Insecticide dissipation from soil and plant surfaces in tropical horticulture of southern Benin, West Africa

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In Sub-Saharan Africa, horticulture provides livelihood opportunities for millions of people, especially in urban and peri-urban areas. Although the vegetable agroecosystems are often characterized by intensive pesticide use, risks resulting therefrom are largely unknown under tropical horticultural conditions. The objective of this study therefore was to study the fate of pesticides in two representative horticultural soils (Acrisol and Arenosol) and plants (*Solanum macrocarpon* L.) after field application and thus to gain first insight on environmental persistence and dispersion of typical insecticides used in vegetable horticulture in Benin, West Africa. On plant surfaces, dissipation was rapid with half lives ranging from 2 to 87 h (α-endosulfan < β-endosulfan < deltamethrin). Soil dissipation was considerably slower than dissipation from plant surfaces with half-lives ranging from 3 (diazinon) to 74 d (total endosulfan), but persistence of pesticides in soil was still reduced compared to temperate climates. Nevertheless, for deltamethrin and endosulfan, a tendency for mid-term accumulation in soil upon repeated applications was observed. The soil and plant surface concentrations of the metabolite endosulfan sulfate increased during the entire trial period, indicating that this compound is a potential long-term pollutant even in tropical environments.

Introduction

For an assessment of the environmental and human safety of pesticide use, it is crucial to elucidate the fate of pesticides in the environment. Pesticide persistence and mobility in soil, for instance, largely determine the risk of groundwater pollution.[1] Extensive research in this field has been conducted in temperate regions, is scarcer for the tropics in general, and is largely missing for Africa in particular.[2] Pesticide dissipation from soil is known to be substantially influenced by climatic conditions and findings established under temperate conditions cannot simply be transferred to tropical environments. Thus, several studies[3,4] found pesticide field half-lives established under tropical conditions to be considerably reduced relative to data from temperate climates, which was attributed to increased volatilization from the soil surface and increased microbial degradation of pesticides in soil, which both are mainly ascribed to higher ambient temperatures in the tropics.[2–4] Pesticide dissipation, and particularly volatilization, from plant surfaces is typically even more rapid than from soil.[5–7] Enhanced volatilization, however, implies a potentially increased dispersion of pesticides in the tropical environment, with the danger of a subsequent deposition in off-site regions after atmospheric transport.[8]

While the overall level of pesticide use in Africa is relatively low,[9] intense pesticide application regimes with minimal compliance with authorization, dosage rates, and prescribed pre-harvest intervals are reported for vegetable production on this continent.[10,11] Missing implementation of pesticide-use legislation and environmental monitoring programs further increase the risk of pesticide misuse. This study focused on small-scale peri-urban vegetable growing in southern Benin, for which prior field diagnoses had specified deltamethrin, endosulfan, and diazinon among the commonly used pesticides in vegetable production.[11,12] Amongst these, only deltamethrin is officially registered in Benin for use on vegetables (Beninese plant protection agency, personal communication). Substantial variations can be observed in pesticide application frequencies (from once in eight weeks to once per week) and application rates (*e.g.* for deltamethrin 44–399 g ha^{-1}, assuming an active ingredient concentration of 12.5 g l^{-1} pesticide formulation) for which overdosing is more common than underdosing (B. James, personal communication).

Although the actual pesticide use may have alarming consequences for farmers' and consumers' health as well as for the environment, comprehensive information on environmental concentrations or fate of pesticides is rare for western Africa. Furthermore, little is known on pesticide volatilization and dissipation rates from plant surfaces in land-use systems of the tropics. A few studies give an overview on concentrations of organochlorine pesticides in soils of Cote d'Ivoire[13] and in water, sediment, and vegetable samples of Ghana.[14,15] The only study related to pesticide dispersion in Benin found an inhibition of the hatching of *Anopheles gambiae* eggs and of the subsequent growth of its larvae in surface water and soil from the largest vegetable growing site in Cotonou, Benin.[16] The authors concluded that probably pesticide residues from agricultural use were responsible for the observed toxic effects. There is no further information available concerning pesticide fate and dispersion in Benin in particular or western Africa in general.

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Therefore, the objective of this study was to investigate the dissipation of selected insecticides (deltamethrin, endosulfan, diazinon, bifenthrin) under typical practice of vegetable growing in southern Benin. Special focus was laid on the soil dynamics of pesticides and their comparison with the ones on plant surfaces.

Materials and methods

Field study

The study area was located in southern Benin, in the greater area of the city of Cotonou. The local climate is classified as a tropical, winter-dry savanna climate with a mean annual temperature of 27.2 °C and a bimodal rainfall which sums up to 1226 mm per year (climate recording of the International Institute of Tropical Agriculture (IITA) station near Cotonou from 1990 to 2006). The field experiments for the present study were conducted from November 2006 to February 2007, *i.e.* during the main dry season. The mean daily minimum temperature during this time was 20.2 °C ± 0.4 standard error (S.E.) and the mean daily maximum temperature was 33.1 °C ± 0.1 S.E. Rain fell on the 17th of February 2007 (17.2 mm), otherwise no precipitation occurred during the study period. The trial was implemented at two sites representing two typical regional soils: a Haplic Acrisol (Udic Kandiustult, AC) at the experimental plots of the IITA in Abomey-Calavi (6°25′N, 2°19′E) and a Haplic Arenosol (Ustic Quarzipsamment, AR) with an intensive history of cultivation and supply of organic amendments at Houéyiho, the biggest commercial peri-urban vegetable production site in Cotonou (6°22′N, 2°23′E) (classification according to WRB[17] and US soil taxonomy,[18] respectively). Table 1 summarizes the basic properties of both soils.

Solanum macrocarpon L. was chosen for cultivation, as it was identified as the dominant local leafy vegetable. In addition, this crop was characterized by inappropriate pesticide applications, being treated up to twelve times with pesticides (mainly insecticides) within the total growth period of ten weeks.[19] The trial was established on fallow soil at the experimental station at IITA and on a vegetable farm at Houéyiho. The dissipation of pesticides from plant surfaces was studied on separate plots to keep the plant canopy intact during the soil dissipation study. Experimental plots were prepared at three replicates at IITA for both trials and at Houéyiho for soil dissipation only. Each plot of *S. macrocarpon* was managed according to local agricultural practices for seed bed preparation, transplanting of seedlings, frequency and quantity of pesticide application, irrigation from the top using watering cans, fertilization, weeding, and harvesting, but plant density was approximately halved to 11 plants m^{-2} as compared to local practice, so that pesticide spray would reach an adequate area of the soil surface during application. Disturbance of the soil was minimized during all cultivation measures; however, occurrence of ponding infiltration and micro-scale erosion could not fully be avoided during irrigation. The latter was done twice daily and total water volume used per day was 5.5 and 10 mm at IITA and Houéyiho, respectively. The mineral fertilizers urea and NPK were used at both sites and compost was used two days after the first pesticide application as an organic amendment at Houéyiho site only. Plants were harvested seven and ten weeks after transplanting by cutting the stems near ground level.

The insecticides bifenthrin, diazinon, deltamethrin, and endosulfan, which is a 7 : 3 mixture of the α- and β-isomers, were used in their locally available commercial formulation. Basic substance properties are provided in Table 2. Among these pesticides, only deltamethrin is officially registered in Benin for use in vegetable cultures. However, vegetable users often disrespect pesticide regulation and consequently the use of all studied pesticides in vegetable cultures has been reported several times from Benin.[12,16,19] Pesticides were applied as a mixture of emulsifiable concentrates using a calibrated backpack sprayer. To minimize application heterogeneities, spraying was done twice in tracks overlapping each other for half of the track width. Application tracks were marked off and a time interval of 10 s was set during which the bed length was sprayed. The beds used to study soil dissipation were treated three times in intervals of ten days, starting four days after transplanting. The beds for plant surface dissipation were treated only once, five weeks after transplanting. Being in the main focus of this study, deltamethrin and endosulfan were used for both trials and applied repeatedly on the beds for soil dissipation (deltamethrin: all applications, 20.1 ± 0.4 S.E. g ha^{-1}; endosulfan: first and second application, 760.3 ± 32.5 S.E. g ha^{-1}). In the soil dissipation trial, diazinon (997 ± 31 S.E. g ha^{-1}) and bifenthrin (50 ± 2 S.E. g ha^{-1}) had to be applied during the third application for reasons of crop protection. Application rates were chosen according to the

Table 1 Properties of the soils under study

Horizon	Depth (cm)	pH (0.01 M $CaCl_2$)	CEC_{pot}[a] ($cmol_c$ kg^{-1} dry soil)	Base saturation (%)	C_{org}[b]	N_{tot}[b]	Texture[c]		
							Sand	Silt	Clay
Acrisol (IITA site)									
A	0–30	6.2	2.9	24	0.65	0.06	89	5	6
B_1	30–90	4.3	3.3	26	0.25	0.03	73	4	23
B_2	90–105	4.4	3.0	23	0.16	0.02	67	6	27
Arenosol (Houéyiho site)									
A	0–15	6.7	3.0	82	0.72	0.07	97	3	0
AC	15–30	6.7	0.5	68	n.d.[d]	n.d.	99	1	0
C	30–90	6.3	0.6	51	n.d.	n.d.	99	1	0

[a] Potential CEC was measured at pH 8.1 with the percolation method according to Mehlich.[41] [b] C and N were analyzed *via* elemental analysis. [c] Texture was determined according to the pipette method of Köhn.[42] [d] Not detectable.

Table 2 Physico-chemical properties and sorption coefficients of the target pesticides[21]

Compound	Water solubility (mg l^{-1})	log K_{ow}	Vapor pressure (mPa at 25 °C)	K_H (Pa m^3 mol^{-1})	K_{oc}[b] (ml g^{-1} OC)	
					Acrisol	Arenosol
Bifenthrin	<0.001	>6.0	0.024	102	>71 200	>62 700
Deltamethrin	<0.0002	4.6	1.24×10^{-5}	0.0313	>71 200	>63 800
Diazinon	60	3.3	12	0.0609	750	1350
α-Endosulfan	0.32	4.7	1.9[a]	1.48	7990	10 600
β-Endosulfan	0.33	4.8	0.09[a]	0.07	11 000	16 700

[a] Source: Sarafin.[43] [b] Sorption coefficient K_d normalized to the organic carbon content of the topsoil, K_d determined for both topsoils in laboratory equilibrium batch experiments in consideration of OECD guidelines.[44]

manufacturer's recommendation, yet were increased for deltamethrin in consideration of local practice. Diazinon was purchased as a combined formulation with bifenthrin and thus it was slightly overdosed to achieve an adequate application rate of bifenthrin.

Soil samples were taken 0, 1, 2, 4, 7, and 10 d after the first and second pesticide application and 0, 1, 2, 4, 7, 10, 13, 16, 24, and 45 d after the third application. From each replicate, five subsamples were taken at random from grid positions using a cylindrical soil auger (8 cm height and 5.5 cm inner diameter), while avoiding double sampling of grid positions. Subsamples were thoroughly mixed before an aliquot was wrapped into aluminum foil and stored in plastic bags on ice until being frozen (< −16 °C) upon arrival at the laboratory within 3 h of sampling. Plant sampling was done immediately before pesticide application (blank matrix) and at 0, 2, 4, 8, 20, 32, and 72 h after application. One sample consisted of six plants per replicate, which were cut at ground level and stored in plastic bags on ice. Upon arrival at the laboratory (<30 min after sampling), the entire plants were cut into smaller pieces (*ca.* 5 cm diameter) which were well mixed before an aliquot was wrapped into aluminum foil, put into a plastic bag and frozen (< −16 °C). All samples remained deep-frozen until sample processing and analysis.

Pesticide analysis

All solvents used were of HPLC grade from J. T Baker (Deventer, the Netherlands); water was purified using a Millipore water treatment system (Molsheim, France). NaCl and anhydrous Na_2SO_4 were of p.a. quality, Na_2SO_4 was activated at 200 °C for 6 h before use. Filters (Schleicher & Schuell 595 ½) were purchased from Schleicher & Schuell (Dassel, Germany) and C18 for flash chromatography (0.04 mm mesh) was obtained from J. T. Baker (Deventer, the Netherlands). Aluminum oxide (Merck, Darmstadt, Germany, 0.063–0.2 mm mesh) and silica (J. T. Baker, Deventer, the Netherlands, 0.063–0.2 mm mesh) were activated at 150 °C for 12 h and then deactivated by adding water (6 and 2%, respectively, w/w) before use. Pesticide standards and the internal standard δ-HCH were purchased from Promochem (Wesel, Germany) at purities >99%. The recovery standard fluorene-d_{10} was obtained from Cambridge Isotope Laboratories (Andover, USA) at a purity of 98%. Pesticide stock solutions were prepared by dissolving the appropriate amount of standard in toluene; working solutions were obtained by dilution of stock solutions with toluene. All standard solutions were kept in amber glass vessels in a freezer at −25 °C. Glassware was rinsed with acetone and ethyl acetate, cleaned in a laboratory dishwasher, and baked at 200 °C for 6 h before use.

Processing of soil samples was carried out according to a method published previously.[20] Plant sample analysis was designed to cover predominantly plant surface residues and was performed according to the following method: The internal standard δ-HCH was sprinkled onto the surface of 2 g of defrosted sample and the solvent was allowed to evaporate before the sample was placed into glass centrifuge jars. Extraction was performed by shaking the plant samples end-over-end for four hours with 40 ml of acetonitrile : water (1 : 1, v/v). Afterwards, the first aliquot of extraction solution was decanted, filtered and transferred into pear-shaped flasks, a fresh aliquot was added and the sample was shaken for another two hours. The combined extracts were then rotary evaporated and the remaining aqueous phase was liquid–liquid-extracted using 60 ml of saturated sodium chloride solution and 25 ml of dichloromethane. The whole procedure was repeated two more times with fresh aliquots of dichloromethane and the combined dichloromethane extracts were again rotary evaporated until only the keeper toluene remained. A clean-up of the extracts was performed using flash chromatography. To this aim, 1 g of aluminum oxide on top of 1 g of silica were wet packed in hexane in 8 ml glass columns. The concentrated sample extract was transferred on the column and washed in using approximately 0.5 ml of hexane. Elution was done with 8 ml of diethyl ether : hexane (1 : 1, v/v) and the eluate was rotary evaporated until only toluene remained. Before transferring the extracts to the autosampler vials, the recovery standard fluorene-d_{10} was added.

Instrumental analysis

For gas chromatography, an Agilent 6890 series GC was used (Agilent, Böblingen, Germany), equipped with a HP 5-MS column (J&W Scientific, USA, length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm). The GC was coupled with an Agilent 5973 inert mass selective detector equipped with an electron impact ion source. Helium was used as carrier gas at a constant flow rate of 0.8 ml min^{-1}. The injector was operated at 250 °C in pulsed splitless mode (pulse time 1 min, pulse pressure 2.5 bar) and the injection volume was 1 μl. The GC oven was programmed as follows: The initial temperature of 85 °C was held for 2.5 minutes. Then, the temperature increased by 20 °C min^{-1} to 290 °C where it was kept for seven minutes. A post-run of five minutes at 300 °C was programmed. The transfer line

temperature was 290 °C and the temperature of the ion source was 230 °C. The MSD was operated in selected ion monitoring (SIM) mode. All calibration standards were prepared in the respective blank matrix to compensate for the instrument's matrix-induced response enhancement. Due to the contamination of the Arenosol blank samples with endosulfan residues, Arenosol samples were also quantified *via* Acrisol matrix-matched calibration standards. Calibration was routinely performed using three- to four-point linear calibration functions showing coefficients of determination ≥ 0.99. With the described method and instruments, routine limits of quantification (RLOQ) were 2.5 μg kg^{-1} dry soil and 25 μg kg^{-1} fresh plant matter for all target compounds. Results were not corrected for extraction method losses (see below).

Statistical analysis

Measured pesticide amounts in vials were converted to concentrations per soil dry weight and plant fresh matter, respectively. The mean concentration of the three replicates and its standard error were routinely calculated. The fitting of model curves to the dissipation data was performed using nonlinear regression (Sigma Plot 9.0, Systat Software GmbH, Erkrath, Germany), which uses the Marquardt–Levenberg algorithm.

First-order functions (eqn (1)) fitted the data in most cases, but sometimes, adding a constant third parameter to the equation (eqn (2)) yielded a better fit.

$$C(t) = C_0 \exp(-kt) \quad (1)$$

$$C(t) = C_1 \exp(-kt) + C_2, \text{ with } C_1 + C_2 = C_0 \quad (2)$$

In these equations, C(t) is the concentration of pesticides still present in the soil at time t, C_0 is the concentration of pesticides at time t = 0, C_1 and C_2 are the fractions of C_0 subjected to the respective dissipation processes and k is the dissipation rate constant. Field half-lives (DT_{50}), *i.e.* the time period in which 50% of the initial pesticide residues have disappeared were calculated from eqn (1) with $DT_{50} = \ln(2)k^{-1}$. For eqn (2), the calculation of DT_{50} was done iteratively. When testing for correlations between pesticide half-lives and pesticides' physico-chemical properties, Spearman's rank correlation was used (Statistica 7, Statsoft, Hamburg, Germany).

Quality assurance

Blank samples were taken of both soils before the experiment in order to assess any pesticide background pollution. The Acrisol proved to be free of the target analytes (<RLOQ for all target compounds) but the Arenosol was found to contain substantial endosulfan residues from former applications. Irrigation water was additionally sampled and minor quantities of all pesticides except deltamethrin were detected, presumably deposited by spray drift. Assuming a bulk density of 1.3 g cm^{-3} soil, this water contamination would correspond to an additional pesticide supply to the sampling layer *via* irrigation water of ≤ 0.07 μg kg^{-1} d^{-1} and was therefore judged negligible.

To validate the analytical methods, recovery experiments (n = 2, fortification at 25 and 250 ppb for soil samples and 100, 1000, and 20 000 ppb for plant samples) were carried out. Recoveries for all pesticides were 90–110% for the Acrisol, 85–100% for the Arenosol (results for endosulfan compounds in the Arenosol calculated from measured value minus mean background contamination) and 85–113% for the plant samples. However, endosulfan–sulfate showed recoveries of 130% in the Arenosol and 160% on plant samples (low spike level). This was probably due to a non-homogeneous bias from the Arenosol's background contamination and to formation of endosulfan–sulfate from α- and β-endosulfan during plant sample processing, respectively. Additionally, overall pesticide recoveries, accounting also for sample handling and transport, were calculated using soil samples that were fortified on-site in Benin (n = 3, fortification at 250 ppb). Overall recoveries ranged from 80% to 103%, and only for β-endosulfan a recovery of 68% was calculated for the Arenosol, presumably again as a result of non-homogeneous bias from this soil's background contamination.

The recovery of the internal standard δ-HCH in the samples was calculated routinely using the recovery standard fluorene-d_{10} and extraction efficiency was judged as normal if recovery of δ-HCH was >80%.

Results and discussion

Dissipation of pesticides from soil

Half-lives of deltamethrin (Fig. 1 and Table 3) ranged from 5.8 to 15 days for both soils and showed a tendency to increase with increasing number of applications. Half-lives pertaining to the Arenosol (mean: 11 d) always exceeded the corresponding values for the Acrisol (mean: 6.9 d). Observed field half-lives of deltamethrin were comparable to those observed for the dissipation from two Brazilian soils (Oxisol: 11.1 d, Arenosol: 11.8 d),[3] yet were considerably reduced compared with those measured in the laboratory (DT_{50} 21–25)[21] or for a Canadian sandy clay soil in a field experiment (DT_{50}: 12–49 d).[22]

Dissipation of endosulfan compounds (Fig. 1 and Table 3) generally proceeded faster for the α-isomer (DT_{50}: 4.8–13 d) than for the β-isomer (DT_{50}: 11–64 d) and faster for the Acrisol than for the Arenosol. The same behavior has been described before in the literature and is presumably due to the higher volatility of α-endosulfan.[23–25] Half-lives of both isomers were elevated by a factor of two for the second application. Endosulfan sulfate, which is often included in the residue calculation as it is the major metabolite of endosulfan on plants[26] and soils[27] and still exhibits toxicity,[28] was obviously more persistent than its parent compounds in our trial. It exhibited increasing concentrations even towards the end of the trial period in the Acrisol (Fig. 1) and reached concentrations of 175 μg kg^{-1} at 55 days after its last application. In spite of information from vegetable farmers about no recent use of endosulfan on our plots, the Arenosol was found to contain high background concentrations of this compound and modeling based on the biased concentrations was not always successful (Table 3). Half-lives of α- and β-endosulfan determined during this trial in the Acrisol were higher than those recorded before in the tropics, *e.g.* for two Brazilian soils (DT_{50} α-endosulfan: 1.7 d)[3] and a Thai Acrisol (DT_{50} β-endosulfan: 4 d),[4] yet were still reduced as compared to laboratory data.[29] Literature values of DT_{50} for endosulfan sulfate range from 99 ± 47 d reported for Australian cotton fields[24] to 151 ± 7 d measured in

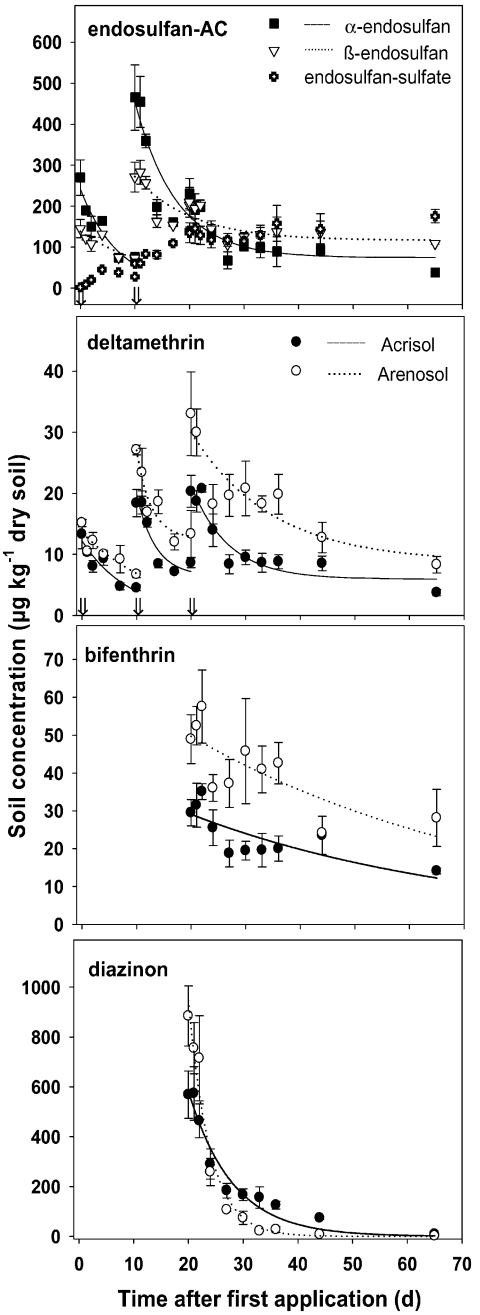

Fig. 1 Pesticide dissipation in soil (n = 3, error bars denote standard errors, ⇓ denotes time of repeated pesticide application, lines represent modeled dissipation).

a laboratory experiment.[29] We can confirm the persistence of this major metabolite in our experiment, observing rising concentrations of endosulfan sulfate until the end of the trial (Fig. 1). We therefore conclude that endosulfan sulfate, and to a lesser degree also β-endosulfan, are potential long-term pollutants in the investigated soils even under tropical conditions.

Dissipation half-lives of bifenthrin were 36 d (AC) and 41 d (AR), thus representing the longest field half-lives of all insecticides in our study. Further data on soil dissipation of bifenthrin in tropical climates were not available, however, DT_{50} in temperate climates ranged from 65 to 125 d.[21] The highest soil concentrations of bifenthrin were measured for both soils on the third day after application (Fig. 1). A similar behavior was observed for a number of pesticides that had been applied on a terrain covered with grass in Thailand[25] and was ascribed to pesticide wash-off by dewfall. Foliar wash-off of pesticides by rain has been reported before,[30] even for poorly water-soluble compounds and with rain setting in several hours after application.[31] We assume that in our study, bifenthrin was also washed off from plants by daily irrigation during the first days after application and soil concentrations thus increased accordingly. The other investigated pesticides supposedly dissipated too rapidly from plant surfaces to produce a similar effect.

Showing field half-lives of 3–6 d in soils, diazinon was the least persistent of all compounds studied. Furthermore, it was the only compound that dissipated faster from the Arenosol than from the Acrisol (Fig. 1 and Table 3), which we attribute to the high vapor pressure (Table 2) and thus volatility of this pesticide. In comparison to the other compounds studied, initial dissipation of diazinon is thought to occur predominantly *via* volatilization, for which the highest rates are measured during the first hour after application.[32] Temperature is a crucial parameter for volatilization and a ten degree increase in soil temperature may result in a 1.8-fold increased volatilization of pesticides applied to moist soil.[5] In our field trial, application at the Arenosol site was conducted onto a darker topsoil and one hour later in the morning than at the Acrisol, both factors leading to higher soil surface temperatures and thus presumably to increased volatilization losses of diazinon at the Arenosol site. In consequence, dissipation of diazinon at our tropical field sites was generally accelerated as compared to dissipation half-lives (11–21 d) measured in the laboratory.[21]

Dissipation of pesticides from plant surfaces

From plant surfaces, α-endosulfan dissipated rapidly and almost completely (DT_{50}: 1.6 h), whereas the initial fast decline of β-endosulfan was followed by a second phase of much slower dissipation, resulting in a half-life of 6.7 h (Table 3, Fig. 2). Endosulfan sulfate did not show a beginning decline during the trial period (72 h) and may therefore be regarded as the main residue component even on plant surfaces. This dissipation pattern was similar to the one described for soil dissipation in this study and to the one observed for the dissipation of endosulfan from cotton foliage in Australia[24] and in tomato leaves in Ghana.[33] The same studies[24,33] quote DT_{50} ranging from 3.9 to 22 h for α-endosulfan and from 22 to 48 h for β-endosulfan and half-lives measured during our study were to our knowledge the shortest published for the dissipation of both isomers from plant surfaces so far. We may conclude that the major part of endosulfan on plant surfaces is lost *via* volatilization during the first 12 h after application under the given experimental conditions, as endosulfan is known to be stable to sunlight.[21] The relative persistence of the metabolite endosulfan sulfate as compared to its parent compounds, which has been reported before,[24,33] was confirmed by our results. Deltamethrin dissipation from plant surfaces led to a half-life of 3.6 d, which means that its dissipation was slightly accelerated in comparison to field data from temperate regions (Canada), where a DT_{50} of 5.1 d was measured on alfalfa plants.[34]

Table 3 Model parameters (standard error in parentheses) of curve fitting, fit quality (R^2) and field half-life of pesticide dissipation from soil and plant surfaces

Compound	Matrix – Application no.	Estimated model parameters C_0 C_1[a] (μg kg $^{-1}$)	C_2	k (d^{-1})	R^2	DT_{50}
Repeated application to soil and single application to plants						
Deltamethrin	AC – 1[b]	12.2	—	0.1133 (0.0266)	0.86[e]	6.1 d
	AC – 2	18.8	—	0.1189 (0.0314)	0.83[e]	5.8 d
	AC – 3	15.3	5.0	0.1462 (0.0529)	0.89[e]	8.9 d
	AR – 1	13.6	—	0.0679 (0.0186)	0.80[e]	10 d
	AR – 2	14.4	12.6	0.3731 (0.1555)	0.89	7.3 d
	AR – 3	21.3	8.7	0.0685 (0.0374)	0.82	15 d
	Plant[c]	1.1	—	0.008 (0.0027)	0.69[e]	87 h
α-Endo-sulfan	AC – 1	242.1	—	0.1435 (0.0342)	0.87[e]	4.8 d
	AC – 2	380.5	74.2	0.1324 (0.0327)	0.85[e]	6.6 d
	AR – 1	350	—	0.0997 (0.0287)	0.79[e]	7.0 d
	AR – 2	488.6	—	0.0526 (0.0067)	0.88[f]	13 d
	Plant[c]	23.7	—	0.4444 (0.0409)	0.99[f]	1.6 h
β-Endo-sulfan	AC – 1	138.5	—	0.0659 (0.0206)	0.76[e]	11 d
	AC – 2	156.1	116	0.0968 (0.0399)	0.75[e]	22 d
	AR – 1	n.m.[d]	n.m.	n.m.	n.m.	n.m.
	AR – 2	436.7	—	0.0108 (0.0046)	0.34[e]	64 d
	Plant[c]	8.6	4.5	0.2172 (0.078)	0.92[e]	6.7 h
Total endosulfan	AC - 1	387.6	—	0.0831 (0.0229)	0.80[e]	8.5 d
	AC - 2	441.7	342	0.1223 (0.0473)	0.76[e]	17 d
	AR - 1	n.m.	n.m.	n.m.	n.m.	n.m.
	AR - 2	1254.2	—	0.0094 (0.0045)	0.28	74 d
	Plant[c]	26.7	10.4	0.4404 (0.0761)	0.98[f]	2.7 h
Single application to soil only						
Bifenthrin	AC	29.2	—	0.0192 (0.0067)	0.57[e]	36 d
	AR	49.7	—	0.0169 (0.0057)	0.59[e]	41 d
Diazinon	AC	582.4	—	0.1247 (0.0158)	0.95[e]	5.5 d
	AR	947.2	—	0.2538 (0.0338)	0.97[e]	2.8 d

[a] C_0 of first order model (eqn (1)), C_1 of modified first order model (eqn (2)). [b] AC – Acrisol, AR – Arenosol, 1, 2, 3 – first, second and third application of pesticides, respectively. [c] C_0, C_1, C_2: mg kg $^{-1}$, k: h^{-1}. [d] Not modeled since curve fitting was not successful. [e] Parameter estimation significant at the 0.05 probability levels. [f] Parameter estimation significant at the 0.01 probability levels.

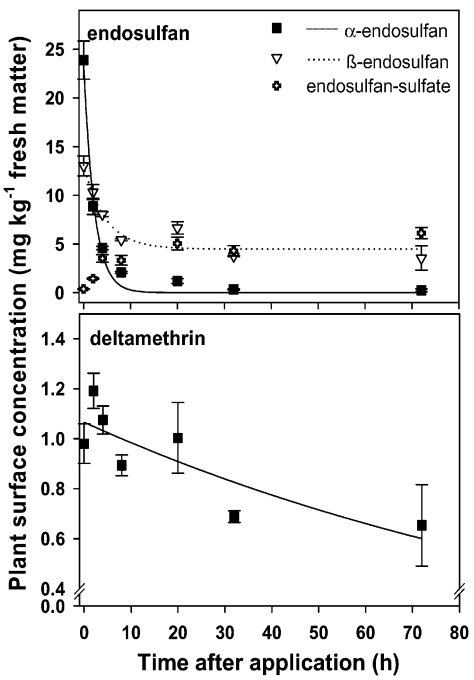

Fig. 2 Pesticide dissipation on plant surfaces (n = 3, error bars denote standard errors, lines represent modeled dissipation).

Comparative discussion

Pesticide field half-lives were in general shortened in comparison with corresponding data from temperate climates and laboratory experiments by a factor of six to ten for most combinations of pesticides and substrates, which is in good agreement with results published for pesticide dissipation from tropical soils of Brazil and Thailand.[3,25] However, half-lives were only reduced by a factor of two to three for bifenthrin from both soils, endosulfan compounds from the Arenosol, diazinon from the Acrisol, and deltamethrin from plant surfaces. Higher volatilization is often held responsible for increased dissipation of pesticides in the tropics[2,25] and the volatilization potential of a pesticide in turn is strongly determined by its Henry's law constant K_H[35] and presumably correlates with its vapor pressure.[32] However, a direct correlation between the observed half-lives and pesticide vapor pressure or K_h could not be established, but existed between DT_{50} and the sorption coefficient normalized to the organic carbon content of the soil K_{oc} (Spearman's R: 0.83). Pesticide adsorption as denoted by K_{oc} is seemingly determining pesticide availability for the sum of all dissipation processes in this environment and thus the overall dissipation rate. This is supported by the observation that dissipation tended to proceed faster from the Acrisol, *i.e.* in the soil showing lower K_{oc} for all pesticides except for deltamethrin and bifenthrin. However, K_{oc}

of the pyrethroids need to be regarded as approximations as they were determined from the routine limits of quantification in batch solutions (Table 2) and thus differences in organic carbon of the two soils account for differences in K_{oc}.

In our study, the accumulation potential of pesticides in soil following repeated applications can be assessed for deltamethrin and endosulfan in the Acrisol. The impact of such practices on microbial pesticide degradation has been discussed controversially in the literature: Adaptation of the microbial community resulting in a faster degradation of pesticides has been suggested[36,37] as well as a build-up of residues that restrains microbial activity and thereby leads to a slower degradation of pesticides in soil.[38] By trend, half-lives increased with increasing number of applications in our study, though comparison of dissipation rates ±S.E. did not reveal substantial differences among the various applications on one soil for both pesticides. However, using the ratio of pesticide concentrations at the end of the last and first sampling period to assess pesticide accumulation[25] after repeated applications reveals a different picture. Accordingly, 300 and 125% of the deltamethrin residues of the first application (10 d after application) were still present in the Arenosol 10 and 45 d after the third application, respectively. For the Acrisol, these values reached 210 and 80%, respectively. For endosulfan, 290 and 50% (α-endosulfan) and 275 and 150% (β-endosulfan) of the residues of the first application (10 d after application) were still present in the Acrisol 10 and 55 d after the second application, respectively, indicating at least a mid-term accumulation potential of both pesticides under the practiced pesticide application regime. More persistent pesticides like bifenthrin, for which repeated applications have also been described,[19] consequently may hold an even greater potential for accumulation.

In general, pesticide dissipation from plant surfaces proceeded considerably faster than from soil (Table 3). This is consistent with findings of earlier studies[6,7] for various compounds and presumably results from augmented pesticide volatilization on plants.[39,32] In our study, $DT_{50soil}/DT_{50plant}$ as a measure of the acceleration of dissipation increased in the following order: deltamethrin < β-endosulfan < α-endosulfan, *i.e.* with increasing vapor pressure and decreasing K_{oc} of the compound. Considering K_{oc} as a measure of substance ability to sorb to the leaf surface, this is in good agreement with findings relating a compound's volatilization from the leaf surface at constant environmental conditions to its vapor pressure and affinity to the lipoid leaf surface.[40]

Deltamethrin residues of 0.6 mg kg^{-1} were measured in *S. macrocarpon* after the recommended pre-harvest interval of three days. These concentrations did not exceed maximum residue levels (MRLs) set by FAO/WHO (2 mg kg^{-1}), yet did not comply with the much stricter European MRLs (0.5 mg kg^{-1}). In part, this was due to the twofold higher than officially recommended application rate of deltamethrin. Yet, the chosen application rate was considered typical for the local horticultural practice (B. James, personal communication) and consequently, health concerns might arise from the consumption of such vegetables. FAO/WHO and European MRLs for the sum of endosulfan (α- + β- + -sulfate) are 0.5 and 0.05 mg kg^{-1}, respectively. Given the fact that (i) concentrations of endosulfan sulfate were still rising after three days (sum of endosulfan compounds at this time: 9.9 mg kg^{-1}), and (ii) dissipation of β-endosulfan apparently had reached a second much slower phase, we speculate that these thresholds might easily be exceeded, even after the 15 d pre-harvest interval prescribed for endosulfan on vegetables *e.g.* in California, and even more so as no official pre-harvest interval exists for the use of endosulfan on vegetables in Benin. Therefore, an application of endosulfan to vegetables in Benin might lead to an unacceptable risk for consumers given the local plant protection practices for *S. macrocarpon*. We conclude that monitoring studies of pesticide residue levels in vegetable products in Benin are urgently required to quantify the exposure of consumers to pesticides *via* this pathway.

Conclusion

In comparison with temperate climates, half-lives of insecticides were reduced by a factor of six to ten for most compounds and matrices, which supposedly resulted from enhanced volatilization, and in part photolysis, under the tropical conditions of this study. For the Acrisol, pesticides may be arranged by increasing persistence as follows: diazinon < α-endosulfan < deltamethrin < β-endosulfan < bifenthrin. For the Arenosol, positions of β-endosulfan and bifenthrin are reversed. Plant surface dissipation proceeded substantially faster than soil dissipation, and endosulfan half-lives on plant surfaces were the shortest reported so far.

As volatilization seemed to exhibit a substantial influence on enhanced pesticide dissipation under test site conditions, we may speculate that adjacent environmental compartments and even remote areas may be exposed to more volatile pesticides in Western Africa *via* atmospheric deposition. Our results furthermore indicated that risks may evolve from accumulation of pesticide residues in soil and on plant surfaces. Further research is thus urgently needed in the field of basic environmental fate and human exposure studies for pesticides in Western Africa under local use conditions. An implementation of a soil and groundwater monitoring program for areas of high vulnerability and pesticide use in Benin is a necessary step to quantify ambient pesticide concentrations and judge related risks for local consumers and the environment.

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