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# Insecticide Dissipation after Repeated Field Application to a Northern Thailand Ultisol

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Nontarget effects of pesticides may occur when the active ingredients have a long persistence in the environment. The half-lives of six insecticides commonly used in Thai fruit orchards under tropical field conditions were determined. A mixture of endosulfan- $\alpha$  and - $\beta$ , chlorpyrifos, malathion, dimethoate, and mevinphos was applied five times in 10-day intervals onto an Ultisol (lychee plantation ground-covered with grass vegetation, northwestern Thailand). On days 1, 3, 5, 7, and 10 after each application, composite samples of the topsoil (0–10 cm) were collected and exhaustively extracted. Fitting a first-order model to the datasets revealed rapid initial dissipation [half-lives from  $2.2 \pm 0.4$  (malathion) to  $5.4 \pm 1.3$  days (chlorpyrifos)]. Volatilization appeared to be a major process of pesticide dissipation, especially for malathion and mevinphos. Because 8% of the applied endosulfan- $\alpha$  and - $\beta$  had been converted to the sulfate metabolite within 1 day after the first application, also microbial degradation contributed significantly to pesticide dissipation. Nevertheless, no trend in half-lives over the five application cycles could be observed, indicating that accelerated microbial degradation did not occur for these insecticides following the five applications. Precipitation and soil moisture were key parameters of dissipation, but dissipation processes were too complex to be generalized for all substances studied. Despite their short half-lives, all pesticides except mevinphos accumulated in soil (up to 656%; endosulfan- $\alpha$ ), and this accumulation correlated significantly with the hydrophobicity of the substances ( $r = 0.88$ ). This was interpreted as an aging process, and it was concluded that pesticide aging must be considered relevant also in tropical environments, where it has received very limited attention so far.

**KEYWORDS:** Field trial; insecticides; organophosphate; organochlorine; persistence; repeated application; Southeast Asia; tropical fruit cropping

## INTRODUCTION

In modern farming, agrochemicals are required to attain sustainable agricultural productivity and to fight insects and other pests (1). This is also true for Thailand, where the cultivation of cash crops is advanced and agricultural products are the most important export goods (2). Because of the high application rates common in Thai agriculture, pesticide residues have been detected widely in soils, surface and ground waters, agricultural products, and even the breast milk of female farmers (3–5). In these studies, organochlorine and organophosphorous pesticides prevailed.

To assess the hazard of ground and surface water contamination by a certain pesticide, its persistence and mobility in soil have to be determined (6, 7). These factors are influenced not only by intrinsic physicochemical properties of the pesticide (e.g., octanol–water partitioning coefficients; 8, 9) but also by biotic and abiotic degradation, microbial biomass, soil pH, and organic matter content as well as concentration of the substance itself (see, e.g., refs 10 and 11). Two of the most crucial controls of pesticide dissipation are soil moisture and temperature (12). Laboratory studies generally do not adequately represent the specific field situation, for example, variable weather conditions, leaching, distinct preferential flow, UV oxidation, and volatilization (13). Consequently, Zabik et al. (14) reported higher dissipation rates of pesticides in the field than in laboratory studies. To determine realistic dissipation rates of pesticides, field studies are therefore necessary (15). However, persistence data from field studies cannot be transferred from one region to another, especially if differences in climate or pedogenic conditions are as substantial as they are between temperate

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regions and the tropics. Nevertheless, pesticide fate in the tropics has rarely been studied (16, 17); the vast majority of studies on the environmental behavior of pesticides focuses exclusively on temperate regions (see, e.g., refs 18–20). Generally, field dissipation half-lives of pesticides in the semiarid and semihumid tropics are shorter than in temperate regions ( $t_{1/2} < 15$  days) (21), because the higher temperatures promote degradation and volatilization of pesticides (22). Data on pesticide dissipation in the humid tropics are almost completely lacking, but dissipation may be, due to better moisture supply, even faster than in dryer tropical environments (compare ref 23). However, rapid dissipation reduces the efficacy of pesticide treatments, so that greater total amounts or higher spraying frequencies than in temperate regions are needed.

Microbial degradation is a major pathway of pesticide dissipation (see, e.g., refs 24 and 25). It is often enhanced after repeated applications (15, 26), because repeated applications may stimulate the growth of microbial populations adapted to the breakdown of specific pesticides (27). Yet, if pesticide applications are repeated so frequently that they result in soil concentrations high enough to have direct toxic effects on the microbial community, half-lives may remain unaffected or even increase (28, 29). To our knowledge, it has never been studied how multiple consecutive applications of insecticides affect pesticide dissipation in the soils of tropical orchards, although, in these systems, repeated treatments are common practice during fruit maturing.

Consequently, the objective of our study was to investigate the influence of repeated applications on the dissipation behavior of selected organochlorine and organophosphorous insecticides in a northern Thai lychee orchard under realistic field conditions. Pesticides were applied in 10-day intervals, and soil was sampled in high temporal resolution in a manner to calculate field half-lives of these pesticides for every sampling cycle. Data were interpreted on the background of physicochemical properties of the pesticides and weather conditions within the application cycles.

## MATERIALS AND METHODS

**Study Area.** We conducted our experiment on a lychee orchard in northern Thailand (18° 53' N, 98° 52' E). The climate of this region is monsoonal with pronounced dry (from November to April) and wet (from May to October) seasons. Mean annual precipitation and temperature are 1600 mm and 21.6 °C, respectively. The elevation of the research site is 800 m above sea level; overall inclination of the westerly exposed slope is about 15°. Due to former rice cultivation about 30 years ago the surface still was terraced with alternating steep and more even sections (“microslopes” and “microplains”, respectively). Lychee trees with an average height of 2.5 m were planted around 10 years ago in a grid of ca. 10 by 10 m. The ground was covered with grass vegetation, which was mowed 2 days before the first application and then every 20 days (between days 7 and 10 of sampling cycles 2 and 4, see below). The soil, which developed on strongly weathered Triassic granites (30), was classified as fine kaolinitic thermic Hapludult (Haplic Acrisol in FAO classification). A more detailed characterization of the soil was given by Ciglasch et al. (31).

**Setup of Research Site.** On the orchard, a 6 by 30 m large area was marked as research site. Soil matrix potential was determined both in microplains and microslopes (see above). Therefore, we installed three tensiometers each in 10 and 45 cm soil depths (12 tensiometers in total) along one of the 30 m long borders of the research plot (Figure 1). To monitor the volumetric water content of the topsoil (0–10 cm), we assigned time domain reflectometry (TDR) measuring points adjacent to the tensiometers (ThetaProbe ML2x, Delta T Devices, Burwell). Additionally, we installed six rain collectors [2.5 L bottles of amber glass with a glass funnel (Ø 14.5 cm) on top]. Each funnel

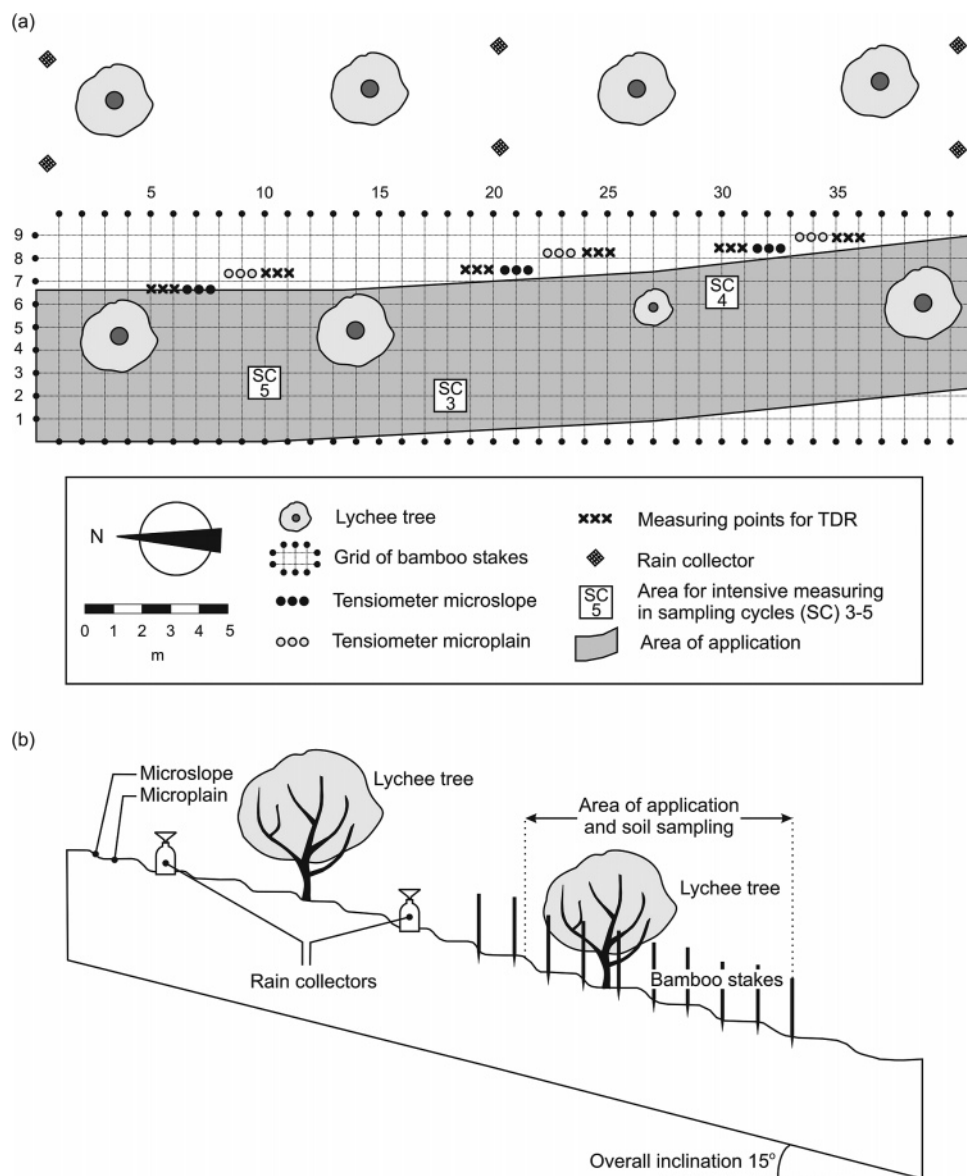
was equipped with a stainless steel mesh to prevent particles from entering the collectors. All instruments were installed adjacent to the area that was to be treated with pesticides, but not on the treated area itself. This was done to avoid contamination of the instruments by pesticides and disturbance of the plot upon reading of the instruments. After this instrumentation, we set up a grid of colored bamboo stakes around the application area to allow orientation during application of pesticides and during soil sampling (Figure 1).

**Pesticide Application and Sampling Strategy.** Beginning on June 19, 2002, a backpack sprayer was used to apply six insecticides in one combined “spraying cocktail” of commercially available formulations directly onto the soil surface (Table 1). Although not an accepted horticultural practice, application of a mixture of several insecticides directly to soils and not the trees enabled a more uniform application method and minimized spray drift. The direct ground application allowed us to spread the pesticides in a reproducible way, especially as straight walking paths for the spraying person had been marked with bamboo stakes (see above). The spray rate was calibrated on the basis of the pace of the applicator required to attain the desired coverage. To assess the quantity of insecticide delivered to the grass surface, six glass fiber filters (GF 6, Ø = 6 cm, Schleicher and Schuell Microscience, Dassel, Germany) were randomly placed on the vegetation before application. Immediately after application, the filters were wrapped in aluminum foil, placed on ice, and brought to the laboratory. There, they were stored at –18 °C until they were transported frozen to Germany for further processing.

Every 10 days the application was repeated; five corresponding sampling cycles (SC1–SC5) were completed. All six insecticides are commonly used by Thai farmers in the study area, and they cover a broad spectrum of physicochemical properties (Table 1). Although the pesticides usually are not applied together in one spraying cocktail, we chose this practice to enable a comparative investigation of insecticide dissipation of six pesticides with different physicochemical properties under the same weather conditions. On our research plot, none of the insecticides had been applied within the past 12 months. The application rates were from ca. 2 (mevinphos) to 6 kg ha<sup>–1</sup> (endosulfan, chlorpyrifos; Table 2). These rates exceeded the recommended rates by a factor of ca. 3–5, which was necessary to ensure initial pesticide concentrations in soil that clearly exceed the limit of detection so that dissipation kinetics could be fitted to the data.

Samples of the topsoil (0–10 cm) were taken with an auger (inner diameter = 3 cm) on days 1, 3, 5, 7, and 10 after each application. Only the inner part of the content of the auger was used, and we thoroughly cleaned the auger before every new use. After the soil samples had been taken on day 10, the subsequent application of pesticides was carried out and the next SC started. Each soil sample consisted of five subsamples. The composite samples were wrapped in aluminum foil, placed on ice, transported to the laboratory, and frozen at –18 °C until further processing. In SC1 and SC2, the individual subsamples were taken at randomly chosen grid points. The grid was defined by the bamboo stakes (Figure 1), and random numbers as coordinates of sampling points had been generated electronically. After the first two SCs, however, we did not continue to collect the subsamples randomly, but took them from “areas of intensive measuring” defined for each sampling cycle SC3–SC5 (size = 1 m<sup>2</sup> each; discussed below). On every sampling day we measured soil matrix potential as well as soil moisture and determined the amount of rainfall that had fallen since the previous sampling.

**Sample Preparation and Analysis of Pesticides.** The filters used to estimate the actual application rate and the uniformity of application were freeze-dried and extracted. The filters were shaken twice with 20 mL of acetone and twice with 20 mL of ethyl acetate (10 min each at 140 strokes per minute) in glass vessels with Teflon-lined screw caps. The extracts were decanted into pear-shaped flasks through glass funnels with glass wool filters. After the funnels had been rinsed with ethyl acetate, a surrogate standard of 5 g of terbutylazine (*N*<sup>2</sup>-*tert*-butyl-6-chloro-*N*<sup>4</sup>-ethyl-1,3,5-triazine-2,4-diamine) in 50 µL of methanol (MeOH) was added to the flasks. Furthermore, we added 150 µL of toluene to prevent the sample from drying up during the following rotoevaporation of the solvents. Thereafter, we washed the residues with ca. 300 µL of toluene into deactivated gas chromatograph (GC)



**Figure 1.** Layout (a) top view (drawn to scale) and (b) cross section (sketch) of sloping plot established in a northern Thailand lychee orchard to determine field half-lives of pesticides repeatedly applied to the soil.

**Table 1.** IUPAC Names and Relevant Physicochemical Properties of Insecticides (53) That Were Repeatedly Applied to a Northern Thai Lychee Orchard in One Combined Spraying “Cocktail”

substance	water solubility (mg L <sup>-1</sup> )	log <i>K</i> <sub>OW</sub>	vapor pressure (mPa)
endosulfan-α [(3α,5α,6α,9α,9aβ)-6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide]	0.33 <sup>b</sup>	4.74	0.83 (20 °C)
endosulfan-β [(3α,5α,6β,9β,9aα)-6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide]		4.79	
chlorpyrifos [O,O-diethyl (O-3,5,6-trichloro-2-pyridinyl) phosphorothioate]	2	4.70	2.7 (25 °C)
malathion [S-1,2-bis(ethoxycarbonyl)ethyl O,O-dimethyl phosphorodithioate]	145	2.75	5.3 (30 °C)
dimethoate (O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate)	24000	0.70	0.25 (25 °C)
mevinphos (1-carbomethoxy-1-propen-2-yl dimethyl phosphate)	cm <sup>a</sup>	0.13	17 (20 °C)

<sup>a</sup> Completely miscible. <sup>b</sup> Value for endosulfan-α + -β.

vials (500 μL). As recovery standard, we added 5 μg of fluoranthene D<sub>10</sub> dissolved in 50 μL of MeOH to the vial. The vials were capped and stored at 4 °C until analyzed.

Although only total soil concentrations were taken into account for this study, we extracted the soil samples sequentially with three solvents of increasing efficiency (32, modified; 33). This was done to investigate field aging of the studied pesticides on the same set of samples in an

upcoming study. Before extraction, the soil was manually homogenized and the gravimetric water content determined. A 10 g oven-dry weight equivalent of soil was weighed in centrifuge tubes with Teflon caps, and 50 mL of 0.01 M CaCl<sub>2</sub> was added. The vials were mechanically shaken for 24 h at room temperature and then centrifuged at 1000g for 10 min. The supernatant was decanted through filter paper (fluted filter 597<sup>1/2</sup>, Schleicher and Schuell) into a solid-phase extraction (SPE)



**Table 2.** Application Rates of Six Insecticides Repeatedly Sprayed on a Lychee Orchard in Northern Thailand<sup>a</sup>

substance	kg (of active ingredient) ha <sup>-1</sup>					mean
	SC1 June 19, 2002	SC2 June 29, 2002	SC3 July 9, 2002	SC4 July 19, 2002	SC5 July 29, 2002	
endosulfan- $\alpha$	4.51 (0.26)	5.14 (0.49)	4.41 (0.50)	4.64 (0.45)	4.84 (0.25)	4.71 (0.18)
endosulfan- $\beta$	2.27 (0.13)	2.56 (0.23)	2.14 (0.24)	2.33 (0.22)	2.35 (0.12)	2.33 (0.09)
chlorpyrifos	5.94 (0.37)	6.83 (0.64)	6.21 (0.76)	6.34 (0.60)	6.76 (0.34)	6.42 (0.25)
malathion	4.02 (0.21)	4.53 (0.42)	4.11 (0.47)	4.18 (0.40)	4.30 (0.23)	4.23 (0.15)
dimethoate	4.27 (0.25)	4.88 (0.49)	4.32 (0.39)	4.76 (0.43)	4.02 (0.21)	4.45 (0.17)
mevinphos	1.79 (0.13)	2.05 (0.27)	1.87 (0.23)	1.99 (0.18)	1.66 (0.10)	1.87 (0.08)

<sup>a</sup> Dates mark the day of application and thereby the beginning of a new sampling cycle (SC 1–5). Data are arithmetic means with standard errors ( $n = 6$  for the individual SCs,  $n = 30$  for the overall mean).

system. This system was composed of 3 mL glass SPE cartridges (Mallinckrodt Baker, Phillipsburg, NJ) with 100 mL reservoirs (amber glass) mounted on top. The solid phase was 300 mg of graphitized nonporous carbon (Carbopack, Supelclean ENVI-Carb SPE Bulk Packing 120/140 mesh particles; Supelco, Bellefonte, PA). The cartridges were conditioned with 5 mL of a mixture of dichloromethane (DCM) and MeOH (9:1 v/v), 2 mL of MeOH, and 15 mL of ascorbic acid [10 mg L<sup>-1</sup>, pH 2, adjusted with 1 M HCl (34, 35)]. After the surrogate standard (5  $\mu$ g of terbuthylazine dissolved in 50  $\mu$ L of MeOH) had been added into the reservoir glasses and the filter rinsed with a surplus of 0.01 M CaCl<sub>2</sub>, the solution was eluted through the column using a vacuum pump (–20 kPa). After elution, the cartridges were dried in a stream of air by increasing the suction to ca. –95 kPa, then wrapped in aluminum foil, and kept at –18 °C until further processing. For re-extraction, we freeze-dried the cartridges and eluted them with 1 mL of MeOH and 6 mL of a mixture of DCM and MeOH (9:1, v/v; 34). The eluate was collected in a pear-shaped flask and spiked with 150  $\mu$ L of toluene as a keeper. The other solvents were rotoevaporated. To exclude residual water from the samples, we inserted an additional drying step. Therefore, we put a plug of glass wool into the outflows of glass funnels, filled the funnels with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and rinsed them with DCM. Afterward, the eluate was transferred onto the salt and thoroughly washed through with DCM. The effluent was collected in pear-shaped flasks, of which the DCM was rotoevaporated once more. The extract was transferred into a GC vial with ca. 300  $\mu$ L of toluene, and the recovery standard (5  $\mu$ g of flouanthene D<sub>10</sub>, dissolved in 50  $\mu$ L of MeOH) was added. Until measurement, the capped vials were stored at 4 °C.

While the SPE was running, the second extraction was conducted with 50 mL of MeOH. The soil pellets that had formed upon centrifugation were resuspended by vigorous manual shaking, and the vials were mechanically shaken for 4 h in the dark. After centrifugation at 1000g for 10 min, the supernatant was filtered through a paper filter into a pear-shaped flask, and the centrifuge vials with remaining soil were put into a refrigerator (4 °C) overnight until further processing. The filters were then washed with MeOH. Afterward, we added the internal surrogate standard (5  $\mu$ g of terbuthylazine dissolved in 50  $\mu$ L of MeOH) and 150  $\mu$ L of toluene as keeper into the flask and rotoevaporated the MeOH. To conduct a liquid–liquid extraction (LLE), we transferred the remaining solution into a separatory funnel, which already contained 5 mL of a saturated KCl solution (ca. 1.5 g of KCl) to promote the transfer of pesticides into the organic phase. Afterward, the flasks were rinsed with 25 mL of DCM, which was also poured into the separatory funnel. The funnels were closed with glass stoppers and shaken horizontally for 10 min before the two phases were allowed to separate for another 10 min. Afterward, the organic (lower) phase was let off into a funnel filled with Na<sub>2</sub>SO<sub>4</sub> as a drying agent; the effluent was collected in a pear-shaped flask. This LLE procedure was repeated twice. Having washed the Na<sub>2</sub>SO<sub>4</sub>-containing funnels with additional DCM, we rotoevaporated the solvent and pipetted the extract into GC vials. Then we added the recovery standard directly into the vials as described above, capped them, and kept them at 4 °C until measurement. The centrifuge vials containing MeOH-extracted soil were filled with 50 mL of a mixture of acetone/ethyl acetate/water (AEW, 9:1:1, v/v/v) on the next day. Further steps of the extraction were carried out analogously to the extraction with MeOH.

Pesticides were analyzed on a GC system with an electron impact mass spectrometer (GC/EI-MSD; 6890-N GC with 5973-N MSD; Agilent Technologies). The column was a HP5-MS (length = 30 m, inner diameter = 250  $\mu$ m, film thickness = 0.25  $\mu$ m; Agilent Technologies) Measuring and quantification were performed according to the procedures of Laabs et al. (36). Briefly, a temperature program from 82 to 280 °C with plateaus at 130 and 160 °C was run (total length = 47 min). The carrier gas was helium (purity = 99.999%) at a constant flux rate (0.8 mL min<sup>-1</sup>). Measurements were conducted in the selected ion monitoring (SIM) mode; quantification was done with the help of the internal standards added to each sample.

**Calculation of Field Half-Lives.** The total quantity of insecticide recovered in the three extracts was summed and the concentration determined on a soil dry weight basis. First-order kinetics were then calculated for all pesticides and sampling cycles using a least-square fit of concentrations versus time (eq 1) using Sigma Plot 7.0 (Jandel GmbH, Erkrath, Germany)

$$c(t) = c_0 e^{-kt} \quad (1)$$

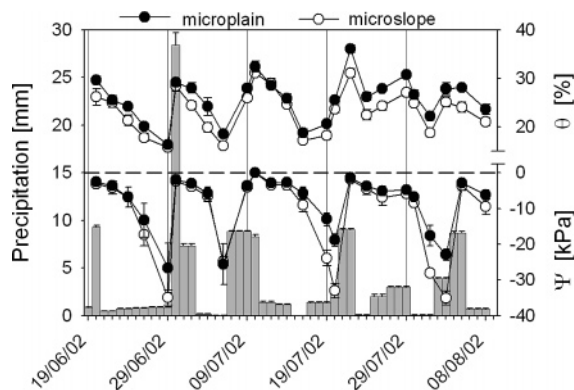
with  $c(t)$  = the concentration of pesticides still present in the soil at time  $t$ ,  $c_0$  = the concentration of pesticides at time  $t = 0$ , and  $k$  = the dissipation rate constant. The quality of the fit was described with the coefficient of correlation  $R^2$ . If  $c(t) = 0.5c_0$ , solving eq 1 for  $t$  yields the field half-life  $t_{1/2}$  (eq 2):

$$t_{1/2} = \ln(2) \times k^{-1} \quad (2)$$

## RESULTS AND DISCUSSION

**Climatic Conditions and Soil Moisture.** Total rainfall in the sampling period (June 19–August 8, 2002) was  $171 \pm 0.6$  mm, which was only ca. 25% of the amount collected in the same period 1 year before (693 mm) (31). Median daily precipitation was 2.7 mm, whereas the arithmetic mean was 6.3 mm, demonstrating the importance of singular heavy rain events. Generally, these heavy rainfalls were separated from each other by several dry days with low or no precipitation. This precipitation pattern resulted in fluctuations of the soil matrix potential  $\Psi$  from –30 to –5 kPa and volumetric water contents from <20 to almost 40% in the 0–10 cm soil depth (Figure 2).

**Variability of Data and Initial Concentration of Pesticides.** The field conditions under which our experiment was conducted can contribute to two kinds of variability: (i) variability of the initial concentration due to heterogeneous application and (ii) spatial variability in pesticide dissipation kinetics. Although heterogeneities in ground vegetation may lead to nonuniform pesticide applications (37), the controls that were placed on the soil surface during applications revealed that the manual spraying was homogeneous and reproducible [standard error (SE) within one application was a maximum of 13.3%; SE between applications was below 5%; Table 2].



**Figure 2.** Precipitation and course of matrix potential  $\psi$  and volumetric water content  $\theta$  in the topsoil (0–10 cm) of an Ultisol in northern Thailand during a study of field dissipation of pesticides, means and standard errors (precipitation,  $n = 6$ ; soil matrix potential,  $n = 3$ ; volumetric water content,  $n = 9$ ). Vertical lines mark the days of pesticide application.

To address spatial heterogeneity, samples were combined from randomly chosen sampling points (see above). In the course of the experiment, however, we observed that the microrelief led to systematic differences in soil moisture: due to higher exposure to sunlight and lower input of rain per area, the micro-slopes were generally drier than the microplains (**Figure 2**). This should directly influence the dissipation of pesticides, because soil moisture is a key parameter for the activity of pesticide-degrading microbes (23), pesticide volatilization (19), and sorption (38). After two sampling cycles, distinct areas of intensive measuring on a microplain were assigned for each of the following three sampling cycles (size = ca. 1 m<sup>2</sup>; **Figure 1**). The microplains were chosen for intensive measuring because they covered a much larger area than the micro-slopes and because pesticide application on an even surface of the microplains can be expected to be more regular than on the micro-slopes. The concentration of soil sampling onto smaller areas improves the comparability of samples taken on different sampling days within a sampling cycle; moving the sampling area from sampling cycle to sampling cycle increases representativeness of the experiment for the whole plot and reduces the risk of influencing the experiment by taking the samples (soil compaction during sampling, creation of artificial “macropores” with the auger).

On the first day after application, the concentrations of the different pesticides in the topsoil (0–10 cm) varied widely, with about 25–40% of the applied dimethoate, chlorpyrifos, and endosulfan ( $\alpha$  and  $\beta$ ) recovered from soil, whereas only 1.6–2.1% of mevinphos and malathion were recovered (**Table 3**). Because the latter two substances have much higher vapor pressures than the other four pesticides studied (**Table 1**), this difference in recovery is mostly due to rapid volatilization in the initial 24 h of large fractions of the applied mevinphos and malathion. Rapid volatilization was favored by the tropical weather conditions under which our experiment was conducted: Volatilization increases with increasing temperature (19) and relative humidity (39), which typically were around 25 °C and 80% during application, respectively (Klaus Spohrer, University of Hohenheim, unpublished data). Furthermore, the ground vegetation of our research plot promoted volatilization because pesticides generally have a lower affinity to plants than to soil (40) and because the stagnant atmospheric boundary layer at the soil surface is thicker than that in the plant canopy (41).

The recovery of the less volatile substances on the first day after application was within the expected range. Racke (42)

reported that initial concentrations of pesticides in soil are ca. 50% of the applied amount. However, according to FOCUS (43), only 10% will be recovered if the soil surface is densely covered with vegetation. Because the rainy season had not yet reached its climax when we conducted our experiments, the ground cover of our research plot was not yet fully developed, so that initial recoveries of pesticides were between the values suggested by Racke (42) and FOCUS (43). The relative recoveries varied from sampling cycle to sampling cycle, which might be partly due to carry-over effects or differences in precipitation within the first 24 h after application (discussed below).

**Dissipation of Pesticides.** After each application of the pesticides, soil pesticide concentrations sharply increased, but decreased again in the course of the subsequent sampling cycle. The dissipation patterns of the different pesticides showed two common characteristics: (i) the highest concentrations of pesticides were not always measured on the first day after application but sometimes after the third day only, and (ii) despite their wide range of physicochemical properties, differences in dissipation from soil were small for the various pesticides we investigated (**Figure 3**, illustrated for endosulfan- $\alpha$  and dimethoate).

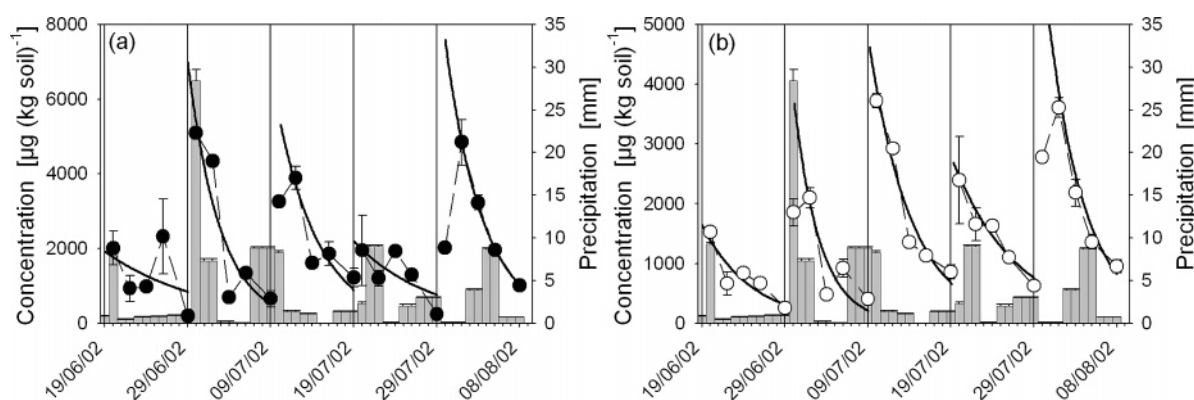
The time lag between application and highest soil concentrations again demonstrates the role of the ground vegetation as a buffer restricting pesticide input to soil. Obviously, precipitation was needed to wash the pesticides from the plant surfaces into the soil. This buffer function of the plant cover is relevant for pesticide fate because volatilization from plants is usually higher than from soil (40, 41). Hence, the precipitation pattern after application influences the scale on which the pesticides affect the environment: If it rains soon after application, the compounds are rapidly washed into the soil. This means that they will mainly act on plot scale, whereas the probability of (air-mediated long-range) transport into remote off-target areas (22, 44) will increase with increasing time between application and wash-off from the plants. It is remarkable, however, that the delayed input of pesticides from plants into the soil did not always coincide with rainfall, which can most clearly be seen at the beginning of sampling cycle 5 (**Figure 3**). Obviously, dewfall was sufficient to transfer pesticides from plants onto the soil, as described by Thompson et al. (45). Yet, because our experiment focused on pesticide dissipation from soil, processes on the plant–soil interface were not studied in detail and are suggested as a topic of upcoming research. The delay between pesticide application and highest concentration in soil had a direct influence on our calculations of field half-lives: whenever we observed this lag, the dissipation kinetics were not fitted from the first, but from the second to the last sampling day within each application cycle.

The dissipation rates of all pesticides in the soil studied were similar in spite of significant differences in their physicochemical properties, as indicated by variations in mean field half-life that were small compared with previous reports in the literature ( $t_{1/2} = 1.4$ –7.2 days). Also, the absolute half-lives were short for all substances, and to our knowledge, we observed the shortest published half-lives of malathion and dimethoate (**Table 4**). We attribute these findings to the humid tropical climate at the experimental site, which increases the probability of rainfall soon after application as well as the total amount of rain. Yet rainfall may affect pesticide concentrations in soil in various ways: Wash-off from plants increases concentrations in topsoil. At the same time microbial activity in moist soil is generally higher than that in dry soil, which promotes pesticide

**Table 3.** Relative Recovery (Percent of Applied) and Concentrations of Repeatedly Applied Insecticides on the First Day of Each Sampling Cycle (SC) in an Ultisol in Northern Thailand (0–10 cm) [Means and Standard Errors ( $n = 2$ )]

substance	$\mu\text{g (kg of soil)}^{-1}$	% of applied <sup>a</sup>	$\mu\text{g (kg of soil)}^{-1}$				
	SC1 June 19, 2002		SC2 June 29, 2002	SC3 July 9, 2002	SC4 July 19, 2002	SC5 July 29, 2002	
endosulfan- $\alpha$	2010 (452)	35.7	5094 (136)	3251 (110)	1951 (942)	2023 (8)	
endosulfan- $\beta$	1076 (168)	38.0	3147 (96)	2658 (171)	1939 (703)	2472 (140)	
endosulfan-sulfate	732 (14)	8.3 <sup>b</sup>	1181 (24)	2202 (250)	2095 (611)	2173 (133)	
endosulfan-lactone	7 (1)	0.1 <sup>b</sup>	42 (3)	26 (1)	39 (10)	113 (1)	
chlorpyrifos	1735 (239)	23.6	3793 (107)	4090 (147)	2230 (857)	2891 (62)	
malathion	107 (11)	2.1	246 (21)	240 (7)	159 (92)	419 (6)	
dimethoate	1527 (9)	28.6	1853 (226)	3722 (116)	2393 (732)	2778 (42)	
mevinphos	37 (9)	1.6	19 (2)	13 (1)	9 (2)	34 (2)	

<sup>a</sup> Bulk density of topsoil:  $0.8 \text{ g cm}^{-3}$  (field estimation); calculated for first SC only because of carry-over of pesticides from SC to SC occurred and because of the lag in pesticide input into soil caused by wash-off from plants (see Figure 3). <sup>b</sup> Based on the sum of applied endosulfan- $\alpha$  +  $\beta$ .



**Figure 3.** Temporal course of concentrations of (a) endosulfan- $\alpha$  and (b) dimethoate in the topsoil (0–10 cm) of a northern Thailand Ultisol after repeated applications. Vertical lines mark the application dates and solid curves the monoexponential dissipation kinetics. Gray bars show the precipitation events during the experiment.

**Table 4.** Field Half-Lives ( $t_{1/2}$ ) of Insecticides in a Repeatedly Treated Tropical Ultisol (Sampling Cycles SC1–5; Dates Refer to the Day of Application)<sup>a</sup>

substance	$t_{1/2}$ (days)						lit.	ref and description
	SC1 June 19, 2002	SC2 June 29, 2002	SC3 July 9, 2002	SC4 July 19, 2002	SC5 July 29, 2002	SC1–5 mean $\pm$ SE		
endosulfan- $\alpha$	nr <sup>b</sup>	2.7 (0.84)	3.5 (0.75)	nr	3.1 (0.95)	$3.1 \pm 0.2$	1.7	(16) Brazil, Ustox
endosulfan- $\beta$	nr	2.9 (0.61)	nr	nr	5.0 (0.84)	$4.0 \pm 1.1$	5.4 <sup>c</sup>	(54) India, sandy loam
chlorpyrifos	nr	2.8 (0.64)	6.1 (0.63)	nr	7.2 (0.82)	$5.4 \pm 1.3$	9.7–12.2 <sup>c</sup>	(26) India, cotton crop soil
malathion	nr	2.6 (0.85)	2.5 (0.93)	nr	1.4 (0.99)	$2.2 \pm 0.4$	0.8	(16) Brazil, Ustox
dimethoate	4.2 (0.76)	2.2 (0.71)	3.5 (0.94)	5.3 (0.70)	3.1 (0.96)	$3.7 \pm 0.5$	12.3	(55) India, loamy sand
mevinphos	2.1 (0.81)	5.3 (0.78)	6.4 (0.89)	1.4 (0.93)	1.4 (0.83)	$3.3 \pm 1.1$	17	(56) tropical conditions simulated in greenhouse, soil pH 6.5
							5.1–7.1	(57) China, loam
							6.7	(58) Japan, Andosol
							11–22	(26) India, cotton crop soil
							1	(59) California, vegetables

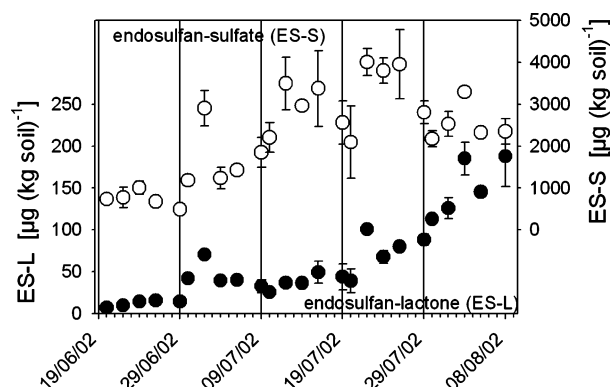
<sup>a</sup>  $t_{1/2}$  values were calculated by fitting monoexponential decay curves to measured soil concentrations. Data were considered to be reliable and are reported here only if the  $r^2$  (given in parentheses for SC1–5) of the fit exceeded 0.60. For comparison, half-lives reported in the literature for field experiments under tropical and subtropical climates are given. <sup>b</sup> Not reliable ( $r^2$  of the monoexponential fitting curve  $< 0.60$ ). <sup>c</sup> Value for endosulfan- $\alpha$  +  $\beta$ .

degradation (12). Excessive rainfall may lead to pesticide leaching or surface runoff (31), which also reduces their concentrations in topsoil. Furthermore, moist soils can (depending on various other boundary conditions and properties of the pesticides) either reduce or enhance the rates of pesticide volatilization (46). Probably, these contrasting effects of rainfall on pesticide dissipation leveled out the differences in dissipation rates between the studied compounds, which probably would have existed under stationary climatic conditions.

An example for the effects of precipitation on the soil concentration of different pesticides is presented in Figure 3:

although the rainstorm of 28.4 mm on June 30, 2002, right after application caused substantial wash-off of the hydrophobic endosulfan- $\alpha$  from plants into the topsoil, the same amount of rain was probably sufficient to leach the more polar dimethoate into deeper soil horizons than investigated in our study. This resulted in a steeper “apparent” increase in the soil concentration of endosulfan- $\alpha$  than of dimethoate. Contrastingly, the much lighter rainfall that occurred after the third application (July 10, 2002) probably washed relatively high amounts of dimethoate into the topsoil, whereas a larger fraction of endosulfan- $\alpha$  than in the second sampling cycle may have remained on the plants.



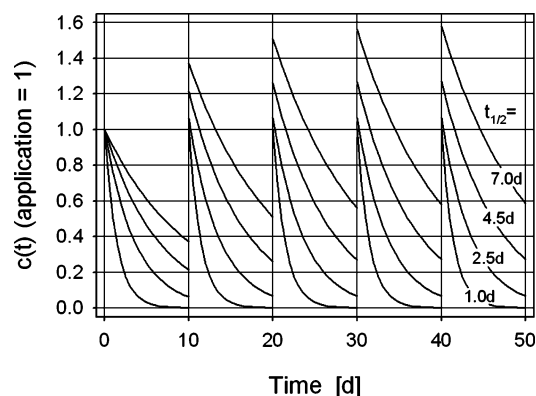


**Figure 4.** Formation of two metabolites of endosulfan, endsulfan-sulfate (○) and endsulfan-lactone (●) in the topsoil (0–10 cm) of a northern Thailand Ultisol. Vertical lines mark the application dates of the parent compound.

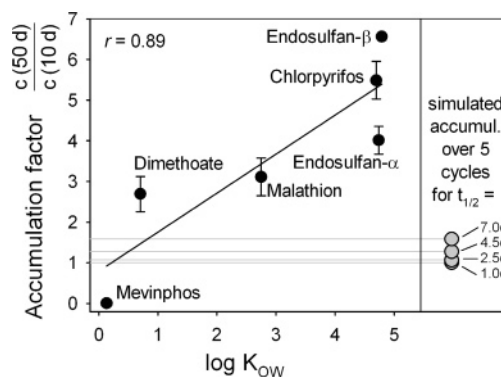
Due to the high relevance of precipitation and other environmental conditions for pesticide dissipation, the effect of microbial adaptation to the degradation of pesticides reported in the literature (see, e.g., ref 15) was completely masked and could not be quantified. Nevertheless, our data clearly indicate that microbial degradation contributed significantly to pesticide dissipation, as both metabolites of endosulfan that we investigated were found in treated soil. Only 1 day after the first application, 8.3% of endosulfan had been converted to endsulfan-sulfate and 0.1% to endsulfan-lactone (Table 3). Whereas the sulfate is a typical microbial metabolite (47), the lactone may also form by photolysis (48). The concentrations of both substances in topsoil increased over time, but the increase was steeper and concentrations fluctuated less for the lactone than for the sulfate (Figure 4). Obviously, the lactone was much more persistent than the sulfate, which is only an intermediate product that underlies further dissipation itself. However, also the half-life of endsulfan-sulfate must be higher than of the parent compound, because, otherwise, it would not accumulate in soil. This is in accordance with the findings of Ghadiri and Rose (49), who reported an accumulation of endsulfan-sulfate in Australian clay soils, and those of Leonard et al. (50), who found that toxicity effects of endsulfan-sulfate in rivers prevail longer than those of the parent compounds.

**Half-Lives and Accumulation of Pesticides.** Because of the multitude of pathways of pesticide dissipation, spatial and temporal variability of environmental conditions, and the small range in field half-lives, we did not observe any correlation between mean dissipation rates of pesticides from topsoil and their physicochemical properties [ $r$  (half-life vs  $\log K_{OW}$ ) = 0.33;  $r$  (half-life vs vapor pressure) = 0.26; not shown].

Therefore, one might come to the conclusion that any pesticide applied to the lychee orchard we worked on will dissipate so rapidly that it will have no adverse effect on off-target ecosystems at all. Yet a comparison between simulated and measured soil concentrations after repeated applications reveals that this conclusion oversimplifies the field situation. If we assumed the field half-lives of two certain pesticides to be 1.4 and 7.2 days, and if these pesticides were applied five times in 10-day intervals, 1 and 61% of one application, respectively, would be present in soil after 50 days (Figure 5). Figure 5 also reveals that the accumulation factor, expressed as concentration at the end of the last sampling cycle divided by the concentration at the end of the first sampling cycle should be 1.01 and 1.60, respectively, for pesticides with field half-lives of 1.4 and 7.2 days. Yet the accumulation factors we calculated



**Figure 5.** Simulation of soil concentrations of pesticides with hypothesized half-lives of 1–7 days after repeated applications in 10-day intervals under the assumption of ideal monoexponential decay.



**Figure 6.** Plot of accumulation of six pesticides in a northern Thailand Ultisol against their logarithmized octanol–water partitioning coefficients after five applications (calculated as concentration at the end of the fifth sampling cycle divided by concentration at the end of the first cycle). For comparison, simulated accumulation factors for pesticides with ideal monoexponential dissipation and half-lives from 1 to 7 days were added in gray (data from Figure 5).

were much higher (up to 6.5, endsulfan- $\beta$ ) for all substances except mevinphos, which fully dissipated in the last sampling cycle, resulting in an accumulation factor of 0 (Figure 6). This means that the monoexponential decay model does not adequately describe the actual pesticide dissipation. Obviously, not all of the pesticides in soil were readily available for dissipation processes. This is in agreement with the literature, where different dissipation kinetics have been suggested for pesticides in different compartments of the soil (e.g., sorbed and in soil solution; 51) or for abiotic dissipation and microbial degradation (52). However, due to the relatively short observation period (five values per sampling cycle), we did not find it reasonable to fit a biexponential dissipation model with four or five free parameters to our data.

The accumulation factors of the individual pesticides closely correlated with their polarities ( $r = 0.89$ ; Figure 6). This means that the deviation from ideal monoexponential decay increased with increasing hydrophobicity of the pesticides. Because hydrophobicity is directly related to binding strength (9), sorption appears to be the major process that determines pesticide accumulation in this tropical soil and deserves further attention.

**Conclusions.** The humid tropical climate promoted pesticide dissipation from the studied Ultisol, so that half-lives were among the shortest published. Pesticide dissipation was influenced by numerous different factors and processes. All of these



had different relevance for the various substances we studied, so that, in total, no differences in dissipation kinetics were observed. Volatilization appeared to be a major pathway of pesticide dissipation, especially for mevinphos and malathion, and it was promoted not only by the high temperatures and relative humidities but also by the ground vegetation. Repeated applications did not affect dissipation rates. Obviously, the weather conditions within the different sampling cycles had a higher influence on pesticide dissipation than microbial adaptation to pesticide degradation, or the microbes already were adapted to pesticide degradation as a result of applications in previous years. However, dissipation was not complete, but increasing accumulation occurred with increasing hydrophobicity of the substances.

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