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Fate of ^{14}C-Labeled Soybean and Corn Pesticides in Tropical Soils of Brazil under Laboratory Conditions

VOLKER LAABS,*,† WULF AMELUNG,† GUNNAR FENT,‡ WOLFGANG ZECH,† AND ROLAND KUBIAK‡

Institute of Soil Science and Soil Geography, University of Bayreuth, 95440 Bayreuth, Germany, and Department of Ecology, SLFA Neustadt/Weinstrasse, Breitenweg 71, 67435 Mussbach, Germany

The dissipation rate of seven currently used soybean and corn pesticides in two tropical soils (Ustox and Psamments) of Brazil was studied in a laboratory incubation experiment. Dissipation half-lives of pesticides ranged between 2 (monocrotofos) and 90 days (endosulfan-β). The contrasting clay contents of the studied tropical soils (130 versus 470 g of clay kg^{-1} of soil) did not influence the dissipation dynamics of pesticides substantially. Mineralization to CO_2 was high [up to 78% of the applied radioactivity (AR)] for the studied organophosphorus compounds and deltamethrin, which also formed considerable amounts of bound residues (>20% of AR) during the 80 days of incubation. The highest portion of nonextractable residues was found for alachlor and simazine (55−60% of AR). In contrast, the nonpolar trifluralin and endosulfan formed only small amounts of bound residues (mostly <20% of AR) but showed the highest dissipation half-lives (>14 days) in the studied soils, also due to a low mineralization rate. When endosulfan-sulfate, as the main metabolite of endosulfan, was considered, the half-life time of endosulfan compounds (sum of -α, -β, and -sulfate) was enhanced to >160 days in both soils. In comparison with the laboratory experiments, dissipation half-life times of chlorpyrifos, endosulfan-α, and trifluralin were shortened by a factor of 10−30 in field trials with the same soils, which was related to the volatilization potential of pesticides from soils.

KEYWORDS: Alachlor; chlorpyrifos; deltamethrin; dissipation; endosulfan; herbicide; insecticide; monocrotofos; persistence; pesticide; simazine; soil; trifluralin; tropical

INTRODUCTION

In the Brazilian *Cerrado* region highly mechanized cash-crop production systems with an intensive use of pesticides are spreading. However, little is known about the fate of these pesticides in representative agricultural soils of this region, such as Oxisols or Psamments. In a recent study, Laabs et al. (*1*) reported short dissipation half-lives (0.6−20 days) for several corn and soybean pesticides in topsoils under tropical field conditions, yet it remains unclear to what degree degradation and/or physical losses contributed to the fast dissipation of pesticides in the field.

The field persistence of pesticides is influenced by many environmental factors (e.g., soil type, climate, and plot exposition) and processes (e.g., degradation, leaching, volatilization, and surface-runoff), which makes a further interpretation of dissipation dynamics difficult. Therefore, the soil dissipation of pesticides is also studied under standardized laboratory conditions to isolate the influences of singular experimental parameters (e.g., soil temperature and soil moisture) on pesticide persistence and to separate the involved dissipation processes, such as chemical degradation, mineralization, and bound-residue formation (see, e.g., refs *2*−*4*). Also, the influence of soil properties (e.g., pH, clay, and organic matter content) on pesticide persistence may be studied in experiments with standardized incubation conditions (see, e.g., ref *5*). Results of such laboratory degradation experiments were frequently used to forecast the dissipation behavior of pesticides under field conditions in pesticide fate modeling (*6*, *7*).

The use of ^{14}C-labeled pesticides in laboratory experiments enables a quantification of pesticide dissipation pathways, such as mineralization, metabolization, and bound-residue (= nonextractable residue) formation of pesticides (see, e.g., refs *2* and *8*). Moreover, it provides an effective tool for an overall quality control of the used analysis methods, by calculation of a material balance for every incubation system. This is possible because the substance-derived radioactivity of pesticides can also be measured as $^{14}CO_2$ (stemming from a complete degradation of the labeled C structure), as radioactive metabolites (representing intermediate degradation products of the parent compounds), and as residual soil radioactivity (belonging to soil-bound pesticide residues of unknown structure). Whereas the mineralization of pesticides to CO_2 is a clearance pathway, the formation of nonextractable residues in soils is a possible sink

* Address correspondence to this author at Covance Laboratories GmbH, Am Kesselfeld 29, 48163 Münster, Germany (telephone +49-251-9798215; fax +49-251-784697; e-mail volker.laabs@covance.com).
† University of Bayreuth.
‡ SLFA Neustadt/Weinstrasse.

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Table 1. Basic Properties of Incubated Soils

soil type	texture (g kg^{-1}) clay	silt[a]	sand	organic carbon (g kg^{-1})	pH (1 M KCl)	CEC_{pot}[b] (mmol$_c$ kg^{-1})	microbial biomass[c] (mg of C kg^{-1})	WHC[d] (g of H_2O g^{-1})
Ustox	470	30	500	22.1	5.1	152	131	0.45
Psamments	130	10	860	9.1	4.2	44	61	0.32

[a] Silt fraction: 2–20 μm. [b] Potential cation exchange capacity determined in 1 M ammonia acetate. [c] Determined according to the method of Anderson and Domsch (*20*) after a 7-day incubation of remoistened soil. [d] Water-holding capacity of soils.

Table 2. Basic Properties of Studied Pesticides[a]

pesticide	labeled position	water solubility (mg L^{-1})	lg K_{OC}[b] (mL g_{OC}^{-1}) Ox	lg K_{OC}[b] (mL g_{OC}^{-1}) Ps	vapor pressure (mPa) (25 °C)
alachlor	*ring*-UL-^{14}C	170	2.3	2.4	2.0
chlorpyrifos	2,6-^{14}C	1.4	3.9	4.1	2.7
deltamethrin	*gem-dimethyl*-^{14}C	0.0002	4.9	5.3	0.00001
endosulfan	6,7,8,9,10-^{14}C	0.32	3.8	4.1	0.83[c]
monocrotofos	(*O-methyl*-^{14}C)$_2$	1000000	1.7	1.6	0.29
simazine	*ring*-UL-^{14}C	6.2	2.4	2.5	0.003
trifluralin	*phenyl*-UL-^{14}C	0.22	3.9	4.4	6.1

[a] According to Tomlin (*50*). [b] Sorption coefficient of pesticides on soils (*1*) normalized to the organic carbon content (OC) of soils (Ox, Ustox; Ps, Psamments). [c] Determined at 20 °C.

for pesticides in the soil compartment after application. However, in some studies such initially bound residues have been remobilized after a subsequent inoculation of the extracted soil with microbes or earthworms (see, e.g., refs *9* and *10*), and it has been shown that a portion of these freed residues may still be the unaltered active ingredient (reviewed in ref *11*). The formation of high portions of bound residues is therefore seen as an undesirable property of agricultural pesticides, and an upper limit of bound-residue formation (70% of applied pesticide radioactivity within 100 days) was established for registration purposes in the European Community (*12*).

The fate of pesticides in tropical soils under laboratory conditions was investigated for some compounds (see, e.g., refs *13*−*15*), which showed similar dissipation dynamics as known from temperate soils, yet until now no comparative studies with tropical soils using several pesticides were conducted. Moreover, comparative data on laboratory and field dissipation times in the tropical soil environment are still lacking.

The objective of this study was an assessment of the pesticide degradability and bound-residue formation in two contrasting agricultural soils of tropical Brazil (Ustox and Psamments) under laboratory conditions. To this aim a laboratory incubation of soils at near optimum moisture conditions for microbial degradation was conducted, which is also required as a trigger experiment regarding the degradability of pesticides in soils during pesticide registration procedures (*16*). Furthermore, the dissipation rates of pesticide parent compounds in the laboratory experiment were compared to field data to assess the influence of field conditions on pesticide persistence.

MATERIALS AND METHODS

Soils. The studied soils were collected from a farm 110 km in the southeast of Cuiabá, Mato Grosso State, Brazil (15° 53′ southern latitude, 55° 16′ western longitude, 800 m above sea level). Samples (0−10 cm) of fine-clayey, mixed, isohyperthermic Typic Haplustox and acid, isohyperthermic Ustic Quartzipsamments (according to ref *17*), corresponding to a Latossolo Vermelho-Amarelo and an Areia Quartzosa in the Brazilian classification system (*18*), were collected from three plots, each located within a 2 km^2 area, and pooled after air-drying and sieving (2 mm) into composite samples. Basic soil characteristics are presented in **Table 1**. Ustox sites had been under a corn−soybean−pasture rotation, whereas Psamments samples were collected from areas that had been used as pasture (degraded) during the past 5 years. Soil samples were stored air-dry in plastic bags (at 15−20 °C) for 4 months until used in the experiment.

Pesticides. For this laboratory study, seven pesticides were chosen, representing a wide spectrum of chemical classes (e.g., triazines, acetanilides, and pyrethroids) and polarities. Radioactive-labeled pesticides were courteously supplied by Aventis CropScience (Frankfurt/Main, Germany) and Dow AgroSciences (Indianapolis, IN), or purchased from Sigma-Aldrich (St. MO) or Promochem (Wesel, Germany). Basic properties and labeling positions of pesticides are presented in **Table 2**. Pesticide stock solutions were prepared in acetone, and their purity was evaluated using thin-layer chromatography (TLC). For all substances, purity was >96% of the applied radioactivity (AR). If necessary, pesticide solutions with too high specific radioactivity were diluted with non-radioactive pesticide solutions to achieve the intended radioactivity level in the application solution.

Incubation Procedure. The soils were equilibrated at 35% of their water-holding capacity (WHC) in open containers in the dark for 7−9 days (at 25 °C) to revitalize and equilibrate the microbial activity of soils before incubation. Under natural field conditions the soils dry out for 3−4 months per year (dry season) and are remoistened only at the beginning of the rainy season, which coincides with the time of the application of most pesticides. Hence, in the incubated soils the microbial community was subject to similar moisture conditions as in the field during the application season. However, for some compounds the soil storage period and the limited nutrient supply in the incubated soil units are known to cause smaller soil degradation rates than in field fresh soils (e.g., reviewed in ref *7*).

Erlenmeyer flasks were used as incubation systems, which were equipped with a soda−lime CO_2 trap at the top (**Figure 1**). Into the lower end of the glass tube was packed 1 g of paraffin-coated glass wool (0.1 g of paraffin oil g^{-1} of glass wool) to adsorb any volatile organic compounds evolving during the incubation. In the upper part, 14 g of soda−lime pellets was used to trap the $^{14}CO_2$ stemming from pesticide mineralization. The systems were sealed airtight at the connection, so that an air exchange with the surroundings was possible only through the soda−lime trap.

The application of pesticides to the soils was achieved by adding 100−400 μL of stock solution to a portion of air-dry soil (equaling 10 g of oven-dry soil mass) in the Erlenmeyer flasks. After evaporation of the acetone, moist preincubated soil (representing 90 g of oven-dry soil mass) was added to the Erlenmeyer flasks and was thoroughly mixed with the treated soil portion. Finally, the soil moisture of the incubated sample was adjusted to 40% of its WHC by adding distilled water drop by drop. The test vessels were incubated at 30 ± 1 °C in

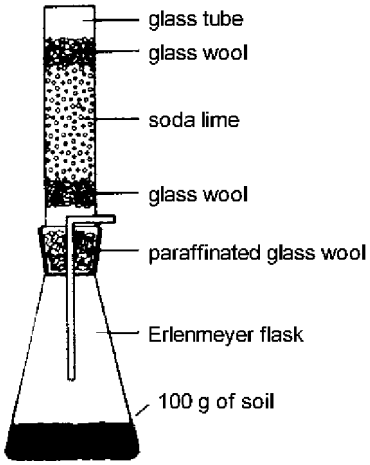

Figure 1. Soil incubation system (modified according to ref *8*).

the dark. The soil moisture content was regularly controlled by weighing the incubation systems. A readjustment of the soil moisture (40% ± 4% WHC) was done every week by adding distilled water to the soil, after the incubation systems had been purged with air (1 min) to trap any $^{14}CO_2$ in the system air phase.

Pesticides were added to the soil according to their maximum dosage of active ingredient (AI) recommended in agriculture: alachlor, 3360 g ha^{-1}; chlorpyrifos, 1500 g ha^{-1}; endosulfan, 1000 g ha^{-1}; monocrotofos, 1100 g ha^{-1}; simazine, 2000 g ha^{-1}; and trifluralin, 1600 g ha^{-1}. Only deltamethrin was used at a 10-fold higher application rate (300 g ha^{-1}), due to its low radioactivity in soil at the recommended rate. In consideration of the sampled soil layer (0−10 cm), the application rates resulted in initial soil concentrations in the experiment of 0.30−3.36 mg kg^{-1} in the Ustox (soil bulk density in the field of 1.00 g cm^{-3}) and 0.24−2.69 mg kg^{-1} in the Psamments (1.25 g cm^{-3}) for the different pesticides.

Sampling and Analysis. At 0, 2, 4, 8, 18, 28, 50, and 80 days after application, incubation systems were sampled to determine the radioactivity in the soil extract, glass wool, soda−lime, and extracted soil. For deltamethrin sampling was done only at 0, 4, 10, 30, and 80 days of incubation, as its apparent inertness in the soil compartment (no leaching, low volatility; see also ref *1*) did not necessitate a high-resolution determination of its soil dissipation. To evaluate the variability of pesticide dissipation in our experiment, replicate incubation systems were sampled at 0, 8, and 80 days after application (for deltamethrin, 0 days). Each sampled incubation system was purged with nitrogen (1 min), and the Erlenmeyer flasks and glass tubes were then frozen (−25 °C, <10 days) until further analysis.

The complete soil sample was extracted by shaking it two times with a mixture of acetone/ethyl acetate/water (150 mL; 2:2:1, v/v/v) for 2 h each. The extraction method was adopted from that of Laabs et al. (*19*), who showed that the used solvent mixture was able to extract the studied pesticides exhaustively from tropical Oxisols (recovery of >85% of the spiked amount using one extraction step). An aliquot of the centrifuged (5000 rpm, 10 min) and pooled extracts was mixed with scintillation cocktail (Ultima Gold XR, Packard, Meriden, CT) and analyzed by liquid scintillation counting (LSC) with automated quench correction (Tri-carb 2300 TR, Packard, Groningen, The Netherlands). The portions of metabolites and parent compounds in the soil extract were determined by TLC analysis using silica plates (Silica Gel 60 F_{254}, layer thickness = 0.25 mm, Merck, Darmstadt, Germany) and *n*-hexane/ethyl acetate 1:1 (v/v) for alachlor, *n*-hexane/toluene 1:1 for chlorpyrifos, toluene/cyclohexane 7:3 for deltamethrin, *n*-hexane/acetone 9:1 for endosulfan and endosulfan-sulfate, acetonitrile/water 3:2 for monocrotofos, *n*-hexane/acetone 1:1 for simazine, and *n*-hexane/acetone 3:1 for trifluralin as mobile phase. The spatial distribution of radioactivity on the TLC plates was measured and integrated by an Instant Imager Analyzer (Packard, Groningen, The Netherlands). Parent compound and endosulfan-sulfate radioactivity was identified by comparing the retention factors of TLC-developed standards with radioactivity spots from chromatograms of soil extracts. All organic solvents used were of Baker-analyzed grade (Baker Chemikalien, Gross-Gerau, Germany). After extraction, each soil sample was dried and ground, and an aliquot was combusted in a Biological Oxidizer (Ox500, Zinsser Analytic, Frankfurt/Main, Germany). The evolved $^{14}CO_2$ was trapped in a scintillation cocktail and analyzed by LSC.

A concentration of soil extracts before LSC and TLC analysis was not necessary, as sufficient radioactivity was extractable from the soils. Exceptions were alachlor and monocrotofos, for which the soil extracts of the sampling dates 28, 50, and 80 days after application had to be concentrated with a rotary evaporator before further analysis. An evaluation of the concentration step showed that this process did not result in a loss of radioactivity or a shift of substance metabolization pattern for these two compounds.

The paraffinated glass wool was extracted with 40 mL of acetone during a 1 h shaking period. An aliquot of the extract was then mixed with scintillation cocktail and analyzed by LSC. To release the bound $^{14}CO_2$, the soda–lime was dissolved in a closed system with 70 mL of 6 M hydrochloric acid (modified according to ref *8*). The evolving gas was purged with CO_2-free air through three subsequently installed vessels filled with a mixture of liquid adsorbent cocktail [mixture of Carbosorb E/Permafluor E$^+$ 1:1 (v/v); Packard, Groningen, The Netherlands]. The three trapping solutions were analyzed by LSC. The efficiency of this method was controlled by LSC-analyzing the remaining acidified solution (adding Ultima Gold AB as scintillation cocktail; Packard, Groningen, The Netherlands) and by measuring the portion of radioactivity in the trapping vessels (possible breakthrough of $^{14}CO_2$). Radioactivity found in the acidified solution was always <0.5% of the applied amount, and the portion of radioactivity measured in the third trapping vessel was in all cases <1% of the amount found in the first vessel, indicating that the released $^{14}CO_2$ was quantitatively trapped during the process.

The limit of quantification of radioactivity in all LSC extracts (e.g., of the soil, the paraffinated glass wool, the soda−lime extract, and the soil combustion) was determined to be ≤0.1% of AR for all compounds, which corresponds to a soil concentration of 0.2−2.7 μg of AI/kg of soil (dependent on the initial soil concentration). The microbial biomass of the studied soils was determined in blank samples corresponding to 0 and 80 days after application (two replicates each) according to the method of Anderson and Domsch (*20*).

Statistical Analysis. Models were fitted to the dissipation data with the help of the Sigma Plot for Windows software package, version 4.01 (Jandel GmbH, Erkrath, Germany), which uses the Marquardt−Levenberg algorithm for parameter estimation. Special attention was paid to avoid overparametrization of models. When possible, curve fitting was done with weighting data-to-model variances by y^{-2} to account for generally smaller deviations of data from the model with increasing time after application. For linear regression and correlation the Spearman and Pearson Product Moment correlation of the software package Statistica for Windows, version 5.1, was used (Jandel GmbH).

RESULTS AND DISCUSSION

The incubation conditions were adopted from recommendations made for studies on pesticide persistence in soils by European regulatory institutions (*16*). Consequently, the soil was incubated in the dark at 40% of its WHC, which is considered to be a suitable soil moisture level for biochemical degradation studies (*16*). However, to take into account higher average soil temperatures in the tropics, the incubation temperature was set at 30 °C. This was approximately the average daily temperature of the topsoil layer (5−15 cm) measured during field experiments in these soils in Brazil (*1*). The microbial biomass of soils after the pre-equilibration phase (131 ± 3 and 61 ± 0 mg of microbial C kg^{-1}) was slightly higher than the one determined at the end of our incubation experiment (116 ± 6 and 43 ± 0 mg of microbial C kg^{-1} for Ustox and Psamments, respectively). Presumably, a beginning substrate limitation caused this decline of microbial biomass, which was frequently reported for laboratory soil incubation experiments (*7*).

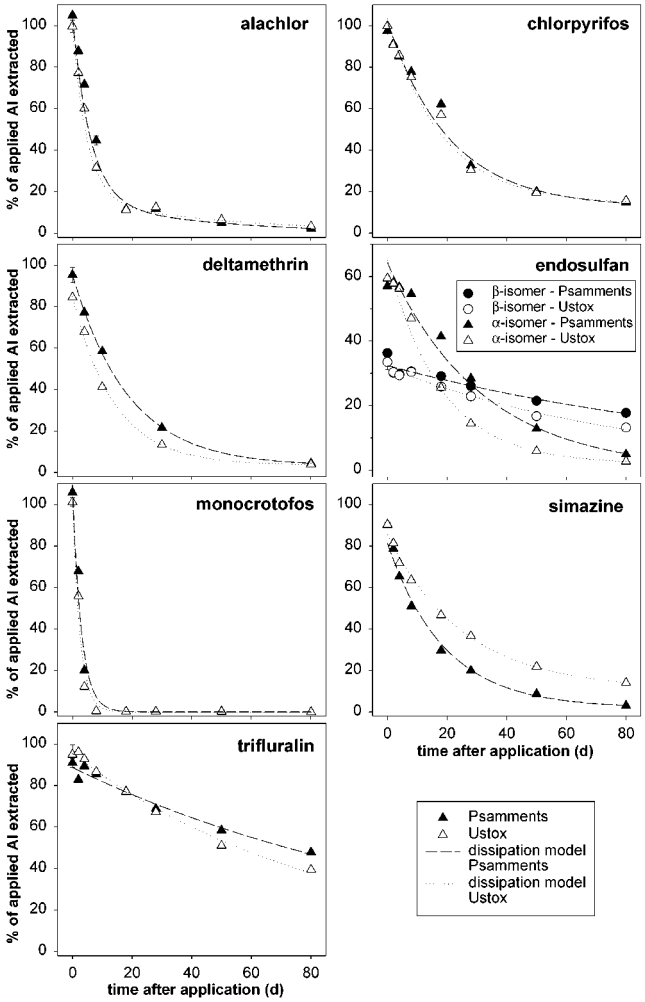

Figure 2. Dissipation of pesticide active ingredient in soils. Error bars (at 0, 8, and 80 days; for deltamethrin at 0 days) denote range of two replicates (for model parameters see **Table 3**).

The average radioactivity balances for the incubation systems were 101% of AR for alachlor, 103% for chlorpyrifos, 90% for deltamethrin, 98% for endosulfan, 96% for monocrotofos, 94% for simazine, and 94% for trifluralin, indicating the validity of the measured data. Replicate differences of the amounts of radioactivity found in the extracted, mineralized, and bound pesticide portions were always <5% of the AR except for monocrotofos in Psamments at 80 days after application, where replicates of the mineralized and bound portion differed by 10% of AR. The extraction efficiency of the used solvent mixture was proven by a high recovery of pesticides from the contaminated soils on 0 days after application (>90% of AR, see **Figures 2** and **3**).

Modeling of Pesticide Dissipation. Pesticide dissipation (percent of AR extracted and identified as AI) was described using a biexponential model as basis. The biexponential model implies that an initial phase of fast pesticide dissipation is followed by a second phase of slower dynamics (*21*). Only the dissipation of alachlor strictly adhered to the biexponential model (**Table 3**; **Figure 2**). Pesticides of intermediate persistence [dissipation half-life (DT_{50}) between 10 and 30 days] followed a monoexponential model with a second, seemingly constant, fraction not yet contributing to the overall pesticide dynamics during the study period. The degradation rate constants of fractions C_2 (see **Table 3**) were not statistically significant when fitted to the data and would need a longer incubation period to gain statistical significance. The dissipation of the most persistent pesticides (endosulfan compounds and trifluralin) followed a pure monoexponential model. This was due to the slow disappearance dynamics of these pesticides, which led to the dominance of their initial dissipation phase throughout the entire incubation period. Monocrotofos showed the fastest dissipation of all compounds (DT_{50} of 2 days), but its disappearance did not decelerate. Therefore, the dissipation of this pesticide could also be modeled by a simple monoexponential function, which adequately described the near complete dissipation of AI until 8 days after application (**Figure 2**).

In samples of Ustox the dissipation half-life times (**Table 3**) increased in the order monocrotofos < alachlor < deltamethrin < endosulfan-α < chlorpyrifos < simazine < trifluralin, endosulfan-β < endosulfan-sum (endosulfan-sum = endosulfan-α + endosulfan-β + endosulfan-sulfate). A similar dissipation ranking of pesticides was observed in Psamments except for simazine, which was substantially less persistent, and except for endosulfan-α, which persisted longer in the sandy soil. The half-life times of pesticide AI were similar in the two studied soils for alachlor, chlorpyrifos, and monocrotofos (**Figure 2**; **Table 3**). The DT_{50} of endosulfan compounds, trifluralin, and deltamethrin was 1.3−2.4 times shorter in Ustox than in Psamments. The faster degradation of these more persistent compounds in the Ustox was presumably caused by a higher microbial activity in the clayey soil. The short lag-phase observed for the dissipation of endosulfan and trifluralin, especially in Psamments during the first days of incubation, might also be related to an initially slower degradation due to limited microbial activity (*6*). Simazine was the only pesticide that persisted longer in the Ustox than in the sandy soil (DT_{50} = 27 vs 14 days), which was caused by an increased metabolization of simazine in the more acidic Psamments (**Figure 3a**). A fast dissipation of triazines in acid soils was also reported by Diaz Diaz et al. (*5*) and Blumhorst and Weber (*2*), the latter observing an increased chemical degradation of atrazine to hydroxyatrazine in such soils. The β-isomer of endosulfan was more persistent in both soils than the α-isomer, remaining in higher soil concentrations since 1 month of incubation, despite its lower application rate (the used standard mixture comprised 69% endosulfan-α and 31% endosulfan-β). The metabolite endosulfan-sulfate was included into the sum of endosulfan compounds for modeling purposes (**Table 3**) because of its known biological activity (*22*). Taking endosulfan-sulfate into consideration, the sum of endosulfan compounds exhibited the highest dissipation half-life time of all pesticides in both soils (>160 days).

Pesticide Dissipation Pattern. The volatilization of the herbicide trifluralin was highest of all pesticides in our experiment, resulting in losses of 4 and 13% of AR in Ustox and Psamments, respectively. The polar herbicides alachlor and simazine exhibited only a negligible volatilization of <0.1% of AR within the 80 days of incubation. Of the investigated herbicides, alachlor and simazine both showed a fast and substantial formation of bound residues during the incubation period, with >55% of the AR bound at 80 days after application in both soils (**Figure 3a**). This process was not that much pronounced for trifluralin, of which only 28 and 14% of AR were not extractable from Ustox and Psamments, respectively, after the 80 days of incubation. A significant mineralization of herbicides to CO_2 occurred only after 18 days of incubation (>1% of AR), leading to similar amounts of alachlor and trifluralin mineralized in both soils (6−12% of applied AR). In contrast, simazine mineralized less rapidly in Psamments as

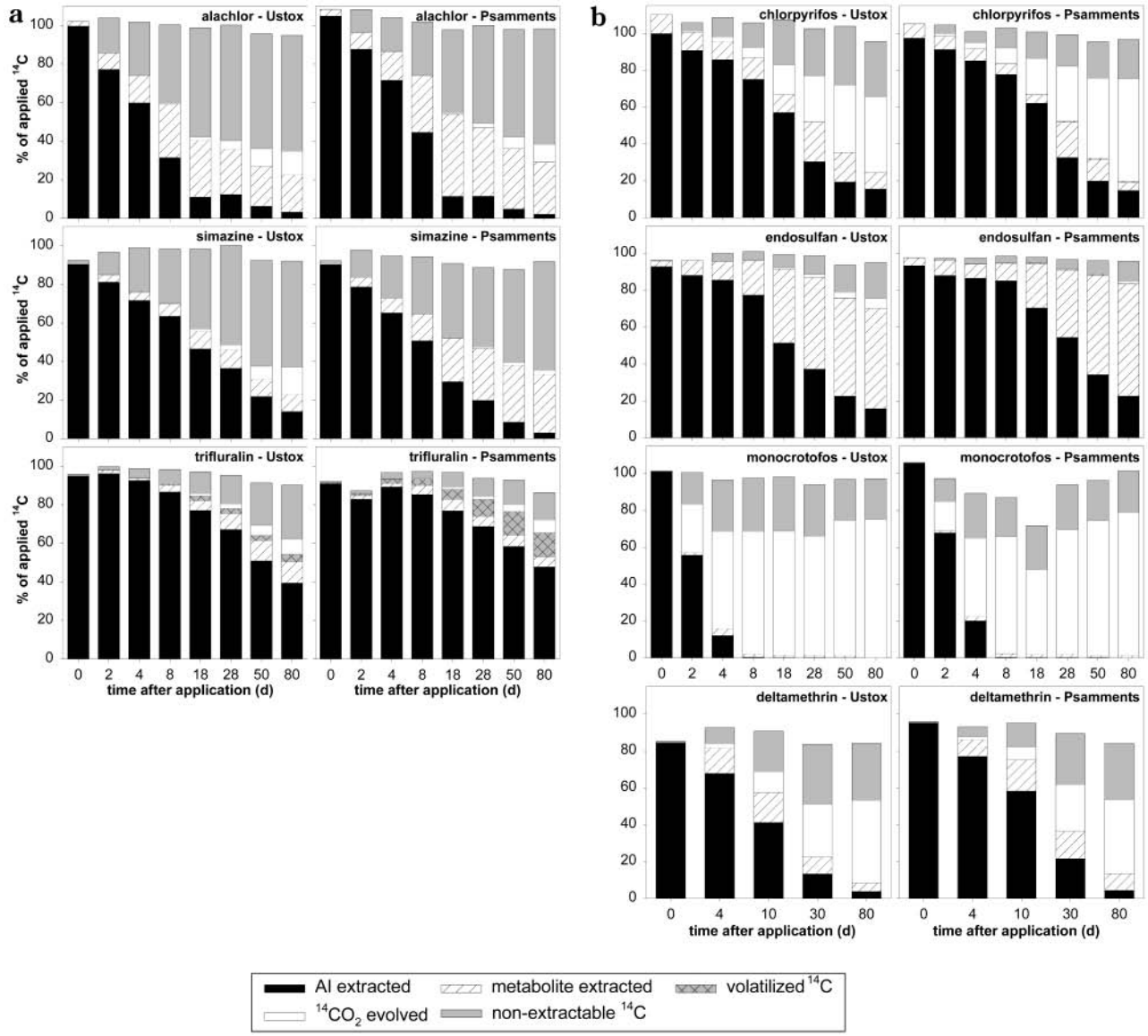

Figure 3. Amount of radioactivity of herbicides (a) and insecticides (b) found as extractable active ingredient, extractable metabolite, volatilized ^{14}C, $^{14}CO_2$, and bound residue during the laboratory incubation experiment.

compared with the Ustox (2 vs 14% of AR), which was related to a higher accumulation of metabolites in the sandy soil. In both soils alachlor degradation also led to significant amounts of transient metabolites (maximum of 29 and 42% of AR in Ustox and Psamments, respectively), which diminished toward the end of the incubation period. Similar metabolization dynamics were observed in the soils for trifluralin, yet involving a lower portion of metabolites (<11% of AR in both soils). When both mineralization and metabolization were considered, trifluralin was the most persistent herbicide in both soils with <20% of AR mineralized or metabolized during the experiment. Alachlor and simazine were more readily degraded, resulting in >29% of the AR found as metabolites or $^{14}CO_2$ after 80 days of incubation.

The insecticides chlorpyrifos and endosulfan volatilized less from Ustox (~0.15% of AR for both compounds) than from Psamments (0.5−0.6% of AR, respectively), as was also observed for trifluralin. Deltamethrin and monocrotofos did not volatilize in significant amounts in this experiment (<0.1% of AR). A higher volatilization of pesticides from sandy than from loamy/clayey soils was also reported by Atienza et al. (*23*) and Chester et al. (*24*). Nevertheless, and similar to the herbicides, volatilization was of minor importance for the total material balance of insecticides in this laboratory study. The bound-residue formation was less pronounced for the insecticides (**Figure 3b**) in comparison to the more polar herbicides alachlor and simazine (**Figure 3a**). Chlorpyrifos, monocrotofos, and deltamethrin all exhibited a similar portion of bound residues in both soils, with 20−30% of AR being nonextractable at the end of the incubation. The apolar organochlorine endosulfan formed fewer bound residues than the other insecticides, and, similar to trifluralin, the bound fraction was higher in the C-rich Ustox (15% of AR) than in the C-poor Psamments (7% of AR). The dissipation of organophosphorus insecticides and pyrethroids was mainly due to the mineralization of their labeled C structure, resulting in a substantial fraction of AR captured as $^{14}CO_2$ for deltamethrin, chlorpyrifos (both >40% of AR), and monocrotofos (>75% of AR in both soils) during the 80 days of incubation. The high mineralization rate observed for monocrotofos during the first incubation week could not be solely attributed to a labile labeling position at its ester-bonded methyl groups, as Lee et al. (*25*) found a similarly high mineralization rate for [3-^{14}C]monocrotofos (60% of AR, after a 16 day incubation) in a degradation study with temperate soils.

Table 3. Pesticide Dissipation Times and Model Parameters

pesticide	soil type[c]	dissipation times[a] (days)			dissipation model parameters[b]				model fit R^2 [d]
		DT_{50}	DT_{75}	DT_{90}	C_1 (fraction)	k_1 ($days^{-1}$)	C_2 (fraction)	k_2 ($days^{-1}$)	
alachlor	Ox	4.3	9.7	26.5	0.84	0.202	0.16	0.019	0.97
	Ps	5.4	11.5	24.9	0.85	0.167	0.15	0.024	0.96
chlorpyrifos	Ox	19.6	43.6	>80[e]	0.86	0.055	0.14	0	0.98
	Ps	21.3	45.9	>80[e]	0.88	0.048	0.12	0	0.98
deltamethrin	Ox	11.0	22.2	40.4	0.96	0.071	0.04	0	1.00
	Ps	14.3	28.6	50.8	0.97	0.054	0.03	0	1.00
endosulfan-α	Ox	13.6	27.2	48.0	0.97	0.056	0.03	0	0.99
	Ps	21.9	43.7	72.6	1.00	0.032	0	0	0.99
endosulfan-β	Ox	*60*	*120*	*198*	1.00	0.012	0	0	0.99
	Ps	*90*	*180*	*299*	1.00	0.008	0	0	0.95
endosulfan-sum[f]	Ox	*161*	*322*	*535*	1.00	0.004	0	0	0.98
	Ps	*385*	*770*	*1280*	1.00	0.002	0	0	0.97
monocrotofos	Ox	1.7	3.5	5.8	1.00	0.399	0	0	0.98
	Ps	2.1	4.1	6.8	1.00	0.337	0	0	0.98
simazine	Ox	26.6	58.1	>80[e]	0.87	0.039	0.13	0	1.00
	Ps	14.2	28.4	49.3	0.98	0.053	0.02	0	0.99
trifluralin	Ox	60	120	199	1.00	0.012	0	0	0.99
	Ps	*87*	*173*	*288*	1.00	0.008	0	0	0.98

[a] Time period for the dissipation of 50 (DT_{50}), 75 (DT_{75}), and 90% (DT_{90}) of the applied amount. Figures printed in *italics* denote dissipation times outside the experimental observation period. [b] Dissipation model: $C(t) = C_1 \exp(-k_1 t) + C_2 \exp(-k_2 t)$, with $C_{1,2}$ as concentrations, t as time after application, and $k_{1,2}$ as degradation rate constants. [c] Ox, Ustox; Ps, Psamments. [d] Coefficient of determination for nonlinear regression. [e] DT_{90} could not be calculated: $C_2 > 0.1C_0$. [f] Endosulfan-sum: sum of concentrations of endosulfan-α, -β, and -sulfate.

In contrast, endosulfan was not readily mineralized in either soil (<6% of AR after 80 days) but was, rather, metabolized to a high degree (54 and 61% of AR after 80 days in Ustox and Psamments, respectively). Endosulfan-sulfate was identified as the main metabolite of endosulfan by TLC in the soil extract, accounting for >90% of total metabolite radioactivity in both soils. The other insecticides formed substantially less amounts of metabolites during the incubation (<22% of AR at all sampling times in both soils), which decreased toward the end of the experiments (<9% of AR at 80 days after application in both soils), indicating their progressing mineralization. Of all the insecticides endosulfan was by far the least degradable compound, when the toxic main metabolite endosulfan-sulfate was considered to be an active ingredient (less than 11 and 6% of AR mineralized or metabolized during the incubation). Chlorpyrifos and deltamethrin exhibited an intermediate and monocrotofos a high degradability with about 50 and 75% of AR, respectively, mineralized or metabolized in both soils during the experiment.

Comparative Evaluation. The few studies on pesticide dissipation in tropical soils mostly confirmed our findings, showing a low mineralization (<2.5% of AR) and high persistence (DT_{50} = 90 days) of endosulfan-α in soils of Thailand and Brazil (*26*, *27*) and a similar persistence of chlorpyrifos (DT_{50} = 22 days) in a sandy soil of India (*28*). As well, the volatilization (18% of AR within 60 days) and dissipation rates (DT_{50} = 60 days) measured for trifluralin in a Brazilian Oxisol (*14*) corroborated our results. However, significantly fewer soil-bound residues were found for trifluralin in their study (<5% of AR within a 90 day incubation), which might be related to the low recovery of radioactivity from the soil (<70% of AR).

For the other compounds, only studies on their dissipation in temperate soils were available, reporting a higher persistence of alachlor (DT_{50} = 5−13 days), deltamethrin (35 days), monocrotofos (4 days), and simazine (40 days) than observed in our experiment (*25*, *29*, *30*,*31*). This finding may be explained by lower incubation temperatures used in these experiments with temperate soils (20−25 °C). It was shown that pesticide DT_{50} values increased by a factor of ∼1.5 for every 5 °C decrease of incubation temperature (see, e.g., ref *32*) and that this relationship could be described by the Arrhenius function (*33*). When the half-life times calculated in our study were corrected by this factor, the persistence of pesticides in the studied tropical soils would be in the same range as reported from temperate soils in laboratory studies (**Table 4**). Also, the relative persistence of pesticides in temperate soils was ranked similarly as compared with our results. Exceptions were simazine, which was less persistent, and endosulfan, which exhibited a higher relative persistence in our experiment. These findings were presumably related to the acidic reaction of the studied tropical

Table 4. Dissipation Half-Life Times of Pesticides in Tropical and Temperate Soils

pesticide	study type[a]	exptl DT_{50}[b] (tropical soils)	lit. DT_{50}[c] (temperate soils)
alachlor	lab	4–5	1–30
	field	4–6	14–49
chlorpyrifos	lab	20–21	10–120
	field	0.6–0.8	10–90
deltamethrin	lab	11–14.	21–25
	field	11–12	na[d]
endosulfan	lab	14–90	30–70
	field	1.6–1.7[e]	10–200
monocrotofos	lab	2	1–5
	field	1–2	13–30
simazine	lab	14–27	27–102
	field	4–17	28–94
trifluralin	lab	60–87	116–201
	field	2–4	60–132

[a] Lab, laboratory study; field, field study. [b] Field experiment data from Laabs et al. (*1*). [c] Literature laboratory data from ref *50*, field data from ref *51*. [d] Data not available. [e] Only the α-isomer was investigated.

soils (pH 4−5), leading to an enhanced chemical degradation of triazines (*2*) and a slower degradation of endosulfan than in soils with higher pH (34).

Most pesticides (alachlor, chlorpyrifos, endosulfan-α, simazine, and trifluralin) formed more bound residues in this experiment as compared to other laboratory studies using lower incubation temperatures (*14*, *35*−*37*, *38*). We attributed this finding to the high incubation temperature chosen for our experiment, as Andréa et al. (*13*) reported steeply increasing portions of bound residues with increasing incubation temperature for atrazine in a study with Brazilian Oxisols. Probably, pesticides formed higher amounts of metabolites by enhanced microbial/chemical degradation during warmer incubation conditions, which were subject to sequestration into the nonextractable fraction in soils (*11*). An increased formation of nonextractable residues at elevated incubation temperatures supports the assumption that, in general, the fraction of bound residues of pesticides may be of increased relevance in the tropics. Especially for pesticides with a high bound residue formation in the studied soils, such as alachlor and simazine (>55% of AR within this experiment), an evaluation of the nature and availability of these residues for leaching processes and bio-uptake in tropical soils warrants further attention.

Comparison of Laboratory and Field Dissipation Data. The persistence of pesticides in tropical soils under field conditions was either lower than (endosulfan-α, trifluralin, chlorpyrifos, and simazine) or similar in comparison to (alachlor, deltamethrin, and monocrotofos) results from our laboratory experiments (**Table 4**). The highest reduction in DT_{50} was observed for trifluralin, followed by endosulfan and chlorpyrifos. Generally, a faster dissipation of pesticides in the field may be caused by additional physical losses, such as surface runoff transport, leaching of pesticide from the sampled top soil layer, and enhanced volatilization. Also, an enhanced microbial/chemical degradation, due to variable soil temperature and moisture conditions, and a soil surface photolysis may accelerate the dissipation of pesticides under field conditions (reviewed in ref *7*).

Losses of the investigated pesticides by leaching from the upper soil layer (10 cm) were low in Ustox (<6% of applied amount) and <10% of the applied amount in Psamments during our field experiments (*1*). Consequently, pesticide leaching could not explain the differences in dissipation half-life times between field and laboratory conditions. Pesticide dissipation by volatilization and surface runoff was not assessed in the field experiment. However, the dissipation half-life time of the most hydrophobic insecticide deltamethrin was not shorter in the field than under laboratory conditions, giving no indication of an eventual (particle-bound) surface runoff loss of pesticides from the experimental plots in our field study. Therefore, volatilization losses of pesticides need to be considered as a cause for the reduced persistence of some pesticides in our field study.

As reviewed by Racke et al. (*39*), volatilization may account for increased substance losses under tropical field conditions relative to temperate climatic conditions. The volatilization of pesticides may be substantially higher in the field in comparison to laboratory conditions, as solar radiation and wind favor the volatilization of pesticides under outdoor conditions (*40*, *41*). Consequently, even pesticides rated as nonvolatile in laboratory experiments (e.g., metolachlor; *42*) may suffer significant volatilization losses from soil (>20% of the applied amount) under field conditions (see, e.g., ref *43*). Volatilization was shown to remove 20−40% of the applied amount of alachlor and chlorpyrifos and up to 90% of the applied amount of trifluralin from field plots during the first days after application (*40*, *44*, *45*). To investigate the influence of pesticide volatilization on their field dissipation, we related their volatility from soil to the differences between pesticide dissipation times under laboratory and under field conditions (**Figure 4**). In this respect, we took the amount of pesticides volatilized during the laboratory experiment as a measure for the relative volatilization potential of pesticides from soils. The strong correlation found for the two parameters suggested that for the more volatile substances, such as trifluralin, endosulfan, and chlorpyrifos, volatilization losses were the main cause of their enhanced dissipation under tropical field conditions. The steeper slope of the regression line for Psamments reflects the increased volatilization losses of pesticides from the sandy soil compared to the clayey Ustox. This finding is in line with the results of Atienza et al. (*23*) and Chester et al. (*24*), who reported that lesser portions of pesticides volatilized from fine-textured soils than from sandy soils. The shorter dissipation time of simazine under field conditions was probably related to an accelerated degradation induced by fluctuations of soil moisture and temperature in the field, which are known to stimulate the microbial degradation of xenobiotics in soil (*46*). Similar results have been reported for other triazines by de Queiroz and Monteiro (*47*) and Di et al. (*48*). Of course, also a substrate limitation of the microbial community in the incubated soil samples might have led to a slower dissipation of simazine in the laboratory than under field conditions.

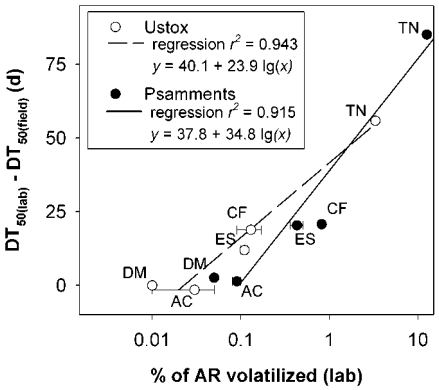

Figure 4. Correlation between the cumulative amounts of applied radioactivity volatilized from soil (during a 80 day incubation in the laboratory, $n = 2$) and the difference between laboratory (lab) and field dissipation half-lives (DT_{50}): AC, alachlor; CF, chlorpyrifos; DM, deltamethrin; ES, endosulfan-α; TN, trifluralin.

The DT_{50} values of pesticides measured in the studied soils under tropical field conditions were shorter by factors of 5−50 than under temperate field conditions for most compounds (**Table 4**). The obvious reason for this discrepancy was a higher soil temperature in the tropics, inducing higher degradation and volatilization rates of pesticides. Whereas pesticide degradation rates are thought to increase by a factor of 2 for a 10 °C increase of soil temperature, volatilization rates have been shown to increase by a factor of 3−4 for the same temperature difference (reviewed in ref *39*). In our field experiments, especially the volatile substances (trifluralin, endosulfan, and chlorpyrifos) showed the most reduced persistence under tropical field conditions as compared to results from temperate regions (**Table 4**). Consequently, we attributed the enhanced soil dissipation of these pesticides in the tropics primarily to volatilization losses. For temperate soils, an estimation of the dissipation half-life times of pesticides under field conditions was achieved using functional relationships between pesticide degradation rates and soil moisture/soil temperature, determined in laboratory experi-

ments (see, e.g., refs *3* and *49*). Our results suggest that for volatile substances also a consideration of their field volatilization losses is required for successful simulations of pesticide persistence under tropical field conditions.

ABBREVIATIONS USED

AC, alachlor; AI, active ingredient; AR, applied radioactivity; $C_{1,2}$, concentrations of pesticides subject to different degradation rates (biexponential model); CF, chlorpyrifos; DM, deltamethrin; DT_{50}, DT_{75}, and DT_{90} dissipation times for 50, 75, and 90% of the applied amount; ES, endosulfan; $k_{1,2}$, pesticide degradation rate constants (biexponential model); K_{OC}, soil sorption coefficient normalized to the organic carbon content of soils; LSC, liquid scintillation counting; M, molar; Ox, oxisols; Ps, psamments; R^2, coefficient of determination for nonlinear regressions; r^2, coefficient of determination for linear regressions; TLC, thin-layer chromatography; TN, trifluralin; WHC, water-holding capacity.

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