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Dissipation of Endosulfan in Field-Grown Tomato (*Lycopersicon esculentum*) and Cropped Soil at Akumadan, Ghana

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The dissipation and persistence of endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide) applied to field-grown tomato (*Lycopersicon esculentum*) were studied at a vegetable-growing location in Ghana. Plant tissue samples and cropped soil collected at 2 h−14 days and 8 h−112 days, respectively, after application, were analyzed by gas chromatography−electron capture detection (^{63}Ni) to determine the content and dissipation rate of endosulfan isomers (α- and β-endosulfan) and the major metabolite, endosulfan sulfate. After two foliar applications of commercial endosulfan at 500 g of active ingredient/hectare, the first-order reaction kinetic was confirmed to describe the dissipation of endosulfan residues in tomato foliage and cropped soil. However, functions that best fit the experimental data were the biphasic process for foliage and the monophasic process for cropped soil. Calculated DT_{50} and DT_{90} values for endosulfan residues in cropped soil were not significantly ($p < 0.05$) different for each of the two isomers.

KEYWORDS: Dissipation; endosulfan; half-life; persistence; soil; tomato (*Lycopersicon esculentum*)

INTRODUCTION

Chlorinated organic pesticides are one of the major groups of chemicals responsible for environmental contamination. Many chlorinated pesticides are highly toxic and considered to be a potential risk to both human health and the environment. Technical endosulfan, a mixture of two stereoisomers, that is, α- and β-endosulfan (**Figure 1a**,**b**) in the approximate ratio of 7:3 (*1*, *2*), is a chlorinated pesticide for control of a large spectrum of insect pests on a wide range of crops (*3*). It is used in many countries throughout the world for the control of pests on fruits, vegetables, tea, tobacco, and cotton (*4*, *5*). Because of such abundant usage, and the potential for accumulation in the environment (endosulfan is not readily detoxified by soil microorganisms), residues are detectable in soils, sediments, and crops at harvest time (*6*, *7*). Although the metabolites of endosulfan, that is, sulfate, diol, ether, hydroxy ether, and lactone, have been shown to occur (*8*, *9*), only the sulfate metabolite (**Figure 1c**) is significant as a residue (*4*).

Endosulfan, which has been found in residue monitoring (*10*, *12*) and food crops studies (*13*), is one of the commonly used chlorinated pesticides on vegetables in Ghana (*14*). At Akumadan (1° 57′ W, 7° 24′ N), a prominent vegetable-farming community in Ghana (*11*), the pesticide is one of the predominant active ingredients used for controlling leaf miners, bollworm, fruit fly, etc., on tomato and has the potential of environmental contamination because of much overuse, abuse, and misuse of the pesticide (*14*). One aspect of the range of studies needed to assess the environmental impact of a pesticide is environmental fate studies, and understanding the persistence and dissipation of the pesticide is an important step forward.

This research uses field experiments to provide insight into the persistence and dissipation of endosulfan applied to field-grown tomato in sandy loam soil under the tropical conditions of Ghana and to answer the following questions: (1) How is endosulfan distributed, qualitatively and quantitatively, in a tomato field following spraying on plant foliage using 1.5 times the labeled rate? (2) Does endosulfan persist in tomato foliage and fruit as total residues to which consumers and/or insects may be exposed? (3) Finally, what are the

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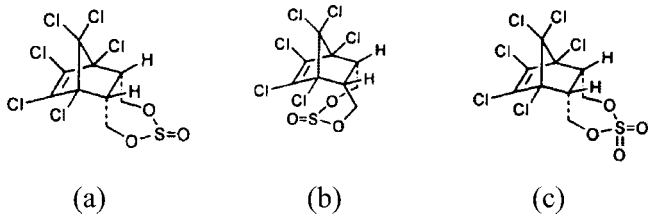

Figure 1. Endosulfan isomers and its sulfate metabolite: (**a**) α-endosulfan; (**b**) β-endosulfan; (**c**) endosulfan sulfate.

persistence and the dissipation rate of endosulfan isomers and major metabolite in tomato foliage and cropped soil?

MATERIALS AND METHODS

Reagents. Analytical standards of α-endosulfan (96.0% purity), β-endosulfan (98.0% purity), and endosulfan sulfate (97.5% purity) were supplied by Dr. Ehrenstorfer GmbH, Augsburg, Germany. Thionex 35 EC/ULV containing 350 g/L active ingredient (ai) of endosulfan (α:β = 1.96:1) was obtained from Hoechst Agrevo Ltd. through a local pesticide dealer at Akumadan. Stock solutions of α- and β-endosulfan and endosulfan sulfate (100 μg/mL) were prepared separately in *n*-hexane. All organic solvents used were of GC grade (Sigma, Münich, Germany; or BDH, VWR International, Poole, U.K.).

Experimental Design and Endosulfan Treatment. The field study was conducted during February−May 2005 at Akumadan. Prespray soil samples (about 200 g dry weight) from 0−10, 10–20, 20–30, and 30–40 cm depths of the experimental field were collected with a corer (5.0 cm diameter) at random and analyzed for water content, pH, organic matter content, texture (clay, silt, and sand contents), and bulk density. Conventional soil analyses were carried out using standard methods. Water content was determined by weight loss after drying in an oven at 110 °C. Measurement of pH (1:2.5 soil/water) was made using a Hach model pH-meter. Soil organic matter was determined according to the Walkley−Black method (*15*); particle size distribution was determined by using the pipet method (*16*) [three sizes were estimated: <0.002 mm (clay), 0.002–0.02 mm (silt), and >0.02 mm (sand)]; and bulk density was determined by weight loss over volume of a cylinder after drying in an oven at 102 °C.

The soil was a sandy loam having 68.5% sand (>0.02 mm), 21.6% silt (0.002–0.02 mm), and 9.9% clay (<0.002 mm); pH 6.5; organic matter of 1.3%; water content of 9.5%; and bulk density of 1.52 g/cm^3 for all segments. Of about 4000 m^2 area prepared for field studies (no endosulfan had been sprayed on the field for over 2 years since September 2002), nine plots each measuring 15 × 15 m were demarcated in a 3 × 3 randomized complete block design for two treatments (T1 and T2) and a control treatment (TC), leaving a border area of about 2.5 m around the plots. Each treatment was replicated three times. On February 9, 2005, 14-day-old tomato seedlings were transplanted at 75 cm apart in rows (row to row distance of 60 cm; 450 plants per plot). On March 12, 2005 (i.e., 31 days after transplanting), endosulfan (Thionex 35 EC/ULV; labeled rate is 2.1 L/ha) was applied on T1 plots from a height of 20–25 cm above the plant canopy at a rate of 3 L/ha (500 g of ai/ha) in 215 L of water on tomato (*Lycopersicon esculentum* var. Power), using a portable backpack sprayer [Knapsack CP 15 L equipped with one conical nozzle operated at 40 psi (275 kPa)]. Before use, the spraying device was calibrated with respect to homogeneity of the spray beam and pumping volume per time unit. The application of pesticide to the plots was executed bandwise and in a criss-cross pattern to ensure a uniform distribution. On March 12 and April 9, 2005 (i.e., 31 and 59 days after transplanting, respectively), the above endosulfan treatment was applied on T2 plots. The second spraying was done at the time of about 50% fruit formation. TC plots were kept as the untreated controls.

Throughout the experiment, the plots were kept free of weeds by hand hoeing, taking care not to disturb the upper layer of soil. The plots were irrigated four times (furrow irrigation). Water was pumped from a reservoir into a head ditch from where the water flowed by gravitation into furrows running across the field. The irrigation water was crosschecked for endosulfan residues. The first irrigation was given on the day of transplanting and thereafter at 21 day intervals. During the experimental period, there was a single rainfall event on April 11, 2005, estimated at 11 mm. Mean relative humidity was 71%; maximum and minimum temperatures averaged 30 and 25 °C, respectively, with a mean of 27 °C during the experimental period.

Sampling for Endosulfan Residues Analysis. After treatment T1, samples of leaves (10 g of fresh weight each) were drawn from each replicate plot at intervals of 0 (2 h after spray), 1, 2, 6, and 14 days. Triplicate tomato leaf samples were collected randomly from the midcanopy of plants from each replicate plot. In addition, whole fruit, root, and stem samples (100–200 g of fresh weight each), and leaf (10

Table 1. Levels and Distribution of Endosulfan (α-Endosulfan, β-Endosulfan, Endosulfan Sulfate, and Sum) in Tomato Plant Parts (Treatment T2)

		residue[a] (mg/kg)			
sample	time[b] (days)	α	β	sulfate	sum[c]
control	0	<0.001[d]	<0.001	<0.001	<0.001
leaves	0	1.110	0.702	0.039	1.851
	1	0.122	0.362	0.086	0.570
	2	0.050	0.085	0.103	0.238
	6	0.017	0.016	0.116	0.149
	14	0.008	0.006	0.020	0.034
fruits	0	0.446	0.428	0.030	0.904
	1	0.297	0.291	0.052	0.647
	2	0.210	0.173	0.266	0.642
	6	0.062	0.037	0.091	0.190
	14	0.031	0.022	0.050	0.103
stems	0	0.126	0.124	0.010	0.260
	1	0.059	0.056	0.055	0.170
	2	0.031	0.026	0.073	0.130
	6	0.006	0.004	0.071	0.081
	14	0.003	<0.001	0.027	0.030
roots	0	0.064	0.047	<0.001	0.111
	1	0.027	0.043	<0.001	0.070
	2	0.015	0.035	<0.001	0.050
	6	<0.001	0.010	0.020	0.030
	14	<0.001	0.003	0.007	0.010
soil	0	0.574	0.221	<0.001	0.795
	1	0.527	0.204	<0.001	0.731
	2	0.527	0.199	<0.001	0.726
	6	0.213	0.067	0.161	0.441
	14	0.057	0.042	0.027	0.126

[a] Mean of triplicate analyses from three replicates. [b] Reference to the second application for T2. [c] α-Endosulfan + β-endosulfan + endosulfan sulfate. [d] Limit of quantification.

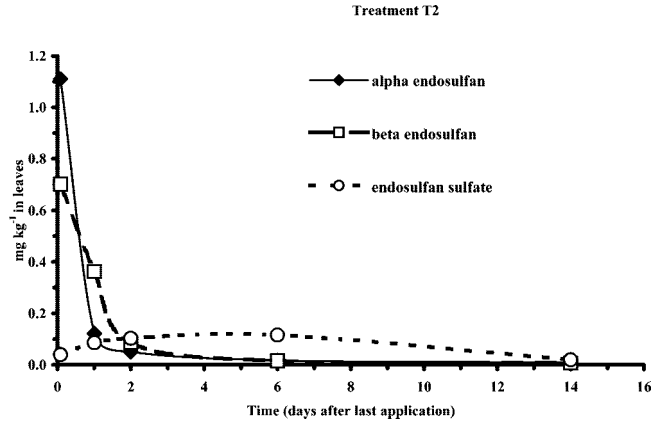

Figure 2. Dissipation of α- and β-endosulfan and endosulfan sulfate in leaves. Maximum concentration of endosulfan sulfate was measured on day 6, which was about 6% of the initial amount of total endosulfan.

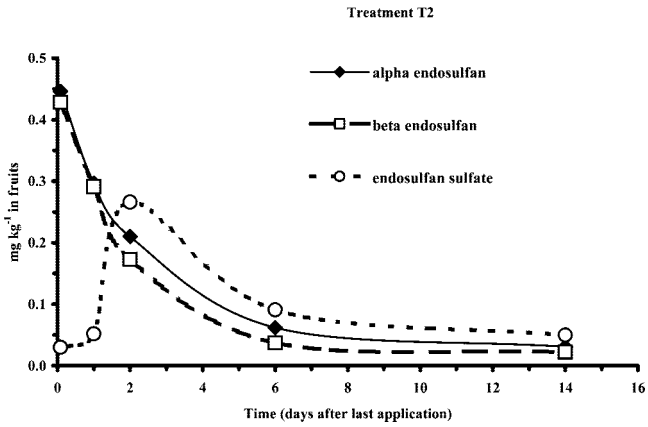

Figure 3. Dissipation of α- and β-endosulfan and endosulfan sulfate in fruits. Maximum concentration of endosulfan sulfate was measured on day 2, which was about 30% of the initial amount of total endosulfan.

g fresh weight) samples were taken randomly at the same time intervals from treatment T2 plots.

Soil samples were drawn at time intervals of 0 (8 h after spray), 1, 2, 6, 14, 28, 56, and 112 days after application from four different levels (0–10, 10–20, 20–30, and 30–40 cm depths) from treatment T1 plots and additionally from the surface (0–10 cm) of treatment T2 plots at intervals of 0 (2 h after spray), 1, 2, 6, and 14 days. One-meter-sided squares were delimited randomly in the 15 × 15 m subplot. In each square, soil cores were taken from the specified soil depths. Thus, within a 15 × 15 m subplot, variable numbers of soil samples (3−10) were taken at the specified times above. All core samples of different depths and treatments were homogenized separately. Each soil sample was a composite of 36 cores (5.0 cm diameter) from 0−10, 10–20, 20–30, and 30–40 cm depths (T1 plots) and 0–10 cm depth (T2 plots). Three replicate samples, about 50 g each, were drawn from each composite.

Sorted samples of soil, leaf, fruit, stem, and root were wrapped in aluminum foil, packed in polythene bags, and transported to the CSIR Water Research Institute Laboratory in Accra (a distance of 349 km) within 24−48 h on ice in clean ice chests. Upon arrival at the laboratory, leaf, fruit, stem, and root samples (peel and flesh) were given a cold water wash with a soft brush to remove adhering soil particles and subsequently kept in a freezer at −4 °C until required for extraction, which was carried out within 24 h. Sorted soil samples were transferred into pans to air-dry at ambient temperature.

Analytical Procedures. Samples of tomato plant parts (roots, stems, leaves, and fruits) were extracted according to procedures described in FAO/IAEA (*17*). Briefly, the frozen samples were thawed, and each plant part (approximately 5 g of fresh weight) was cut (or chopped in the case of leaf) into small pieces and homogenized in a mortar. The plant parts were transferred to a pre-extracted Whatman cellulose extraction thimble; lipids were extracted for 8 h with methanol (200 mL) in a Soxhlet apparatus cycling four or five times per hour. The extract was passed through a preconditioned SPE column (Bond Elute C-18 3 cm^3/500 mg; Varian, Palo Alto, CA) (*11*). Residues trapped in the column were eluted with *n*-hexane (1.5 mL) into a glass vial and brought to volume (2 mL) with *n*-hexane for analysis by gas chromatography.

Air-dried soil samples were ground in a mortar and sieved (2 mm). About 5 g representative sieved samples were weighed into extraction thimbles and extracted for 8 h with methanol (200 mL) in a Soxhlet apparatus as described above for plant samples. The extract was passed through a preconditioned SPE column and treated in the same way as described above for plant parts.

Analyses were performed with a Perkin-Elmer AutoSystem gas chromatograph equipped with a ^{63}Ni electron capture detector. Separations were on a 30 m × 0.32 mm i.d. capillary column with 0.25 μm methyl phenyl phase (Perkin-Elmer Elite-225). The gas flow (helium) was set to 16 mL/min through the column and at 30 mL/min makeup (Nitrogen) through the detector. Sample volumes (1 μL) were injected in a split mode at 250 °C, and the oven temperature was programmed as follows: 100 °C for 1 min, increased to 150 °C (10 °C/min), 250 °C (5 °C/min), then at 30 °C/min to 300 °C (held 10 min). The detector temperature was 350 °C. The retention times (RT) of each of the endosulfan isomers and the sulfate metabolite were compared with those of the external standards, and the data were recorded. The RT of α- and β-endosulfan and endosulfan sulfate were observed as 22.6, 25.2, and 26.8 min, respectively.

In recovery experiments, soil and plant samples from the control plot fortified at levels of 0.1 and 0.5 mg/kg were used. Each fortification level was prepared in three replicates. Chopped or cut plant parts and sieved soil samples were placed in 250 mL standard joint borosilicate bottles and fortified by the addition of appropriate volumes of previously prepared stock solutions of endosulfan. The bottles were capped, manually shaken to ensure thorough mixing, and stored in a deep freezer at −4 °C for 24 h to simulate residue sample storage conditions. The recovery values (mean ± SE) observed were 102.5 ± 2.1, 87.6 ± 1.3, and 84.5 ± 1.2% for α- and β-endosulfan and endosulfan sulfate, respectively, using a fortified soil sample, whereas these values were 85.6 ± 1.3, 84.3 ± 0.9, and 86.5 ± 1.1% for plant samples. Residue data were not corrected for efficiency of recovery. The limit of quantification was 0.001 mg/kg for each of the endosulfan isomers and the metabolite sulfate.

Residues concentrations in soil (milligrams per kilogram of dry weight) and plant samples (milligrams per kilogram of fresh weight) (treatment T2) were converted to loadings per field area in milligrans per hectare. To determine the total mass of active ingredient in soil and plant the following calculations were used:

$$M_{as} = C \times \text{assumed area sprayed} \quad (1)$$

$$M_{ap} = C \times \text{assumed area sprayed} \times \text{crop yield} \quad (2)$$

M_{as} = total mass of active ingredient in soil; M_{ap} = total mass of active ingredient in plant; C = concentration of unit sample in each constituent (mg/kg/m^2 of soil or mg/kg/plant); assumed area sprayed = (15 × 15 m plot size) × 3 number plots; and crop yield = 450 plants per plot (15 × 15m area). To determine the mass of active ingredient per hectare, it is multiplied by 14.8. From the residue loadings in the samples it was possible to estimate the proportion of endosulfan in each constituent of the tomato field ecosystem in one season.

The dissipation of endosulfan in tomato foliage and cropped soil was determined by a nonlinear regression of the pesticide residue concentration against time (treatment T1) implemented in Microsoft Excel. The statistical parameters, r^2, k, and C_0 were determined using an iterative nonlinear regression procedure using SPSS software (SPSS software, version 12.0.1 for Windows, SPSS Inc., Chicago, IL). DT_{50} and DT_{90} values for α- and β-isomers were also calculated.

RESULTS

In **Table 1**, endosulfan residue contents in and their distribution among leaves, fruits, stems, roots, and soil in the course of the experiment (T2 plots) are presented. Shortly after treatment, highest total endosulfan residue contents were found in the leaves, followed by fruits, soil, stems, and roots. Among the plant parts, leaves had the highest content of total endosulfan residues, followed by fruits, stems, and roots. For tomato leaves a sharp decline in the total endosulfan contents was observed within 24 h, followed by a relatively slow decline to the termination of the experiment.

In **Figures 2** and **3**, the dissipation of residues of endosulfan isomers and their metabolite sulfate in foliage and fruit is presented. Residue levels of endosulfan in tomato declined over the 14 day study period. Two hours after treatment, the α-isomer was more abundant than the β-isomer in tomato leaves and fruits. Initial residues of α-endosulfan were 1.11 and 0.45 mg/kg in leaves and fruits, respectively. Initial residues of β-endosulfan were 0.70 and 0.43 mg/kg in fruits, respectively. Endosulfan sulfate was detectable in tomato leaves and fruits analyzed (**Figures 2** and **3**).

Table 2. Dissipation of Endosulfan in Tomato Cropped Soil in T_1 (500 g of Active Ingredient Given 31 Days after Transplanting)

		endosulfan residues[a] (mg/kg)				
days after spraying	depth (cm)	α-endosulfan	β-endosulfan	endosulfan sulfate	Σ endosulfan	dissipation (%)
control plot	0–40	<0.001[b]	<0.001	<0.001	<0.001	
0 (8 h)	0–10	2.30 ± 0.34	0.88 ± 0.11	<0.001	3.18 ± 0.23	
1	0–10	2.11 ± 0.11	0.82 ± 0.07	<0.001	2.92 ± 0.18	8.1
2	0–10	2.11 ± 0.06	0.80 ± 0.07	<0.001	2.90 ± 0.12	8.8
6	0–10	0.85 ± 0.11	0.27 ± 0.01	0.65 ± 0.08	1.77 ± 0.19	44.5
14	0–10	0.23 ± 0.01	0.13 ± 0.01	0.11 ± 0.01	0.47 ± 0.01	
	10–20	<0.001	0.03 ± 0.00	<0.001	0.03 ± 0.00	
	20–30	<0.001	0.01 ± 0.00	<0.001	0.01 ± 0.000.51	84.3
28	0–10	<0.001	0.04 ± 0.00	0.11 ± 0.01	0.15 ± 0.01	
	10–20	<0.001	<0.001	<0.001	<0.001 0.15	95.2
56	0–10	<0.001	0.01 ± 0.00	0.07 ± 0.01	0.08 ± 0.01	
	10–20	<0.001	<0.001	<0.001	<0.001 0.08	97.6
112	0–10	<0.001	<0.001	0.04 ± 0.00	0.04 ± 0.00	
	10–20	<0.001	<0.001	<0.001	<0.001	
	20–30	<0.001	<0.001	<0.001	<0.001	
	30–40	<0.001	<0.001	<0.001	<0.001 0.04	98.7

[a] Mean (±SD) of three replicates. [b] Limit of quantification.

Residue levels of endosulfan isomers in tomato leaves declined very rapidly in the first 2 days, and the rate of dissipation slowed. The sulfate metabolite of endosulfan was detectable almost immediately after treatment, its concentration increasing rapidly in the first 6 days, reaching 6% of the initial residues in foliage, and then decreased at the termination of the experiment (**Figure 2**).

In tomato fruits, initial total endosulfan residues was above 0.50 mg/kg 2 h after treatment and consisted primarily of the α- and β-isomers, whereras only a relatively trace residue level of endosulfan sulfate metabolite was detected 2 h following treatment. Residues of the sulfate metabolite 2 days after treatment constituted about 30% of the initial amount of total endosulfan in tomato fruits (**Figure 3**).

As evident from the data (T1 plots) given in **Table 2** endosulfan parent isomers and their sulfate breakdown product did not move beyond a 30 cm depth. Endosulfan α-isomer remained confined in the 0–10 cm layer. The β-isomer of endosulfan leached down to 30 cm until 28 days of experimentation. The amount present in the 20–30 cm layer was markedly lower than that in the 0–10 cm layer. Endosulfan sulfate metabolite did not leach beyond 10 cm.

A chemical balance budget made using the data in **Table 1** (T2 plots) from a late application of endosulfan (April 9, 2005) (at time $t = 14$ days) showed that most of the residues of the pesticide were found in the tomato plant system (74%), whereas only a relatively small proportion (26%) was found in cropped soil of the amount (0.5%) that remained on-field. In the tomato plant system, the distribution of total endosulfan residues followed the order fruits (43%) > leaves (14%) > stem (13%) > root (4%).

DISCUSSION

In the interpretation of the results of this study, the word 'in' has been used to mean 'in', 'on', or 'in and on'. Our study did not differentiate whether residues were situated on outer surfaces of plant tissues or were taken up into the tissues of the plant. However, several authors have reported endosulfan residues, including metabolites, in, on, or in and on tomato plant tissues (*3*, *18*, *19*) as well as in, on, or in and on tissues of other plants and in soil (*3*, *20*–*26*).

Shortly after treatment of endosulfan on field-grown tomato using Thionex (35 EC/ULV) formulation, the levels of total endosulfan residues were markedly higher in leaves than in fruits, stems, or roots due, partly, to the foliar application of the pesticide. The other reasons could be the horizontal position of the lamina of the leaves as well as the difference in surface area between leaves and other tissues of the plant (*18*, *25*). However, at the termination of the experiment, endosulfan residue levels were about 3−10 times higher in fruits than in other tissues. Miglioranza et al. (*27*) found that high carotenoid levels (lipophilic substances) are responsible for retaining chlorinated hydrocarbons in the body and peel of vegetables, and we believe this to explain the higher endosulfan residue levels in fruits than in leaves at the termination of the experiment.

The measurement of endosulfan (a persistent organochlorine compound) in tomato fruit (a vegetable crop) is of great importance as its uptake is a major pathway for a toxic substance into the food chain leading to human exposure (*28*). The Codex Committee on Pesticide Residues (CCPR) considers a total endosulfan concentration of 0.50 mg/kg in tomato to be the maximum residue level (MRL) [CCPR (https://secure.pesticides.gov.uk/MRLs)]. After treatment, the residue level of total endosulfan in fruit was 0.90 mg/Kkg, and at harvest time, that is, 2 weeks later (according to the preharvest interval), it was 0.10 mg/kg, which is markedly lower than the Codex MRL. However, a definite conclusion on the safety of the consumption of field-grown tomato cannot be reached because high application rates of endosulfan (1000 g of ai/ha, 5–10 kg per seasonal total for tomato by some farmers at Akumadan) are reported (*14*). The human dietary exposure to pesticides from the consumption of vegetables is the subject of another publication (Ntow et al., unpublished results).

The endosulfan formulation used (Thionex) contained two isomers, α- and β-isomers, with a higher relative amount of α-isomer than β-isomer (α-isomer/β-isomer = 1.96:1). During the first 2 h following pesticide treatment, the residue level of

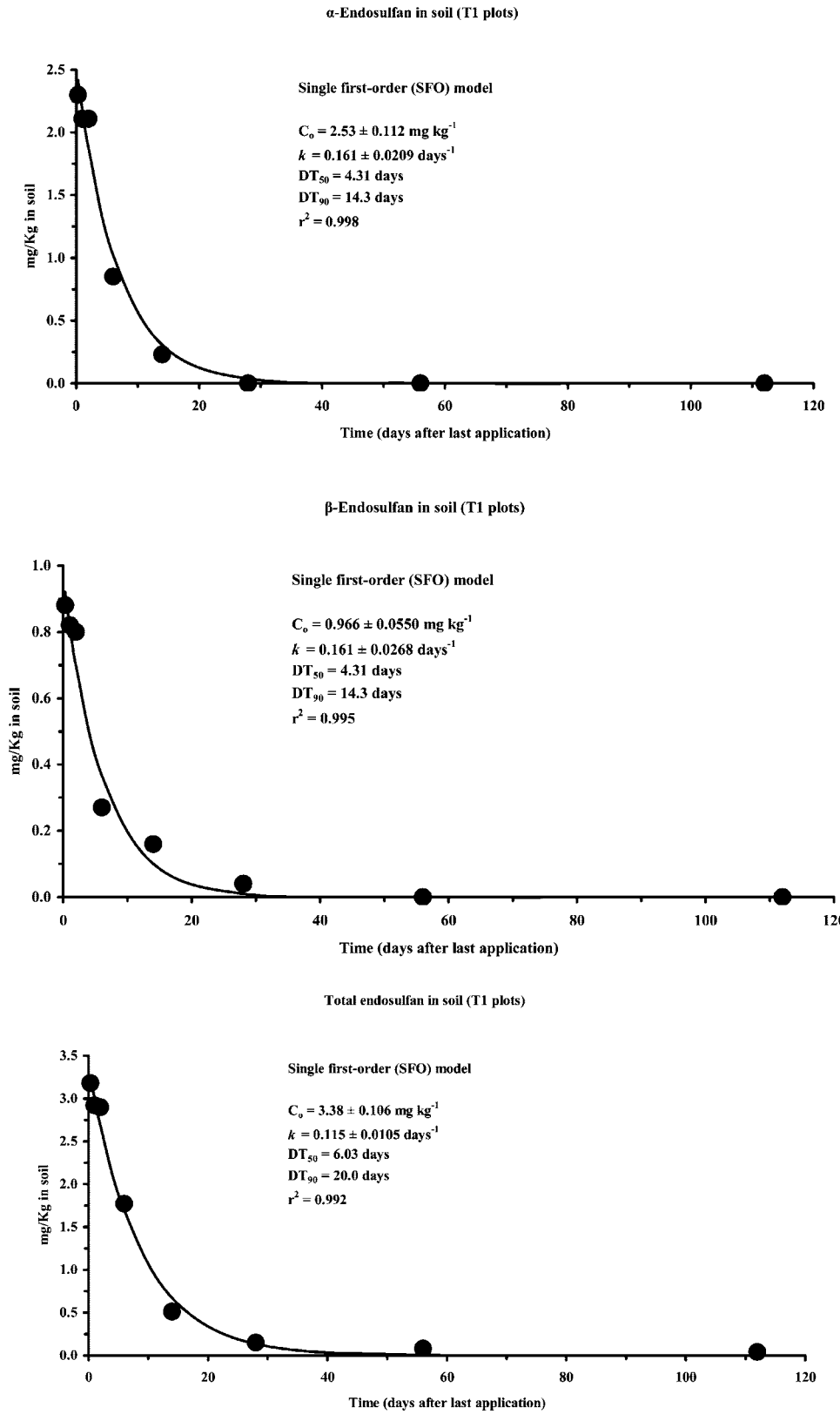

Figure 4. Monophasic dissipation of (**a**, top) α-endosulfan, (**b**, middle) β-endosulfan, and (**c**, bottom) total endosulfan residues in tomato cropped soil.

α-endosulfan was higher than that determined for β-endosulfan in leaves, but from day 2, residue levels found for both isomers were, in general, similar (**Figure 2**; **Table 1**). In fruits, residue levels of α- and β-endosulfan were very similar during the entire 14 day period of experimentation, although levels of α-endosulfan were, in general, higher than those determined for β-endosulfan (**Figure 3**; **Table 1**). According to Antonious et al. (*18*), Kathpal et al. (*26*), and Kimber et al. (*29*), although the endosulfan α-isomer is about 70% of the active ingredient in commercial formulations, it is found in solid surfaces at appreciable levels only immediately after spraying, due to its high volatility. Endosulfan α-isomer is more volatile (vp = 0.006 mmHg at 20 °C) and less water-soluble (2.29 mg/L at 22 °C) compared to the β-isomer (vp = 0.003 mmHg at 20 °C

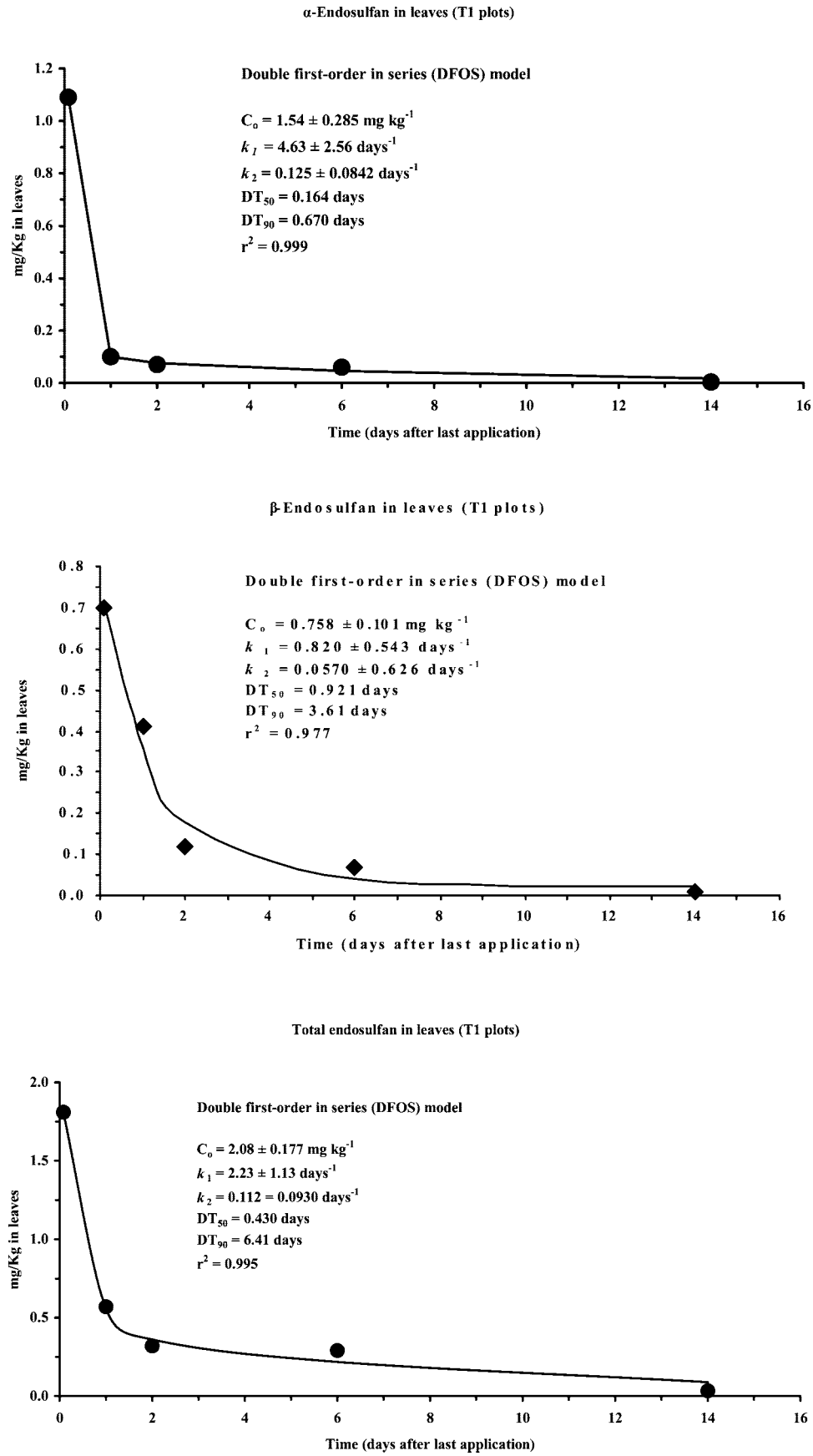

Figure 5. Biphasic dissipation of (**a**, top) α-endosulfan, (**b**, middle) β-endosulfan, and (**c**, bottom) total endosulfan residues in tomato foliage.

and water solubility = 31.1 mg/L at 22 °C) (*18*, *30*). Endosulfan was converted to the sulfate metabolite in foliage and fruit of tomato in 2 h, following treatment. In both foliage and fruit, this breakdown product of endosulfan persisted until the termination of the experiment at 14 days. Oxidation of the parent compounds (*2*) causes an initial buildup in the sulfate metabolite,

which reaches a peak in 6 and 2 days in foliage and fruit, respectively, after application. Given that endosulfan sulfate is formed in many natural environments through biological oxidation and that it is only slowly degraded, both chemically and biologically (*31*), it may represent a predominant residue of endosulfan in aerobic environments.

To describe the dissipation of residues of endosulfan isomers in tomato foliage and cropped soil, a monophasic dissipation model in first-order kinetics derived from eq 3 (*32*) was used.

$$C_t = C_0 e^{-kt} \quad (3)$$

C_0 is the *y*-intercept value, C_t is the concentration of endosulfan residues in matrix at time t (mg/kg), t is the postapplication time (days), and k is the slope of the dissipation line. DT_{50} and DT_{90} values and the dissipation rate constant (k) were determined from the slope of a nonlinear regression plot of C_t versus t.

In tomato cropped soil, endosulfan dissipation followed an essentially first-order kinetic. As can be seen in **Figure 4** in cropped soil the concentration of endosulfan gradually decreased with time during the study period of 120 days. The calculated DT_{50} and DT_{90} values for endosulfan in tomato cropped soil were not significantly ($p < 0.05$) different for each of the two isomers [4.31 (±0.105), 14.3 (±0.105) days for the α-isomer, respectively; 4.31 (±0.0255), 14.3 (±0.0255) days for the β-isomer, respectively] in cropped soil (**Figure 4a**,**b**). These findings suggest that, in this experiment, α-endosulfan and β-endosulfan did not differ in persistence in cropped soil.

However, in tomato foliage, endosulfan concentration also decreased with time, but more rapidly initially and then slowly (**Figure 2**). This deviation of foliage dissipation kinetic from first-order kinetic, with exhibition of biexponential (two-stage) dissipation kinetic, has been often observed for endosulfan (*2*, *18*). Some authors (*2*, *33*) explain this biphasic model through an initial rapid volatilization phase followed by a slower rate of dissipation. The high volatilization rate of endosulfan has been reported from solid surfaces as well as aqueous systems (*20*, *24*, *30*).

Thus, in tomato foliage, dissipation of endosulfan was described by a biphasic model (*32*)

$$C_t/C_0 = a e^{-k_1 t} + (1 - a) e^{-k_2 t} \quad (4)$$

where C_0 is the initial concentration of endosulfan (mg/kg), C_t is the concentration at time t (mg/kg), t is the postapplication time (days), k_1 and k_2 are fast and slow dissipation rate constants, and a is a constant (*32*). Relatively better correlation coefficients were obtained when the dissipation was fitted to two nonlinear phases. **Figure 5** shows the nonlinear relationships together with the values of the statistical parameters calculated for endosulfan parent isomers and total endosulfan using the model. The biphasic shape of endosulfan dissipation curves had earlier been reported by some authors (*2*, *18*, *26*) to describe the two-phase dissipation of pesticides in foliage and soils, when an initial period of fast pesticide loss is followed by a phase of slower dissipation.

To assess the vertical movement of endosulfan, soil core concentrations were measured to judge the pesticide content in different soil layers in relation to the applied amount (**Table 2**). Endosulfan was not detected beyond a 30 cm depth of soil at Akumadan. We attributed this finding to its high soil adsorption coefficient, $K_{oc} = 12400$ [EXTOXNET (http://extoxnet.orst.edu/pips/ghindex.html)], which presumably led to concentrations below the quantification limit in the subsoil layers.

The results of the chemical balance budget (at time $t = 14$ days) after two foliar applications (T2) of endosulfan (total load of 1000 g of ai/ha) as Thionex (35 EC/ULV) formulation indicates that a greater percentage (99.5%) of endosulfan dissipates from a tomato field with only a small percentage (0.5%) remaining on-field 2 weeks after the last spraying (74% in plant and 26% in soil). We suggest that the dissipation occurred through volatilization and degradation of the pesticide in either plants or soil microorganisms. In the study, there was no significant off-site movement of in-furrow irrigation water. Additionally, there was only one small rainfall (11 mm) during the study. Therefore, there was little potential for endosulfan foliar wash-off. As has been discussed in previous sections, the dissipation of endosulfan in foliage is characterized by an initial rapid volatilization phase. In our investigation, endosulfan loss through volatilization was not measured. Several authors (*2*, *34*, *35*) have held the concept that volatilization is a significant route of pesticide loss in the field, particularly when it is applied to the surfaces of soils or plants (*36*), and this may explain how traces of endosulfan have been found in areas never sprayed such as the Artic (*37*) and remote areas around the world (*38*). In a study (*2*) of the fate and transport of endosulfan in an Australian cotton field, the authors found approximately 70% of endosulfan dissipating through volatilization, with only a small percentage (8.5%) remaining on-field a month after four foliar applications of Thiodan ULV (total load of 3000 g of ai/ha). Further studies are needed to quantify volatilization to estimate a total field balance.

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LITERATURE CITED

(1) Shetty, P. K.; Mitra, J.; Murthy, N. B. K.; Namitha, K. K.; Savitha, K. N.; Raghu, K. Biodegradation of cyclodiene insecticide endosulfan by *Mucor thermohyalospora* MTCC 1384. *Curr. Sci.* **2000**, *79*, 1381–1383.

(2) Kennedy, I. R.; Sánchez-Bayo, F.; Kimber, S. W.; Hugo, L.; Ahmad, N. Off-site movement of endosulfan from irrigated cotton in New South Wales. *J. Environ. Qual.* **2001**, *30*, 683–696.

(3) Aguilera-del Real, A.; Valverde-García, A.; Fernandez-Alba, A. R.; Camacho-Ferre, F. Behaviour of endosulfan residues in peppers, cucumbers and cherry tomatoes grown in greenhouse: evaluation by decline curves. *Pestic. Sci.* **1997**, *51*, 194–200.

(4) Antonious, G. F.; Byers, M. E. Fate and movement of endosulfan under field conditions. *Environ. Toxicol. Chem.* **1997**, *16*, 644–649.

(5) Sethunathan, N.; Megharaj, M.; Chen, Z.; Singh, N.; Kookana, R. S.; Naidu, R. Persistence of endosulfan and endosulfan sulfate in soil as affected by moisture regime and organic matter addition. *Bull. Environ. Contam. Toxicol.* **2002**, *68*, 725–731.

(6) Goebel, H.; Gorbach, S. G.; Knauf, W.; Rimpau, R. H.; Huttenbach, H. Properties, effects, residues, and analytics of the insecticide endosulfan. *Residue Rev.* **1982**, *83*, 1–165.

(7) Toxicological profile for endosulfan; U.S. Department of Health and Human Services, Agency for Toxic Substance and Disease Registry, Atlanta, GA, 1990.

(8) Maier-Bode, H. Properties, effect, residues and analytics of the insecticide endosulfan. *Residue Rev.* **1968**, *22*, 2–44.

(9) Schuphan, I.; Ballschmiter, K.; Tolg, G. Zum metabolismus des endosulfans in Ratten and Mausen. *Z. Naturforsch. B* **1968**, *23*, 701–706.

(10) Osafo, S.; Frimpong, E. Lindane and endosulfan residues in water and fish in the Ashanti Region of Ghana. *J. Ghana Sci. Assoc.* **1998**, *1*, 135–140.
(11) Ntow, W. J. Organchlorine pesticides in water, sediment, crops and human fluids in a farming community in Ghana. *Arch. Environ. Contam. Toxicol.* **2001**, *40*, 557–563.
(12) Ntow, W. J. Pesticide residues in Volta Lake, Ghana. *Lakes Reservoirs: Res. Manag.* **2005**, *10*, 243–248.
(13) Amoah, P.; Drechsel, P.; Abaidoo, R. C.; Ntow, W. J. Pesticide and pathogen contamination of vegetables in Ghana's urban markets. *Arch. Environ. Contam. Toxicol.* **2006**, *50*, 1–6.
(14) Ntow, W. J.; Gijzen, H. J.; Kelderman, P.; Drechsel, P. Farmer perceptions and pesticide use practices in vegetable production in Ghana. *Pest Manag. Sci.* **2006**, *62*, 356–365.
(15) Jackson, M. L. *Soil Chemical Analysis*; Prentice Hall: Englewood Cliffs, NJ, 1958.
(16) Day, P. R. Particle fractionation and particle-size analysis. In *Methods of Soil Analysis*; Black, C. A., Ed.; American Society of Agronomy: Madison, WI, 1965; pp 545–567.
(17) FAO/IAEA. *Organochlorine Insecticides in African Agroecosystems*; FAO: Geneva, Switzerland, 1997; pp93–230.
(18) Antonious, G. F.; Byers, M. E.; Snyder, J. C. Residues and fate of endosulfan on field-grown pepper and tomato. *Pestic. Sci.* **1998**, *54*, 61–67.
(19) Gonzalez, M.; Miglioranza, K. S. B.; Aizpún de Moreno, J. E.; Moreno, V. J. Occurrence and distribution of organochlorine pesticides (OCPs) in tomato (*Lycopersicon esculentum*) crops from organic production. *J. Agric. Food Chem.* **2003**, *51*, 1353–1359.
(20) Beard, J. E.; Ware, G. W. Fate of endosulfan on plants and glass. *J. Agric. Food Chem.* **1969**, *17*, 216–220.
(21) Stewart, D. K. R.; Cairns, K. G. Endosulfan persistence in soil and uptake by potato tubers. *J. Agric. Food Chem.* **1974**, *22*, 984–986.
(22) Chopra, N. M.; Mahfouz, A. M. Metabolism of endosulfan I, endosulfan II, and endosulfan sulfate in tobacco leaf. *J. Agric. Food Chem.* **1977**, *25*, 32–36.
(23) Martens, R. Degradation of endosulfan-8,9-^{14}C in soil under different conditions. *Bull. Environ. Contam. Toxicol.* **1977**, *17*, 438–446.
(24) Singh, P. P.; Battu, R. S.; Singh, B.; Kalra, R. L. Fate and interconversion of endosulfan I, II and sulfate on gram crop (*Cicer arietinum* Linn.) in subtropical environment. *Bull. Environ. Contam. Toxicol.* **1991**, *47*, 711–716.
(25) Raha, P.; Banejee, H.; Das, A. K.; Adityachaudhury, N. Persistence kinetics of endosulfan, fenvalerate, and decamethrin in and on eggplant (*Solanum melongena* L.). *J. Agric. Food. Chem.* **1993**, *41*, 923–928.
(26) Kathpal, T. S.; Singh, A.; Dhankhar, J. S.; Singh, G. Fate of endosulfan in cotton soil under sub-tropical conditions of northern India. *Pestic. Sci.* **1997**, *50*, 21–27.
(27) Miglioranza, K. S. B.; Aizpún de Moreno, J. E.; Moreno, V. J.; Osterrieth, M. L.; Escalante, A. H. Fate of organochlorine pesticides in soils and terrestrial biota of "Los Padres" pond watershed, Argentina. *Environ. Pollut.* **1999**, *105*, 91–99.
(28) Donker, M. H.; Eijsackers, H.; Heimbach, F. Ecotoxicology of soil organisms; *SETAC Special Publication Series*, 1994; Chapter 14.
(29) Kimber, S. W. L.; Coleman, S.; Coldwell, R. L.; Kennedy, I. R. The environmental fate of endosulfan sprayed on cotton. *Eighth International Congress on Pesticide Chemistry*; IUPAC: Washington, DC, July 4−9, 1994; pp 1–263.
(30) Guerin, F. G.; Kennedy, I. V. Distribution and dissipation of endosulfan and related cyclodienes in sterile aqueous systems: implications for studies on biodegradation. *J. Agric. Food Chem.* **1992**, *40*, 2315–2323.
(31) Miles, J. R. W.; Moy, P. Degradation of endosulfan and its metabolites by a mixed culture of soil microorganisms. *Bull. Environ. Contam. Toxicol.* **1979**, *23*, 013–019.
(32) Morrica, P.; Fidente, P.; Seccia, S.; Ventriglia, M. Degradation of imazosulfuron in different soils − HPLC determination. *Biomed. Chromatogr.* **2002**, *16*, 489–494.
(33) Ghadiri, H.; Rose, C. W.; Connel, D. W. Controlled environment study of the degradation of endosulfan in soils. In *Challenging the Future*; Constable, G. A., Forrester, N. W., Eds.; Proceedings of the 1st World Cotton Research Conference; CSIRO: Canberra, Australia, 1994; pp 583–588.
(34) Farmer, W. J.; Igue, K.; Spencer, W. F.; Martin, J. P. Volatility of organochlorine insecticides from soil: effects of concentration, temperature, air flow rates and vapor pressure. *Soil Sci. Soc. Am. Proc.* **1972**, *36*, 443–447.
(35) Spencer, W. F.; Farmer, W. J.; Claith, M. M. Pesticide volatilisation. *Residue Rev.* **1973**, *49*, 1–47.
(36) Roger, P. A.; Bhuiyan, S. I. Behavior of pesticides in rice-based agroecosystems: a review. In *Impact of Pesticides on Farmer Health and the Rice Environment*; Pingali, P. L., Roger, P. A., Eds.; Kluwer Academic Publishers: Boston, MA, 1995; pp 111–148.
(37) Jantunen, L. M. M.; Bidleman, T. F. Organochlorine pesticides and enantiomers of chiral pesticides in Artic Ocean water. *Arch. Environ. Contam. Toxicol.* **1998**, *35*, 218–228.
(38) Simonich, S. L.; Hites, R. A. Global distribution of persistent organochlorine compounds. *Science* **1995**, *269*, 1851–1854.

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