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Dissipation kinetics, residue modeling and human intake of endosulfan applied to okra (*Abelmoschus esculentus*)



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Variability of pesticide residues in harvested okra fruits and leaves was observed.
- The uptake and distribution of endosulfan mixtures was studied using dynamiCROP.
- Slower dissipation rate of endosulfan mixtures was seen at single than double dosage.
- A better fitting of regressions was found for endosulfan mixtures on fruits.
- Endosulfan residues were less than 10 g intake per kg of applied pesticides.

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ABSTRACT

The non-judicious application of the harmful pesticide endosulfan on okra, one of India's most consumed vegetable crops, has resulted in the frequent detection of residues in food samples. This can lead to resistance and the resurgence of various pests and diseases. In this context, combined dissipation and residue dynamics of different endosulfan components or mixtures (isomers and metabolites) in crop compartments are not yet well understood. To address this research gap, the present study evaluates the dissipation and persistence behavior of different endosulfan isomers (alpha, beta-isomers) and major metabolite (endosulfan sulfate) on okra during 2017 and 2018. The half-life of endosulfan on okra leaves was found to be between 1.79 and 3.47 days. Half of the endosulfan deposits on okra fruits at the recommended doses were dissipated after 2.39 days compared to 1.99 days at double recommended doses (mean of 2017 and 2018 residue data). Measured endosulfan residues were evaluated against the dynamic plant uptake model dynamiCROP. The better fits were observed between modeled and measured residues for fruits (R² from 0.57 to 0.88). We also report fractions of endosulfan components ingested by humans after crop harvest. Intake fractions range from 0.0001–7.2 g_{intake}/kg of applied pesticide. Our results can evaluate pesticide residues in different crops grown for human consumption, including their isomers and metabolites. They can be combined with dose-response information to evaluate human exposure and/or health risk assessment.

1. Introduction

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Okra (*Abelmoschus esculentus* (L.) Moench), is one of the most important commercial vegetables grown in tropical to warm-temperate regions because of its nutritive value. According to Elkhalifa et al. (2021) and Gill

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Received 4 April 2022; Received in revised form 16 April 2022; Accepted 25 April 2022 Available online 28 April 2022 0048-9697/© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/). et al. (2020), the annual average world production of okra is estimated to be \geq 7.8 million tons, of which India contributes >70% and ranks first with average productivity of ~12 million tons/ha grown on ~0.5 million ha (Dsouza et al., 2022; Singh et al., 2021). The commercial cultivation of okra is often affected by different insect pests (whitefly, leafhopper, shoot and fruit borer, aphids), which lead to yield losses up to >70-80% (Das et al., 2021; Singh et al., 2021). The occurrences of non-approved (banned) pesticides residues (stemming from their excessive and non-judicious use in the past decades) in milk, meat, dairy products, and other agricultural products has alarmed scientists to ponder about hazardous consequences to human/animal health and the ecosystem (Sethi et al., 2022; Sarkar et al., 2022), where such pesticides also feed into the global pressure of chemical pollution on human and environmental health (Kosnik et al., 2022; Persson et al., 2022; Fantke and Illner, 2019). The contamination of the human diet and natural resources with the organochlorine pesticides endosulfan was found in >1100 vegetable samples in India, above the maximum permissible limits (>60-70 ppb) (Dhananjayan and Ravichandran, 2014; Jayaraj et al., 2016). Mobilization of deposited contaminants, biomagnification of such lipophilic and persistent pesticide, ingestion of contaminated feed, fodder, and water, and long-range transport might be attributed to the occurrence of diastereomeric pesticide residues in the environment and food commodities (Dores et al., 2016; Kumari et al., 2022; Kang et al., 2022; Vaikosen et al., 2019).

In recent years, the presence of organochlorine pesticides above European Union (EU) maximum residue limits (MRLs) (\geq 100–1000 ppb) in different analyzed fruits and vegetable samples (\geq 6000) of the Eastern Mediterranean and South Asian countries has created a major bottleneck in the international trade other than imparting environmental and human health hazards (European Food Safety Authority (EFSA) et al., 2020; Gill et al., 2020). The international expert scientific groups (FAO/WHO) have reported that organochlorine residues such as endosulfan and heptachlor were found to the level of \geq 500 ppb in >10 agricultural commodities from 4 countries (Heshmati et al., 2020; Philippe et al., 2021). Endosulfan had been phased out from India in May 2011 and was declared as persistent organic pollutants (POPs) by the Stockholm Convention in 2011. Although, organochlorine pesticides have been banned in India as per section 5 of the Insecticide Act 1968; however, cases of endosulfan poisoning, its frequent occurrence in breast milk, and use for pest control over rice crops in India are still a grave concern (Keswani et al., 2022; Sharma et al., 2022).

The occurrence, fate/distribution, and ecological impact of endosulfan (6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3benzodio-3-oxide), its isomers (α and β , 70:30), and toxic metabolites (endosulfan sulfate (ES)) in the food chain have been discussed in the past decades due to their widespread application in modern agri-horticultural operation, highly persistent nature, bioaccumulation, and biomagnification potential (Philippe et al., 2021; Sathishkumar et al., 2021; Wong et al., 2021). The fate of pesticides in the environment is usually governed by dissipation (e.g. mineralization, soil sorption), which in turn also controls the leaching of chemicals (Fantke et al., 2013; Jacobsen et al., 2015). Researchers have developed different models for predicting the environmental fate of agricultural pesticides in food crops and plant components using different physico-chemical parameters such as degradation, phase partitioning, and intermedia transport (Kumari et al., 2022; Feng et al., 2019; Wani et al., 2019; Fantke and Jolliet, 2016). The limitations (long field trials and crop-growth periods) of DT₅₀ determination from lab studies have motivated researchers to discuss consumer risk assessment based on residue and half-life (HL) data using a variety of crop uptake models (Fantke et al., 2011a; Feng et al., 2019; Juraske et al., 2012). These models simulate pesticide distribution in particular crops and are used to calculate pesticides intake and related health risks for the interpretation of the consumption residues of pesticides/or their behavior in the crops and environment (e.g. Fantke and Jolliet, 2016; Gentil-Sergent et al., 2022; Li and Fantke, 2022).

To understand the mechanistic/heterogeneous distribution of chemicals in the plant-environment systems, and to simulate the pesticides uptake and translocation as a function of time, the dynamic plant uptake and exposure model dynamiCROP was developed by Fantke et al. (2011a, 2011b, 2012a, 2012b); Fantke and Jolliet (2016). A transparent matrix algebra framework is used in this model to solve the mass balance for a given set of pesticide-crop combinations, providing as output an evolution of pesticide residues in different crop components and related human exposure factors, as applied in various studies (e.g. Pang et al., 2020; Feng et al., 2019; Luo et al., 2021; Gentil et al., 2020; Itoiz et al., 2012).

To protect the environment and to promote human safety it is important not only to understand the dissipation and residue kinetics of active ingredients (and their isomers) but the information about persistence behavior of associated metabolites on the edible portions of plants also help to indicate the magnitude of exposure for the relevant population. The comparative study of dissipation half-lives of 333 pesticides from plants under field conditions has assessed the modeling of the residue data over time and compared them against measured residues (Fantke et al., 2014; Fantke and Juraske, 2013; Lewis and Tzilivakis, 2017). Although there were some field studies on endosulfan pesticide residues in the past decades, most of the studies had been reported in temperate regions (Lu et al., 2021; Gentil-Sergent et al., 2022; Feng et al., 2021). There is a paucity of analytical data on pesticide-plant dissipation assessment particularly for residual endosulfan isomers and metabolite in the tropical region. Additionally, scanty information is available about the endosulfan residues (considering their long persistence and occurrence in environmental/food samples) in edible garden vegetables like okra in the study area. Above all, there are still no federal water quality guidelines available in India for endosulfan degradation products instead of their frequent occurrence in surface and groundwater. Endosulfan is being smuggled into the different Indian states through porous borders. It results in frequent occurrence of vegetables, highlighting the importance of adoption of good agricultural practices, monitoring of harmful chemicals in food commodities, and implementing food safety and standards regulations to protect ecosystem and/or human health (Menezes et al., 2017; Sharma et al., 2022).

To address these gaps, the present study was designed for providing a better understanding of residue dynamics and related exposures of endosulfan including all its isomers and metabolite in okra. Therefore, the objectives of the present study are the following a) to measure uptake and dissipation kinetics of endosulfan components or mixtures (isomers and major metabolite) in okra; b) to model the evolution of residues of endosulfan and its components using the dynamiCROP plant uptake model and compare measured against modeled results, and c) to estimate related exposure due to residues in okra fruits harvested for human consumption as input for health risk and impact assessments.

2. Materials and methods

2.1. Field experiment

In line with recent reporting requirements (Fantke et al., 2016), we provide relevant study site characteristics. The experiment for the residue dynamics and dissipation analysis of endosulfan (CAS number:115-29-7) was carried out at the experimental farm of Dr. Y.S. Parmar, University of Horticulture and Forestry, Nauni, Solan (H.P.) during the summer season (June to September) of 2017 and 2018. The experimental site is located in the mid-hill zone of Himachal Pradesh, India (30° 51' N Latitude and 76° 11' E Longitude) with an altitude of 1200 to 1550 m above mean sea level, representing a sub-tropical to sub-temperate climate. The area usually receives an average annual rainfall of 1000 to1400 mm and an average annual temperature of 15.2 to 17.4 °C. The soil of the region is Typic Eutrochrept (subgroup) (USDA soil taxonomy classification), gravel sandy loam in texture, and enriched in high organic matter with near-neutral pH (top 15 cm soil layer) (Galbraith et al., 2018).

The experiment was conducted in Randomized Complete Block Design (RCBD), consisting of 3 treatments (1 control and 2 test treatments) and 3 replications with a high-yield okra cultivar (*Arka anamika*) in a plant spacing of 30 cm \times 50 cm (planting density 7 to 8 plants/m²) as per the

recommended agronomic package of practices of mid-hill zones (Joshi et al., 2021; Rana et al., 2017). Emulsifiable formulations of 2.85 g/L endosulfan (Endosulfan 35 EC (Endocel), with a purity of 35% m/m, batch No. C-168, Excel Crop Care Limited, Mumbai, INDIA) were applied as a foliar spray in the experimental plot at 0.5 kg a.i./ha and 1.0 kg a.i./ha for the management of fruit borer and sucking insect pests. The pesticide application was performed manually using knapsack sprayers (volume: 16 L) which contains ~45.6 g of formulation mixtures. Approximately, 0.5 kg of okra samples were randomly collected at 0, 1, 3, 5, and 7 days after initial spraying (spraying volume: 2.85 mL/L). Samples were collected and stored at -20 °C for further analysis. The details of the weather parameters and data of okra cultivation (field trial) are provided in Table S1.

2.2. Analytical measurement and method validation

Working standard solutions (mixtures) of α - (Endosulfan I), β - endosulfan (Endosulfan II), and endosulfan sulfate (ES) were prepared in the concentrations of 0.1 and 0.01 mg/L from 1000 mg/L reference standard stock solution. Other than endosulfan sulfate, some of the endosulfan metabolites (endosulfan diol, endosulfan ether, endosulfan lactone) also have a toxic effect similar to the endosulfan isomers. Still, the present study only focuses on endosulfan sulfate. This is because the chemical properties of endosulfan sulfate are similar to its parent compound, endosulfan, and endosulfan is often considered a suitable surrogate to develop risk assessment/exposure and toxicological values for endosulfan sulfate (Park et al., 2021; US EPA, 2007). A mass of 50 g of substrates (fruits/leaves) was homogenized three times for 2 min with 150, 100 and 100 mL of hexane/isopropyl alcohol (2:1 v/v). All three extracts were pooled and filtered through Whatman no. 1 filter paper (Grade No. 1, Size 110 mm Quantitative Filter Paper Sheet, 11 Micron, Pack of 100 (12.5 cm)) using mild suction. Three samples were extracted and a fourth one was stored at -40 °C for future use considering the sample losses during processing. Each extract was transferred to 1 L separating funnels, diluted with 100 mL distilled water, and the lower aqueous layer was discarded, dried (the hexane layer) over anhydrous Na2SO4, and collected in a distillation flask. Then, the hexane extract was concentrated in a rotary evaporator (Buchi, R-205 V, Germany) and the residue was redissolved in a mixture of 45 mL hexane and 5 mL acetone mixture (v/v). To this partition process, 0.5 g activated charcoal (Sigma-Aldrich, DARCO®, 100 mesh particle size, powder) was added and the flask was placed on a rotary shaker (REMI, Mumbai, India) (180 rpm, 15 min), then filtered (0.22 µm millipore cellulose filter), and the residue washed with 3 \times 15 mL hexane:acetone (9:1 v/v). The organic extract was again concentrated at 30 °C and then redissolved in 5 mL hexane for gas-liquid chromatography (GLC) analysis (Hewlett Packard HP 5890 Series II Gas Chromatograph) equipped with an OV-17 capillary column (15 m \times 0.32 mm inner diameter \times 0.50 μm film thickness) and flame ionization detector (FID) detector. The limits of detection (LODs) for the studied pesticide (and isomer mixtures along with its metabolite), was 0.026 mg/kg for Endosulfan I, 0.025 mg/kg for Endosulfan II, and 0.024 mg/kg for ES. The gas chromatography for each run was performed using 2 to 10 µg equivalent plant material per injection. The chromatogram of endosulfan, details of the GLC parameters, and program conditions (flow rate, column/oven/detector temperature, lineargradient parameters, detector details) are provided in the supplementary information (Table S2, Fig. S1).

Okra fruit samples (50 g) were fortified at three different levels of concentrations i.e. 0.2, 1 and 5 mg/kg. The six-point calibration curve was also prepared to validate the linearity of the method over a concentration range from 0.2 to 5 µg/mL, whereas the ruggedness of the analytical method (on GC analysis) was <2% (\leq 1.25%RSD). Each fortification level was replicated three times from each matrix to statistically validate and evaluate the accuracy of the method. Analytical quality control measurements have justified that the average recoveries of studied pesticide (and its isomer mixture based on active ingredient) were in the range between 62% and 96.5%. The samples were processed as per the procedure described above and peak areas were used to calibrate the integrator using external standard (ESTD) for listing the corrected quantities of endosulfan isomers and metabolite in unknown samples.

2.3. Dissipation kinetics and waiting period calculation

A set of kinetic models was applied to estimate kinetic parameters $(DT_{50}/t_{1/2} \text{ values}, M_0 \text{ and dissipation rate constants k})$ from the measured endosulfan residues (over 7 days after application) on the harvested components (fruits, leaves) of the edible food crop. For calculating the half-life (HL) value, residual concentrations were plotted as a function of time and the data points were approximated in a regression equation. This helps in the determination of the dissipation end-points (and trends) of parent compounds following an approximately exponential decrease of residues over time through a pseudo first-order kinetics (SFO) exponential model (Kaushik et al., 2019; Mukherjee et al., 2016; Torabi et al., 2021). This regression uses the natural logarithm on the measured concentration, which is commonly used in the interpretation of the pesticide fate models. Some researchers have reported that residue dynamics in some cases do not follow first-order kinetics, but rather more complex, e.g. bi-phasic kinetics or bi-exponential or double first-order in parallel (DFOP) kinetics (Fantke and Juraske, 2013; Torabi et al., 2021), which might be attributed to slow sorption, limited microbial activities, seasonal changes, and diffusion processes. The variations of first-order degradation rate constants with different soil/plant sub-compartments and description of rate-coefficients by gamma-distribution depict the bi-phasic pattern of pesticide degradation, which often considers the pattern of decline of total pesticide concentrations through time- or concentration-dependent endpoints (trigger value or modeling input) (Briones and Sarmah, 2019; Sathishkumar et al., 2021; Torabi et al., 2021). The respective regression (and integrated) equations and corresponding model descriptions (of kinetic models) for deriving estimates of parameters to plot and calculate the half-lives $(t_{1/2})$ for pesticide isomers and metabolite on harvested single compartment (either fruits or leaves) are shown in Table S3.

The calculations for a waiting period (the minimum time required for the residues to reach the maximum permissible level or below MRL/the tolerance limit) were performed according to guidelines proposed by Hoskins (1961). The $t_{\rm si}$ value was calculated as follow:

$$t_{\rm si} = \frac{\ln k_2 - \log_{\rm tol}}{k_i} \tag{1}$$

where, t_{si} = time taken in days by the insecticides to reach tolerance limit; k_2 = initial deposit; $log_{tol} = log$ of proposed tolerance limit; k_i = regression coefficient.

2.4. Effects of household processing on endosulfan residues

Common household processing (peeling, washing, baking, canning, cooking, milling, blanching, etc.) of fruits and vegetables have been reported as one of the effective decontamination operations, which are considered as an important food safety aspect both from a regulatory and public concern perspective (Ahlawat et al., 2019; Vijayasree et al., 2013). In the present study, the effect of running tap water washing on endosulfan residues (isomers only as no metabolites formed on 0 day) was studied on samples of 0 d (same day of application, after 1 h) for the single and double dosages (0.5 and 1 kg a.i./ha) levels. 50 g samples (n = 3) were washed in running water for 5 min and then processed according to the procedures described in Ahlawat et al. (2019) and Kaushik et al. (2019). After washing, the samples were cooked in beakers for 10 min and then processed for analysis for the endosulfan residues. The removal efficiency (%) of pesticide residues due to processing was calculated as:

Removal efficiency (%) =
$$\frac{\text{Residues in processed sample}}{\text{Residues in unprocessed sample}} \times 100$$
 (2)

The details of pesticides dissipation through household processing are discussed in the supplementary information (Table S4, SI.1).

2.5. Estimating residue dynamics using a modeling approach

For modeling residues of measured pesticides, the dynamiCROP (dynamic multi-crop plant uptake and exposure) model was used and adapted to okra. Three types of input parameters were used, namely substance properties (for the different endosulfan isomers/metabolite), crop characteristics (for okra) and environmental characteristics (Fantke et al., 2011a, 2011b). For our study, physicochemical properties, such as molecular weight (g/mol), soil organic carbon/water partition coefficient (L/kg), total mass of applied substance (kg/m²), N-octanol/water partition coefficient, air/water partition coefficient were derived from Feng et al. (2019); Lewis and Tzilivakis (2017) and Rani et al. (2019) (Table 1). Degradation half-lives ($t_{1/2}$, d) in air, water, soil, plant surface (leaves) and plant interior (i.e. fruits) were estimated from fitted measured data (kinetic-models based half-lives).

The crop-specific parameters or agricultural produce (okra) intrinsic data (leaf area indices at different stages of the plant, lipid/water content of roots/stem/leaf/fruit, the density of different plant parts, etc.), boundary conditions/auxiliary parameters, processes of pesticides in okra crop were derived from Fantke et al. (2011 a, 2011b) and included them in the dynamiCROP (Table S5).

The crop input parameters for okra were compared with the tomato (as a reference crop), considering as both herbaceous vegetables for which only fruits are consumed globally. Additionally, for tomato many crop uptake models were developed which discussed the pesticides behavior in the crop-environment ecosystems (Fantke et al., 2011a; Feng et al., 2019).

2.6. Estimating exposure using harvest and intake fractions

Human exposure to a fraction of applied pesticide is mainly related to consumption of agricultural produce which accumulates residual pesticide concentrations in harvested crop components. This residual amount in harvest in relation to applied pesticide mass is expressed as harvest fraction, hF(t) (kg_{in harvest}/kg_{applied}) with t = time between pesticide application and crop harvest:

$$hF(t) = \frac{m_{\text{residue}}(t)}{m_{\text{applied}} + m_{\text{background}}}$$
(3)

where, $m_{\text{residue}}(t)$ (kg/m²), m_{applied} (kg/m²) and $m_{\text{background}}$ (kg/m²) denote the residual mass of applied pesticide in okra fruit components at harvest time; total mass of applied pesticide and background mass of pesticides from previous application respectively (Fantke et al., 2011b; Fantke et al., 2013; Fantke and Jolliet, 2016). In order to evaluate the exposure to a specific pesticide application, we set $m_{\text{background}} = 0$.

Food processing can reduce pesticide residues, and food processing factors are used to relate the residues in consumed, processed food samples to the residues in an unprocessed harvested food sample. The mass fraction of applied pesticide which is finally consumed after all domestic food processing is defined as intake fraction iF(t) (kg_{intake}/kg_{applied}), where time *t* again refers to the time between pesticide application and crop harvest:

$$iF(t) = hF(t) \times pf \tag{4}$$

where pf is a food processing factor (kgintake/kgharvest). Washing activities followed by prolonged cooking may have positive effects on dislodging of pesticides from the fruit surface. A similar effect was observed by Xiao et al. (2021) and Nehra et al. (2021), who has described that loosely held pesticides on the peel/outer surface (adsorbed by dust particles) of the fruits/vegetables can easily be removed by washing, peeling, and trimming. However, the thermal treatment i.e. cooking/steaming usually was effective for pesticides that penetrate inside the cuticle, and a maximum of 66-90% removal of chlorpyriphos, cyhalothrin, or hexythiazox, endosulfan, aldrin, phosalone, metalaxyl, tetrachlorvinphos, benalaxyl, and procymidone have been reported by Vijayasree et al. (2013), Nguyen et al. (2020) and Rana et al. (2017) on apple, apricot, okra, grape, plume and peper. From these reported values of residual pesticides on different fruits and vegetables, we have selected an average food processing factor of 0.56 for our study, which denotes high reduction of pesticides after domestic processing of 56%, acknowledging that this is an uncertain value as pesticide reduction from harvested crops via food processing varies among pesticides (and their isomers), crops and crop components.

2.7. Statistical interpretation

The goodness-of-fit assessment of the kinetic models was performed by statistical enumeration as described in Hu et al. (2021), and Torabi et al. (2021). Coefficient of determination (R^2 value) and Scaled Root Mean Squared Error (SRMSE) were applied to determine the model accuracy. The R^2 value can be calculated as below:

$$R^2 = 1 - \frac{RSS}{TSS} \tag{5}$$

where RSS = Residuals sum of squares; TSS = Total sum of squares. The *SRMSE* is calculated as follows:

$$SRMSE = \frac{1}{\overline{o}} \sqrt{\frac{\sum_{i=1}^{n} \left(C_i - O_i\right)^2}{n}}$$
(6)

where *C* = calculated values; *O* = observed values; \overline{o} = mean of all observed values; *n* = number of values.

Table 1

Substance-specific model parameters input in dynamiCROP (Feng et al., 2019; Lewis and Tzilivakis, 2017; Rani et al., 2019).

Substance	Endosulfan	α-Endosulfan	β-Endosulfan	Endosulfan sulfate		
IUPAC name	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodio-3-oxide					
CAS RN	115-29-7	959–98-8	33,213-65-9	1031-07-8		
Total mass of substances (kg/m^{-2})	10^{-4}	10 ⁻⁴	10 ⁻⁴	10 ⁻⁴		
Molecular weight (g/mol)	406.9	406.9	406.9	422.9		
pK _a class	Neutral	Neutral	Neutral	Neutral		
Air/water partition coefficient (Kair/water)	$3.3 * 10^{-4}$	$3.3 * 10^{-4}$	$3.3 * 10^{-4}$	$4.6 * 10^{-4}$		
N-Octanol/water partition coeeficient (Koctanol/water)	$5.6 * 10^4$	$5.5 * 10^4$	$6.8 * 10^3$	$4.6 * 10^3$		
Soil organic carbon/water partition coefficient (K _{oc/water}) (L/kg)	$1.2 * 10^4$	$1.2 * 10^4$	$1.1 * 10^4$	$5.2 * 10^3$		
$t_{1/2}$ (air) (d) ^a	1.47	1.47	1.47	0.87		
$t_{1/2}$ (soil) (d) ^a	86	86	105	124		
$t_{1/2}$ (plant surface) (d) ^a	3.81	0.92	3.84	10.2		
t _{1/2} (plant interior) (d) ^a	3.81	0.78	1.87	6.95		

^a Present study derived data.

3. Results and discussion

3.1. Measured residues (isomers) and dissipation of endosulfan metabolite in okra

Mean residue levels (measured over 7 days) and uncertainty ranges were calculated through the regression equation (Table S3), which also provided half-lives (along with the intercept and rate constant values) and R² values for each plotted set of regressions (Fig. 1-b). Half-lives for endosulfan mixtures (two isomers and one major metabolite) were calculated and the average for each component was used as input for the dynamiCROP model. To assess pesticide dissipation in harvested plant compartments, the active ingredient contents were quantified in a hexane/isopropyl alcohol mixture. Vijavasree et al. (2013) and Kaushik et al. (2019) have hypothesized that the extraction of pesticides from plant parts (fruits and leaves) through hexane/isopropyl alcohol (low polarity solvents) mixture often represents the potentially low polarity residues/fractions in the soil-plant system. In the present dissipation study of endosulfan (and its α - and β - isomers i.e. Endosulfan I and II) and ES in okra (fruit and leaves) at both doses showed significant difference (p < 0.05; t-test) in dissipation patterns. In the present study, the half-life values range from 0.66 to 23.1 days (R² values from 0.79 to 0.99) for fruits and leaves, respectively. Our results support the findings of Fantke and Juraske (2013) and Doucette et al. (2018), which reported dissipation half-life values (at 95% confidence interval) of 346 pesticides in 183 plant species, namely that the slowest dissipation was always observed for leaves compared to fruits irrespective of different crop seasons. However, this effect was more significant for the 2018 crop season in our study (p < 0.05; t-test). For the high application dose (double dose, i.e. 1.0 kg a.i./ha), the dissipation rate of endosulfan substantially increased (~1.3 fold increase in mean deposits) compared to single dose, although no significant differences between half-life values were observed for the 2017 crop season (p > 0.05; t-test). Initial deposits of insecticides depend upon several factors e.g. concentration, formulation, weather conditions, substrate characteristics, type of sprayer used, the distance between nozzle and plant surface, and properties of active substances carrier as reported by Doucette et al. (2018), and Bajwa and Sandhu (2014). Bajwa and Sandhu (2014) and Jacobsen et al. (2015) have hypothesized that initial concentrations of applied pesticides, the pesticide transfer pathways (aerial diffusion, stem transfer) are often used as input parameters for the determination of dissipation kinetics in risk and impact assessment models.

Theoretically, the dissipation of pesticides in leaves often depends on the vapor pressure of each pesticide. For many pesticides with low vapor pressure, removal from leaves can be slower (although of having high gaseous exchange) than removal via e.g. transpiration inside plants, although other studies have found contradictory results and found that the HL values are influenced by the initial deposits, growth/physiology of plants, and ambient environmental conditions (Bajwa and Sandhu, 2014; Kaushik et al., 2019; Mukherjee et al., 2015). Similar observations were found in our study, where frequent harvesting (every third day) and faster growth of fruits (increased size) compared to leaves might be attributed to the growth dilution effect ("apparent elimination"), which resulted in the large reduction (~30%) of endosulfan residues (fast dissipation) in harvested fruits. The kinetic parameters for the dissipation study of pesticides that were obtained from the fitting kinetics to the SFO model are enlisted in Table S6.

From Table S6, it can be seen that although for most of the cases dissipation kinetics were well defined/explained by the SFO model. Nevertheless, better fits were not observed for the residue dynamics of Endosulfan-II and ES (both single and double application doses) in leaves for the 2018 crop season. It was observed that no ES was found on the day of spray, whereas the residues of ES were first detected on the first day after spray and there after until day 7 (days of the determination of end-points for measured residue), indicating that microsomal mixed-function oxidases (MFO) activity were higher in the okra crop (Mukherjee et al., 2015; Weber et al., 2010). The high dissipation half-life of ES among all endosulfan mixtures can be explained by its stereoselective biotic transformation (mediated by MFO) and persistent nature (Bajwa and Sandhu, 2014; Sathishkumar et al., 2021; Weber et al., 2010).

Considering the measured data points for endosulfan (and isomer mixtures) and dissipation half-lives between two crop seasons (2017 and 2018), it is observed that fast dissipation rates (i.e. \sim 95%) from both leaves and fruits in 2017 might result from high temperature and precipitation events (Table S1 and Fig. 1). In general, the persistence of pesticide deposits is influenced by environmental factors such as light, temperature, relative humidity, precipitation, substrate characteristics along the physical properties of insecticides (Torabi et al., 2021; Bajwa and Sandhu, 2014; Kaushik et al., 2019; Sathishkumar et al., 2021). Some studies have explained dissipation in plants with zero-/ first-/pseudo first-order kinetics using non-linear regression analysis. However, in vegetable crops compared to natural herbs and trees usually >3–4 orders of magnitude of variability in geometric means of pesticide dissipation HL have been reported (Bajwa and Sandhu, 2014; Rana et al., 2017; Joshi et al., 2021). Similarly, Gill et al. (2020), Vijavasree et al. (2013), and Ahlawat et al. (2019) have documented that residual concentration curves and related dissipation in plants (eggplant, tomato, pepper, grape, cotton) are often approximated through biexponential/biphasic models for largely persistent pesticides-plant species combinations, which might be attributed to the species characteristics, quick volatilization, and photodecomposition processes.



Fig. 1. Dissipation curves of endosulfan mixtures (Endosulfan I, Endosulfan II, and Endosulfan sulfate) in okra fruits during two crop seasons (2017 and 2018) derived from field trial data.



Fig. 1 (continued)

3.2. Modeled pesticide mass evolution in okra

Using the dynamiCROP model and utilizing the experimental data related to the okra-specific input parameters, the residue concentrations of endosulfan mixtures were estimated. The dynamiCROP model includes eight compartments, with leaf deposit, fruit deposit, soil, air as source compartments, which together with leaf, stem, root, fruit compartments can receive some of the initially applied pesticide components/mass. In our study, we have evaluated the distribution and transfer of endosulfan mixtures among these compartments and analyzed their behavior in okra in three different sections: the initial, middle, and long periods (Fig. 2). The initial term (at time t = 0) of this model is characterized by initial distribution processes of pesticides that solely depend on the crop varieties/characteristics after the application. For okra, the distinct distribution of endosulfan mixtures between the above compartments indicated the easy/rapid entry and accumulation of endosulfan II and endosulfan sulfate into the air, soil, leaf surface, fruit surface, leaf, and fruit compartments immediately after application of endosulfan (active ingredient) (Table 2, Fig. 2). The quick degradation of endosulfan I and II were observed in air, leaf surface, fruit surface, leaf, and fruit with a residence time of <1 day (Table 2). For leaf and fruit, quick degradation was observed in the case of endosulfan I compared to other components. There was a clear growth/accumulation trend of endosulfan II and endosulfan sulfate in the fruit mostly sourced from fruit surface and air which reached a maximum value of $\geq 7 \text{ mg/kg}$ in 0.1 days. The entry of endosulfan II and endosulfan sulfate into the root and stem was after ≥ 8 and 1 days, respectively, which was mainly driven by the slow root uptake from the soil and xylem flow driven translocation into the stem. The concentration of endosulfan I was decreased until

harvest for leaf and fruit after reaching the maximum point, which might be attributed to the dissipation dynamics of pesticides through volatilization and growth dilution processes (in the middle term of the described model) (Fig. 2).

The longer time of residence of endosulfan II and endosulfan sulfate in fruits (and fruit surface) compared to endosulfan I indicated that mass evolution of pesticides in crops was affected by pesticides physicochemical properties mostly Kow and Kaw. Feng et al. (2019); Kalra and Kaur (2022) and Simoglou and Roditakis (2022) have reported that usually nonvolatile and non-polar pesticides can accumulate rapidly in the leaf and/ or fruit surfaces, whereas their entry into the leaf or fruit interior is often protected by cuticles (can also protect crops from loss of water). The maximum concentration (8.8 mg/kg) of endosulfan II in fruits was reached at 0.1 days; after that, the concentration decreased at different rates in various compartments until harvest in the middle term and finally the soil was found to drive the overall residue dynamics (longest residence time among all compartments) for all endosulfan components in the long term. From Table 2, we can see that endosulfan I appeared shortly in the leaf, accumulated quickly, and reached its maximum value of 6.4 mg/kg after 0.1 days. In general, the reduced concentrations of pesticides in air and leaf surface over the three different periods (initial, middle, and long) might be due to the gaseous exchange between leaf and air along with the diffusive mass transfer from leaf surface to leaf interior.

3.3. Comparison of measured and modeled residues

The modeled and measured residues were calculated at 0, 1, 3, 5, and 7 days after the application of pesticides. We have observed some deviations in the measured and modeled error values, which might be attributed to the uncertainty of the measurements and the high variability in modeled residues. Such variations in corresponding modeled residual concentrations might be due to the sensitivity analysis, optimization of parameters (and different estimation processes i.e. higher-tier approaches), substance features, and environmental conditions. The measured and modeled residue concentrations of endosulfan mixtures for okra show a good overall correlation (Fig. 3). The better fit was obtained in the case of fruits (with R² values of 0.84 to 0.96 and residual standard error (ER) values between 0.60 and 1.47) as compared to leaves (R² values of 0.57 to 0.88). However, residual standard error values were higher for fruits than for leaves (the latter had ER values between 0.41 and 0.5). Due to the later formation of endosulfan sulfate (after 1 day), the residue data at t = 0 did not contain required information of endosulfan sulfate. The difference between modeled and measured data might be attributed to the different factors such as formulation of pesticides, types of pesticide application, various crop types (and their phenotypic divergence). Considering the leafy vegetable foliage as an important component of primary pesticide receiver, the removal of pesticides through volatilization and transpiration play an important role in the modeling of pesticide degradation. From Table S5, we can see that comparison of nominal values of some important cropspecific model input parameters (most importantly, $\mathrm{LAI}_{\mathrm{t0}},\,\mathrm{LAI}_{\mathrm{app}},$ and LAIharv) showed reasonable similarity for the studied (okra) and other crops (e.g. tomato), based on Fantke et al. (2011 a, b, 2014, and 2016); Maduwanthi and Karunarathna (2019) and Salau and Makinde (2016). Hence, such data were applied as model input where okra-specific data were lacking or insufficient. It is usually found that pesticide dissipation from fruits depends on the characteristics of pesticides, fruit's physicochemical (water content and pH), and rheological/functional properties. In the present study, we can observe that the deposition/transfer of pesticides on okra or tomato (as a reference) crops happens through the stem or fruit surface. Feng et al. (2019) and Briz-Cid et al. (2021) have reported that a correlation was observed between pH and measured organochlorine pesticides on the selected leafy vegetables and fruits (lemon, apple). The dissipation of lindane, Lamda-cyhalothrin, 2, 4 DDT, dieldrin, aldrin, heptachlor and α -endosulfan was accelerated (HL was 3–5 times shorter) within the pH range from 4.48–5.86, though the effect was non-significant (p >0.05; t-test) when pH was >5.92 (Briz-Cid et al., 2021; Sarangapani et al.,



Fig. 2. Overall mass evolution of endosulfan mixtures (Endosulfan I, Endosulfan II and Endosulfan sulfate) in okra crop compartments, plotted based on reported average halflives across field trial scenarios.

Table 2

Modeled results of endosulfan mixtures (Endosulfan I, Endosulfan II and Endosulfan sulfate) in okra obtained from dynamiCROP. Harvest fractions (hF) include okra leaves and fruits as harvested crop components, while subsequent human intake fractions (iF) consider only okra fruits for human consumption.

Model parameters		Endosulfan	Endosulfan I	Endosulfan II	Endosulfan sulfate
Residence times in	Air	0.67	0.59	0.9	1.0
receiving	Soil	117	117	141	152
compartments (d)	Leaf	0.03	0.01	0.02	0.02
	surface				
	Fruit	0.8	0.2	0.6	3.1
	surface				
	Leaf	3.7	0.8	1.4	1.5
	Fruit	3.3	0.7	1.4	4.5
	Stem	1.2	0.6	0.4	0.3
	Root	3.2	0.8	1.1	1.5
Time for maximum	t _{leaf}	0.3	0.1	0.1	0.1
residue mass (d)	t _{max,}	0.1	0.1	0.1	0.1
	fruit				
	t _{max,}	2.0	1.0	1.0	1.0
	stem				
	t _{max,}	13.0	4.0	8.0	9.0
	root				
Residue at harvest time	Leaf	8.9	0.02	0.97	1.3
(mg/kg)	Fruit	2.9	0.01	0.8	7.0
Residue at maximum	Leaf	44.1	26.9	39.7	37.9
time (mg/kg)	Fruit	10.6	6.4	8.8	7.4
$hF_t (g_{in harvest}/kg_{applied})$ $(t = 21 d)^a$	Fruit	1.3	0.00013	0.023	13
$iF_t (g_{intake}/kg_{applied})$ (t = 21 d) ^a	Fruit	0.7	0.0001	0.01	7.2

^a For better interpretability, harvest fractions and intake fractions were converted from kg/kg to g/kg.

2020; Hendawi et al., 2018). Although in our work we did not study the effect of pH on pesticide dissipation, we can hypothesize that hydrolysis and plant transpiration might be the most influencing factor for dissipation of the endosulfan mixtures considering their similar properties with the above mentioned organochlorine pesticides.

The transpiration coefficient, shape/size, water content of the fruits, and leaf growth stages are the important harvest parameters that showed different values for okra from tomato (Table S5), though Feng et al. (2019); Kalra and Kaur (2022) and Simoglou and Roditakis (2022) have documented that cucumber and Chinese cabbage growth can be modeled using some growth parameters of tomato as a reference crop. It is crucial to update some okra-specific data in future studies which can discuss the pesticide transfer and deposition behavior in okra using the critical environmental data.

3.4. Pesticide fractions in crop harvest and taken in by humans

To discuss the human exposure from food crop consumption, harvest fractions (*hF*) and human intake fractions (*iF*) were estimated. From our study, we found that the values of hF for different endosulfan mixtures were between 0.00013 and 13 g pesticide residue in the harvest per kg applied (Table 2), which gives a maximum of 1.3% of applied pesticide that is found as residue in the crop components at denoted harvest time. We note that actual crop harvest time under current agricultural conditions is 21 days used for the residue analysis in the present study i.e. for human exposure evaluation, the realistic harvest time for endosulfan on okra has taken (Sharma and Choudhury, 2018; Heshmati et al., 2020). In the present study, a waiting period for consumption of okra fruit as vegetable crop was calculated (1.1–3.0 days) based on the Codex MRL value of 2 mg/kg in common fruits and vegetables (Doucette et al., 2018; Joshi et al., 2021). This waiting period was within the reported value of 1–5 days as suggested by Jiang et al. (2020) and Heshmati et al. (2020) on okra. On the contrary,



Fig. 3. Modeled vs. measured residue concentrations (mg/kg) of endosulfan mixtures (Endosulfan I, Endosulfan II and Endosulfan sulfate) in okra.

slightly higher waiting periods (5–8 days) of ready-mix formulation of deltamethrin and endosulfan on tomato and eggplant fruits were reported by Wani et al. (2019) and Nehra et al. (2021). These large variations in magnitude usually reflect differences among substance properties (K_{aw}, K_{ow}) and half-lives in the individual harvested crop components. With that, our study is in line with the observations of Juraske and Sanjuán (2011) and Mutungi et al. (2022) who have reported that the harvest fractions of organochlorine, hydroxyanilide, imidazolinone, and imidazolinone pesticide residues on various crops (wheat, cucumber, potato, apple, lettuce) usually varied along with the crop components.

Based on the assumption that harvested okra fruits are further processed for human consumption (as compared to harvested okra leaves), related human intake fractions ranged from 0.0001 to 7.2 $g_{intake}/kg_{applied}$ (endosulfan sulfate showed one order of magnitude higher iF than other components), which denotes the given amount of pesticide mass ingested via consumption of edible crops after the application of 1 kg of pesticides (Table 2). 7.2 g intake per kg applied is an equivalent of 0.72% of the applied mass being taken in by humans via consumption of the relevant harvested crop components. This variation in values is usually caused by the differences in physicochemical properties and harvested crop component characteristics of pesticides which usually demonstrates the exposure of endosulfan residues from food consumption after direct application of pesticide treatments. Household processing steps applied in the present study (washing and cooking) reduced pesticide residues in crop harvest by \geq 55% before human consumption (Endosulfan I) (Table S4, SI.1). As can be seen in Table S4, the residue reduction effect was not statistically different for double-dose treatment and combined activities of washing and cooking. Gasparotto et al. (2022); Yong et al. (2022) and Feng et al. (2019) have reported that pesticide intake fractions for various fruits and vegetables like tomato and potato usually varies between 0.02 and 6 g_{intake}/kg_{applied}. Our results for okra corroborate these observations.

4. Conclusion

Pesticide residue dynamics of endosulfan components (isomers and metabolites) in okra crop were evaluated through analytical quality control measurements and method validation process utilizing extraction (and partitioning) through hexane and GLC measurements. The effect of simple decontamination processes like washing and boiling/cooking on the deposits of endosulfan was determined to influence the residue levels in the processed commodity. On okra leaves, a 1.4 to 1.9-fold increase in deposit was observed for higher doses over normal doses during the two years of investigation (2017 and 2018). The dissipation pattern of endosulfan showed that it degraded very fast (first-order kinetics) and by day 7 it had degraded by ~91.5%. After the combined washing and cooking process >55% reduction of endosulfan residues on okra fruits has been observed. The dynamiCROP model, which was used to simulate residue dynamics of endosulfan mixture, suggests that the model may be appropriately applied to leafy vegetable crops, though more research is required to adapt relevant crop-specific parameters, such as leaf area index. Since the uptake and distribution of pesticides are generally complex in fruit and vegetable crops, the comparison of residue trends between measurements and model estimates based on any reference crop might not be suitable, while the use of parameters related to the actual crop under study need to be used. The diverse variations in the magnitude of hF and iF usually reflect differences among substance properties and crop components. The scientific methodology used in the present study can form a suitable basis to help in the assessment of the safety of persistent and banned pesticide residues (can contaminate food-chain through soil-water-crop nexus) for edible fruits and vegetables. Therefore, the present study provides input for understanding suitable pesticide application patterns to minimize human exposure.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2022.155591.

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