Fate of Pesticides in Tropical Soils of Brazil under Field Conditions

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ABSTRACT

The potential of pesticides for nonpoint ground water pollution depends on their dissipation and leaching behavior in soils. We investigated the fate of 10 pesticides in two tropical soils of contrasting texture in the Brazilian Cerrado region near Cuiabá during an 80-d period, employing topsoil dissipation studies, soil core analyses, and lysimeter experiments. Dissipation of pesticides was rapid, with field half-lives ranging from 0.8 to 20 d in Ustox and 0.6 to 11.8 d in Psamments soils. Soil core analyses showed progressive leaching of polar pesticides in Psamments, whereas in Ustox pesticides were rapidly transported to 40 cm soil depth regardless of their sorption properties, suggesting that leaching was caused by preferential flow. In lysimeter experiments (35 cm soil depth), cumulative leaching was generally low, with ≤0.02% and ≤0.19% of the applied amounts leached in Ustox and Psamments, respectively. In both soils, all pesticides but the pyrethroids were detected in percolate at 35 cm soil depth within the first 6 d after application. Cumulative efflux and mean concentrations of pesticides in percolate were closely correlated with their Groundwater Ubiquity Score (GUS). The presence of alachlor (2-chloro-2′,6′-diethyl-N-methoxymethylacetanilide), atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide], simazine [2-chloro-4,6-bis(ethylamino)-1,3,5-triazine], and trifluralin (2,6-dinitro-N,N-dipropyl-4-trifluoromethylaniline) throughout the soil profile and in percolate of wick lysimeters at 95 cm soil depth indicated that a nonpoint pollution of ground water resources in tropical Brazil cannot be ruled out for these substances.

I N THE Brazilian Cerrado region, more than 30 million hectares are used for cereal and soybean [*Glycine max* (L.) Merr.] production (Resck, 1998). The rapid agricultural development of this region has led to an increased use of pesticides in Brazil, which now ranks among the five largest agrochemical markets in the world (Racke et al., 1997). The intensive use of pesticides in agriculture may cause contamination of ground water resources due to their leaching through the soils into aquifer regions. Ground water pollution by pesticides has been extensively studied in temperate regions (reviewed by van den Berg and van der Linden, 1994; Ritter, 1990), whereas data from tropical areas are lacking almost completely. Recent results of Lanchote et al. (2000) and Li et al. (2001) proved the contamination of ground water in the tropics with triazines, which underlines the fact that nonpoint pollution of ground water may be of concern in tropical regions, too.

To assess the risk of ground water contamination by pesticides, their persistence and mobility in soil need to be determined (Roberts, 1996). Laboratory studies are often not adequate to this aim, because variable climatic conditions and processes like volatilization, UV oxidation, leaching, and pronounced preferential flow transport may influence pesticide persistence and mobility under outdoor conditions (Beulke et al., 2000; Flury, 1996). In temperate regions, many studies were conducted to assess the leaching potential of pesticides in field experiments and to evaluate the influence of soil properties, soil management, and application mode on pesticide output from soils (e.g., Bowman, 1990; Gish et al., 1995; Johnson and Pepperman, 1995). However, relatively few data were reported so far on pesticide fate under the specific climatic and pedological conditions in the tropics (reviewed by Racke et al., 1997). Recently, Laabs et al. (2000) reported in a comparative study short field dissipation half-lives of pesticides ($t_{0.5} < 15$ d) and a moderate short-term leaching of polar herbicides to the subsoil of one Ustox in tropical Brazil. However, data on medium to long-term leaching of pesticides in representative soils of the tropics are completely lacking for most compounds in the literature.

The leaching of pesticides in the field may be assessed by direct ground water sampling, a soil core analysis, or lysimeter–suction cup studies. A sole soil core analysis may not yield meaningful results in respect to pesticide movement in the soil, because inhomogeneously distributed preferential flow pathways of pesticides may be missed by the coring process (Flury, 1996). However, by this method, the progressive vertical translocation of pesticides into the subsoil may be assessed under field conditions. To account for pesticide transport along preferential flow pathways, pesticide concentrations need to be monitored in percolating soil water. Suction cups are inefficient samplers when preferential–macropore flow occurs immediately after rainfall events and when a continuous vacuum source is not available in the field. In these cases, free-draining pan lysimeters have been recommended to sample fast percolating soil water. However, at unsaturated soil conditions a saturation zone immediately above the pan lysimeter needs to develop before water may percolate (Barbee and Brown, 1986). For the assessment of the progressive vertical transport of pesticides as well as their leading edge in soils, a combined study with soil coring and lysimeters has to be considered (Flury, 1996).

The objective of our study was a comparative assessment of the field dissipation and mobility of 10 corn (*Zea mays* L.) and soybean pesticides in two contrasting soil types of the Brazilian Cerrados. To this aim a combined topsoil dissipation, soil coring, and lysimeter experiment was conducted on Ustox and Psamments soils,

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Table 1. Basic characteristics of the studied soils.

| Soil | Horizon | Texture | | | Organic carbon | Total nitrogen | pH (1 M KCl) | CEC$_{pot}$‡ | Bulk density |
		Sand	Silt†	Clay					
					g kg^{-1}			cmol$_c$ kg^{-1}	g cm^{-3}
Haplustox (n = 3)									
0–10 cm	A	424–546	25–43	429–540	16.3–30.6	1.0–2.2	4.8–5.6	12.1–17.5	0.94–1.04
40–50 cm	BA	445–533	26–71	423–484	10.4–11.1	0.6–0.7	4.7–5.1	8.9–9.9	0.96–1.06
90–100 cm	Bo	427–525	11–53	461–520	7.0–8.2	0.4–0.5	5.0–5.6	5.1–8.8	0.87–0.98
Quartzipsamments (n = 3)									
0–10 cm	A	846–885	10–18	97–144	7.1–10.2	0.7–0.9	4.2–4.3	3.7–5.1	1.23–1.25
40–50 cm	C$_1$	839–893	52–54	53–108	4.2–4.8	0.4–0.5	4.4–4.5	2.6–3.4	1.23–1.32
90–100 cm	C$_2$	842–895	0–52	52–158	2.7–3.5	0.3–0.4	4.6–4.8	1.8–2.9	1.20–1.26

† 2–20 μm.
‡ Potential cation exchange capacity (measured with 1 M ammonium acetate).

which are the dominant soils used for cropping in the Cerrado landscape (Resck, 1998).

MATERIALS AND METHODS

Study Area, Soils, and Plot Design

The experimental site is situated in the southeastern part of Mato Grosso State (15°53′ S, 55°16′ W; 800 m above mean sea level), in the central-western region of Brazil. Climatic conditions are of the savanna type with a clearly distinguished rainy (November–April) and dry (May–October) season. Mean annual temperature is ca. 23°C and the mean annual precipitation is ca. 1900 mm. Typical soils in the top positions of the plateaus are Ustox (with 600–700 g kg^{-1} clay), which become increasingly more sandy proceeding to the shallow stream beds, where Psamments (with >800 g kg^{-1} sand) are encountered in the vicinity of streams. On basis of a preliminary soil survey we chose three sites on each fine-clayey, mixed, isohyperthermic Typic Haplustox and acid, isohyperthermic Ustic Quartzipsamments (Soil Survey Staff, 1998; Latossolo vermelho-amarelo and Areia Quartzosa according to Brazilian classification; Estado de Mato Grosso, 1995) for the plot and lysimeter experiments; basic soil characteristics are summarized in Table 1. Plots were located within a slightly inclined (<2%) 2-km^2 area, with the three plots on sandy soils, due to geological conditions, generally in the down-slope direction of the respective plots on Ustox. The plots (64 m^2 each) were situated in different land slots or fields, with a minimum distance of 150 m in between. Ustox had formerly been used in a corn–soybean–pasture rotation, whereas the Psamments had been under degraded pasture for the last five years. Because of the different land use in the season before our experiment, surface soil layers (0–15 cm) of all plots were uniformly dug up and harrowed two weeks before the start of the experiment, regardless of previous soil treatment by the farmer. After raking and removal of all vegetation, application lanes were marked off and a trench was opened for lysimeter installation on one side of each plot. The ground water table within the study area was located at least 5 m below the soil surface during the rainy season.

Each trench was equipped with two pan lysimeters (e.g., Barbee and Brown, 1986) at 35 cm soil depth and two pan lysimeters, as well as one wick lysimeter (e.g., Holder et al., 1991), at 95 cm depth. At two trenches per soil type, an additional wick lysimeter at 35 cm soil depth was installed. Due to customs-related problems, wick lysimeters could be installed only 22 d after application. The free-draining lysimeters consisted of stainless steel pans (25 by 25 cm) that were filled with acid-washed quartz pebbles and quartz sand to ensure good contact to the soil above (see lower part of Fig. 1). Wick lysimeters had the same design, but were additionally

equipped with a glass fiber wick of 50 cm length, whose top end was fixed at the soil–lysimeter interface on a fine stainless-steel mesh (Fig. 1). A fiber glass cloth (GF8; Schleicher & Schuell, Dassel, Germany) was put upon the spread-out wick end (one braid each to the lysimeter corners) to enhance the lateral transport of water to the wick braids at the soil–lysimeter interface (Holder et al., 1991). The glass fiber cloth was partly cut out in between the wick braids to avoid a possible plugging of the whole lysimeter contact area due to particle transport during preferential flow events. The glass fiber wick was comprised of six individual braids of glass fiber cable (LK3.0; Schott Glas, Wiesbaden, Germany), which were unified and rebraided into four strings. In preliminary laboratory experiments, wicks of 30 cm length were able to draw water from ceramic plates against −10 cm water column (data not shown), although at very low flow rates (ca. 2 mL h^{-1}).

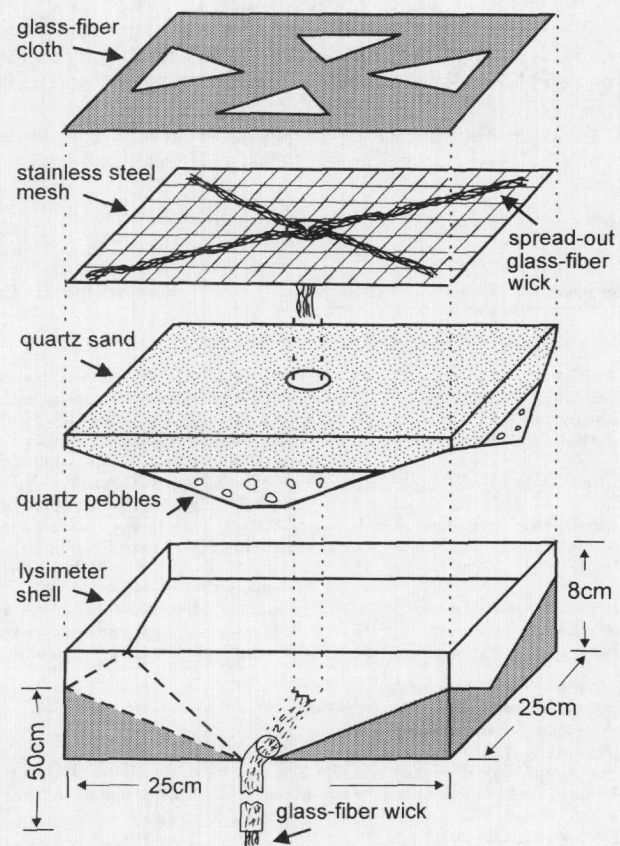Lysimeters were installed sideways from the trench walls

Fig. 1. Schematic diagram of the wick lysimeter.

to preserve undisturbed soil conditions in the soil column above. For the lysimeters in 35 cm soil depth, stainless steel plates were pushed into the soil to define vertical boundaries of the soil monolith. Lower lysimeters (in 95 cm soil depth) were installed onto 10-cm-tall stainless steel collars (25 by 25 cm), which had been pressed into the soil from below with a hydraulic jack. These collars hindered any lateral outflow of water from the soil column right above the sampling device (saturation zone). The trench walls between and above the lysimeters were covered by plastic foil to minimize lateral evaporation of water. Percolates were collected in amber glass bottles, which had been rinsed with ethyl acetate and baked at 300°C for 2 h before use.

At all plots rain collectors were installed (1 m above ground), and at three plots air temperatures (minimum and maximum) were measured (1 m above ground). Climatic data of the study period were recorded in 2-d intervals and soil temperatures were measured on two plots (5 and 15 cm soil depth) during 30 d of the study period. Within the study period (18 Dec. 1998 to 8 Mar. 1999) mean daily maximum air temperatures were 34.8°C, and mean minimum air temperatures 19.7°C. Precipitation was not significantly different between Ustox and Psamment sites and averaged 8.4 mm d^{-1}. Daily soil temperatures (measured once at every sampling date between 1000 and 1700 h) were on average 32.8°C at 5 cm depth for both soils and 27.4 and 29.2°C at 15 cm depth for clayey and sandy soils, respectively.

Experimental Layout and Sampling Strategy

Pesticides were applied to the plots on 18 Dec. 1998 in aqueous mixtures of commercial products using a hand-held spraying apparatus. Before use, the spraying device was calibrated in respect to homogeneity of spray beam and pumping volume per time unit. The application of pesticides to the plots was executed band-wise and in a criss-cross pattern to ensure a uniform distribution. Pesticide names, application dose, and basic physical–chemical properties are presented in Table 2.

To assess the dissipation of pesticides in soil, composite samples (10 singular samples of 200 cm^3 each, 0–8 cm soil

depth) were collected 0, 1, 2, 4, 6, 8, 12, 18, 28, 50, and 80 d after application. Sampling positions were randomly chosen from free grid positions of the marked application lanes and were always located near the center of the respective application bands to avoid no- or double-application areas near the band edges. After homogenization of soil samples, aliquots were wrapped in aluminum foil, put into plastic bags, and immediately stored on ice for a maximum of 5 h during field work and transport to the laboratory. In the laboratory, samples were kept at -20°C until processing.

To measure the vertical translocation of pesticides in the soil profile, composite samples (five subsamples of about 200 cm^3 each) of the 0- to 10-, 10- to 20-, 20- to 30-, and 30- to 40-cm soil depth were taken 6, 14, 24, 34, 52, and 80 d after application. The soil sampling was done using a tempered steel soil corer (50-cm length, 5-cm inner diameter); only the inner part of the soil core was sampled to avoid contamination of the sample by material from other soil depths. After the coring process the corer was scrubbed clean with paper towels when needed. Soil samples were otherwise handled as described above.

Lysimeter percolate was sampled every 2 d. Percolate samples of duplicate free-draining lysimeters were pooled into one sample for each trench. After noting the percolate volume, samples were immediately stored on ice (<5 h) and later kept at -20°C until extraction in the laboratory (<3-d storage period).

Analysis of Pesticides

Pesticides were extracted from soil by a solvent mixture of acetone, ethylacetate and water (2:2:1 [v/v/v]) and analyzed following the method of Laabs et al. (1999). For all substances the mean recovery was in the range of 85% (simazine) to 110% (λ-cyhalothrin) (±2.2% mean standard error, SE) and 83% (trifluralin) to 97% (deltamethrin) (±1.4% mean SE) of the spiked amount (400 µg kg^{-1}, $n = 3$) for Ustox and Psamments, respectively (data not shown). Water samples (<1-L volume) were solid-phase extracted with a bonded silica phase (Bakerbond C18; Baker Chemicals, Gross-Gerau, Germany) and pesticides were analyzed as outlined by Laabs et al. (2000).

Table 2. Basic properties of pesticides and application data.

Pesticide	Trade name	Type†	Nomenclature (IUPAC)	Water solubility‡	Vapor pressure‡,§,¶	K_{oc}# Ox	K_{oc}# Ps	Application rate
				mg L^{-1}	mPa (25°C)	— mL g$_{oc}^{-1}$ —		g (a.i.††) ha^{-1}
Alachlor	Lasso	H	2-chloro-2',6'-diethyl-N-methoxymethylacetanilide	240	2.0	222	243	3 360
Atrazine	Triamex	H	2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine	33	0.04‡‡	189	234	2 000
Chlorpyrifos	Lorsban	I	O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate	0.4	2.5	7 250	14 000	1 500
λ-Cyhalothrin	Karate	I	α-cyano-3-phenoxybenzyl 3-(2-chloro-3,3,3-trifluoropropenyl)-2, 2-dimethylcyclopropanecarboxylate	0.005	0.0002‡‡	>80 000	137 000	30
Deltamethrin	Decis	I	(S)-α-cyano-3-phenoxybenzyl (1R,3R)-3-(2,2-dibromovinyl)-2, 2-dimethylcyclopropan-1-carboxylate	0.002	0.002	79 000	181 000	20
Endosulfan α	Thiodan	I	6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano, 2,4,3-benzodioxathiepin 3-oxide	0.32	0.83‡‡	5 710	13 800	650
Metolachlor	Dual	H	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide	530	1.7	123	217	3 840
Monocrotofos	Nuvacron	I	3-(dimethoxyphosphinyloxy)-N-methylisocrotonamide	1 000 000	0.98	48	41	1 100
Simazine	Triamex	H	2-chloro-4,6-bis(ethylamino)-1,3,5-triazine	6.2	0.003	269	337	2 000
Trifluralin	Trifluralina	H	2,6-dinitro-N,N-dipropyl-4-trifluoromethylaniline	0.3	6.1	8 020	22 500	1 600

† H, herbicide; I, insecticide.
‡ According to Hornsby et al. (1996).
§ According to Hartley and Kidd (1987).
¶ According to Tomlin (2000).
# Soil sorption coefficient normalized to the organic carbon (OC) content of soils; determined for laboratory reference soils of study area (Ox: Typic Haplustox; Ps: Ustic Quartzipsamments) in batch experiments according to OECD guidelines (Organisation for Economic Co-operation and Development, 1981).
†† Active ingredient.
‡‡ Measured at 20°C.

Recovery of individual pesticides from spiked water samples (n = 3) was in the range of 65% (chlorpyrifos) to 108% (alachlor) of the spiked amount (1 μg L^{-1}) with a mean SE of ±1.1% (data not shown).

Internal standards (α-HCH: α-1,2,3,4,5,6 hexachlorocyclohexane; terbuthylazine: 2-tert-butylamino-4-chloro-6-ethylamino1,3,5-triazine; and ditalimfos: O,O-diethyl phthalimidophosphonothioate) were added to samples in organic solvents prior to extraction to facilitate pesticide quantification and control the sample processing quality by determining the recovery of internal standards. Mean recovery of internal standards during our study was 82 and 85% of the spiked amount for lysimeter samples and soil samples, respectively. Routine limits of quantification were 0.01 (e.g., simazine, atrazine) to 0.05 ng (monocrotofos), dependent on pesticide properties, with an injection volume of 1 μL. Internal standards and analytical pesticide standards were supplied courtesy of Aventis Crop Science (Frankfurt/Main, Germany), Dow Agrosciences (Norfolk, UK), Novartis Crop Protection (Basel, Switzerland), or purchased from Promochem (Wesel, Germany) with a purity greater than 95%. All organic solvents used were of "picograde" purity.

Statistical Analysis

The Mann–Whitney U Test, Spearman correlation, and Pearson Product Moment correlation were executed with the software package Statistica for Windows (Statsoft, 1996). Dissipation curves were fitted for individual pesticides and soils by nonlinear regression with the Sigma Plot for Windows 4.01 curve fitting package (SPSS, 1997), employing the Marquardt–Levenberg algorithm. Special attention was given to avoid overparametrization as indicated by high p and dependency values. Curve fitting was usually done weighting y data with y^{-2} to account for generally smaller deviations of y with increasing time after application. Consequently, the curve fit was optimized to predict pesticide concentrations in soil accurately until the end of the study period with the minimum of parameters needed.

RESULTS AND DISCUSSION

Pesticides were applied to the experimental plots in mixtures of commercial formulations. As it is a common agricultural practice to apply several pesticides at the same time (e.g., commercial mixtures of atrazine + simazine, endosulfan + λ-cyhalothrin, alachlor + trifluralin), the presence of substantial amounts of several pesticides in soils is the usual case in modern agriculture. We assumed that the consecutive application of all pesticides to the same plots did not influence substantially their individual dissipation and leaching behavior in comparison with their fate in normal agriculture. The structural differences between pesticides (Harper, 1994) and their fast dissipation during the first week after application (with dissipation of about 50% of the applied amount for most of the pesticides) should have prevented a saturation of soil sorption sites for individual pesticides in respect to mobility studies. The simultaneous application of pesticides onto the same plots has the advantage to facilitate the comparison of pesticide dissipation and leaching under exactly the same soil chemical and physical conditions, which yields additional information regarding differences in transport behavior between pesticides of different polarity (Flury, 1996).

The precision of the pesticide application was assessed by calculating their recovery from concentrations in soil samples taken immediately after application (0 d, 0–8 cm soil depth). The recovery from both soils was between 72 and 117% of the calculated application amount for all pesticides, indicating an acceptable precision of application and analysis of pesticides, as well as a valid soil sampling strategy to measure representative soil concentrations. An exception was monocrotofos, whose recovery lay between 45 and 66% of the applied amount, presumably due to the extremely fast dissipation of this substance (Lee et al., 1990; Laabs et al., 2000).

Dissipation of Pesticides

Pesticide dissipation was modeled using mono- and bi-exponential decay models derived from Eq. [1]. The latter model was adopted from Nose (1987) to describe the multisite–multicompartment dissipation of pesticides in soils, when an initial period of fast pesticide loss is followed by phases of slower dissipation:

$$C(t) = C_1 \exp(-k_1 t) + C_2 \exp(-k_2 t) + C_3 \quad [1]$$

with $C_1 + C_2 + C_3 = C_0$. In this formula, t represents time, $C(t)$ denotes the concentration of pesticide still present in the soil at time t, k_1 and k_2 are the dissipation rate constants ($k_1 > k_2$), C_0 is the initial concentration of pesticides in the soil, and C_1, C_2, and C_3 are the fractions of the initial pesticide concentration subject to the respective dissipation rates.

For most pesticides and soils, bi-exponential dissipation models yielded the best fit (Table 3). Topsoil dissipation data and fitted models are exemplarily shown for metolachlor in Fig. 2. Dissipation rate constants pertaining to the second phase (k_2) were between 5 and 40 times smaller than those fitted for the first phase (k_1), indicating a substantial slowdown in dissipation dynamics after the initial phase for most pesticides. Fractions of pesticides subject to the initial fast dissipation processes (C_1) were between 98 and 18% of the applied amount. The initial phase dominated by fast dissipation has been attributed to surface losses (runoff, volatilization, and photodegradation), whereas the slower disappearance afterwards has been related to degradation processes (microbial, chemical) within the soil (Hill and Schaalje, 1985). Monocrotofos dissipation was better described by a simple exponential decay model, due to its very fast and complete dissipation within the first 60 d after application. Dissipation of metolachlor and simazine in Ustox also followed a mono-exponential model with a second pesticide fraction not yet contributing to dissipation dynamics. This, however, has to be attributed to their relative persistence in this soil, which resulted in the dominance of the initial loss phase throughout the study period. The "constant" fractions (see also C_3 for trifluralin and chlorpyrifos) are logically not undegradable, but their slow dissipation did not yet influence the overall pesticide disappearance within the study period.

Table 3. Pesticide dissipation (0–8 cm); standard errors are shown in parentheses ($n = 3$). Different letters (a, b) indicate significantly different values (between soils), $p < 0.05$, Mann-Whitney U test.

Pesticide	Soil[†]	Mean dissipation times[‡]			Dissipation curve parameters[§] (means)						Fit quality r^2	Temperate[¶] $t_{0.5}$
		$t_{0.5}$	$t_{0.75}$	$t_{0.9}$	C_0	C_1	k_1	C_2	k_2	C_3		
		d			µg kg^{-1}	% of C_0	mean rate	% of C_0	mean rate	% of C_0		d
Alachlor	Ox	5.9a (0.5)	12.0a (0.9)	20.5a (1.7)	3288	97.9	0.122a	2.1	0.014a	0	0.99	15
	Ps	4.1b (0.2)	8.2b (0.3)	14.0b (0.6)	2668	97.9	0.175b	2.1	0.023b	0	0.97	
Atrazine	Ox	7.4a (1.8)	29.4a (5.9)	62.7a (11.0)	1659	50.2	0.526a	49.8	0.026a	0	0.98	60
	Ps	2.2b (0.3)	5.1b (0.8)	14.0b (2.7)	1369	83.1	0.406a	16.9	0.040b	0	0.97	
Chlorpyrifos	Ox	0.8a (0.2)	1.8a (0.4)	9.5a (2.4)	1573	81.2	1.443a	18.3	0.073a	0.5	0.98	30
	Ps	0.6a (0.0)	1.3a (0.1)	2.5b (0.1)	1076	92.7	1.244a	7.2	0.086a	0.1	0.99	
λ-Cyhalothrin	Ox	10.8a (1.3)	29.3a (0.6)	53.6a (1.3)	35.0	23.8	1.084a	76.2	0.038a	0	0.98	30
	Ps	8.5a (1.7)	23.5b (2.3)	43.3b (3.3)	28.4	23.0	2.725a	77.0	0.047a	0	0.99	
Deltamethrin	Ox	11.1a (0.9)	27.3a (1.2)	48.7a (3.1)	29.1	18.1	1.473a	81.9	0.044a	0	0.98	40
	Ps	11.8a (1.3)	30.5a (2.8)	56.2a (4.6)	21.9	25.3	1.507a	74.7	0.036a	0	0.98	
Endosulfan α	Ox	1.7a (0.3)	8.5a (1.6)	25.9a (1.4)	642	58.9	1.228a	39.9	0.058a	1.2	0.98	50
	Ps	1.6a (0.2)	5.9a (1.4)	26.2a (1.6)	498	69.7	0.759a	30.3	0.042a	0	0.99	
Metolachlor	Ox	20.0a (1.6)	42.3a (4.0)	82.7a (10.3)	3395	94.0	0.038a	6.0	0	0	0.99	90
	Ps	7.9b (1.2)	18.2b (1.7)	41.4b (1.1)	3022	70.1	0.152b	29.9	0.029	0	0.98	
Monocrotofos	Ox	1.7a (0.2)	3.4a (0.4)	5.6a (0.6)	492	100.0	0.421a	0	0	0	0.99	30
	Ps	1.2a (0.1)	2.3a (0.2)	3.8a (0.3)	581	100.0	0.609a	0	0	0	0.99	
Simazine	Ox	16.9a (0.7)	36.9a (3.3)	73.7a (13.2)#	1448	92.6	0.046a	7.4	0	0	0.98	60
	Ps	4.4b (0.8)	10.0b (1.6)	22.7b (2.5)	1348	79.5	0.213b	20.5	0.035	0	0.99	
Trifluralin	Ox	4.0a (0.5)	16.4a (2.9)	60.5a (20.0)#	1471	48.9	0.539a	44.9	0.053a	6.2	0.97	60
	Ps	1.5b (0.2)	6.1b (1.0)	26.6b (2.1)	1166	67.6	0.966a	29.3	0.055a	3.1	0.99	

† Ox, Ustox; Ps, Psamments.
‡ $t_{0.5}$, $t_{0.75}$, $t_{0.9}$ denote the time after which 50, 75, and 90% of the applied amount dissipated.
§ C_0, soil concentration at 0 d after application; $C_{1,2,3}$, soil fractions of different dissipation dynamics; $k_{1,2}$, dissipation rates.
¶ Field dissipation data according to Hornsby et al. (1996), for deltamethrin according to Hill and Schaalje (1985).
# For one Oxisol plot, $t_{0.9}$ was assumed to be 100 d, as the calculation was not possible according to the fitted model: $C_2,C_3 > 0.1C_0$.

Generally, differences of degradation rate constants and fractions among substances were greater than those between the two soils.

Initial dissipation from the topsoil layer, as indicated by low $t_{0.5}$ values, was fastest for the organophosphorus compounds (monocrotofos, chlorpyrifos), followed by endosulfan α and trifluralin, although they exhibited a marked slowdown in dissipation (Table 3). The most persistent substances during the study period were metolachlor, simazine, atrazine, and trifluralin in the Ustox ($t_{0.9} > 60$ d) and deltamethrin, λ-cyhalothrin, metolachlor, trifluralin, and endosulfan α in the Psamments ($t_{0.9} > 26$ d). Topsoil dissipation of pesticides generally proceeded faster in the Psamments than in the Ustox with the exception of deltamethrin, endosulfan α, and monocrotofos, for which no statistically significant differences between the dissipation times ($t_{0.9}$) in the two studied soils existed (Table 3). For the more polar herbicides (alachlor, metolachlor, atrazine, and simazine), a higher persistence in the Ustox than in the Psamments may be attributed to an increased loss of pesticides to deeper soil layers in the latter soil, due to its lower organic carbon content and therefore lower sorption coefficient. For some more volatile pesticides, such as trifluralin, alachlor, and chlorpyrifos, a higher volatilization rate from sandy soils in comparison with clayey soils may also explain the differences in dissipation half-lives (Atienza et al., 2001).

Soil Core Analysis of Pesticide Leaching

To assess the vertical movement of pesticides, soil core concentrations were measured to judge the pesticide content in different soil layers in relation to the applied amount (Fig. 3). Monocrotofos and deltamethrin were never detected beyond 20 cm soil depth and only sporadically in the layer of 10 to 20 cm in both soils (data not shown). For deltamethrin we attributed this finding to its very high K_{OC} and low application rate, which presumably led to concentrations below the detection limit in the subsoil layers. Monocrotofos could probably not be detected in lower soil layers due to its fast and complete degradation (Table 3) and its relatively high routine limit of quantification in soil samples (4 µg kg^{-1}).

In Psamments subsoils, we measured higher proportions of the moderately polar herbicides metolachlor, alachlor, atrazine, and simazine than in the respective
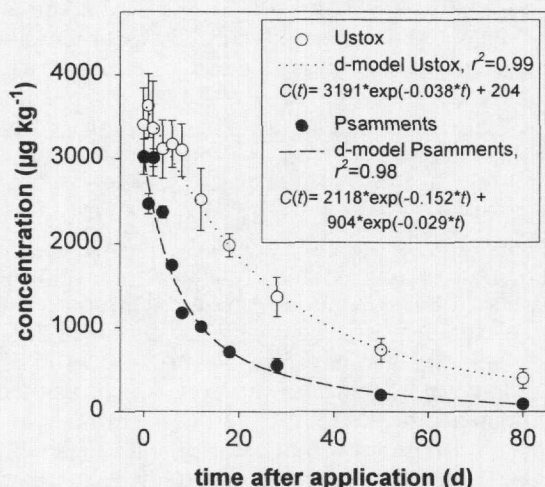

Fig. 2. Dissipation of metolachlor in topsoil (0–8 cm) of Ustox and Psamments soils (error bars denote standard errors, $n = 3$).
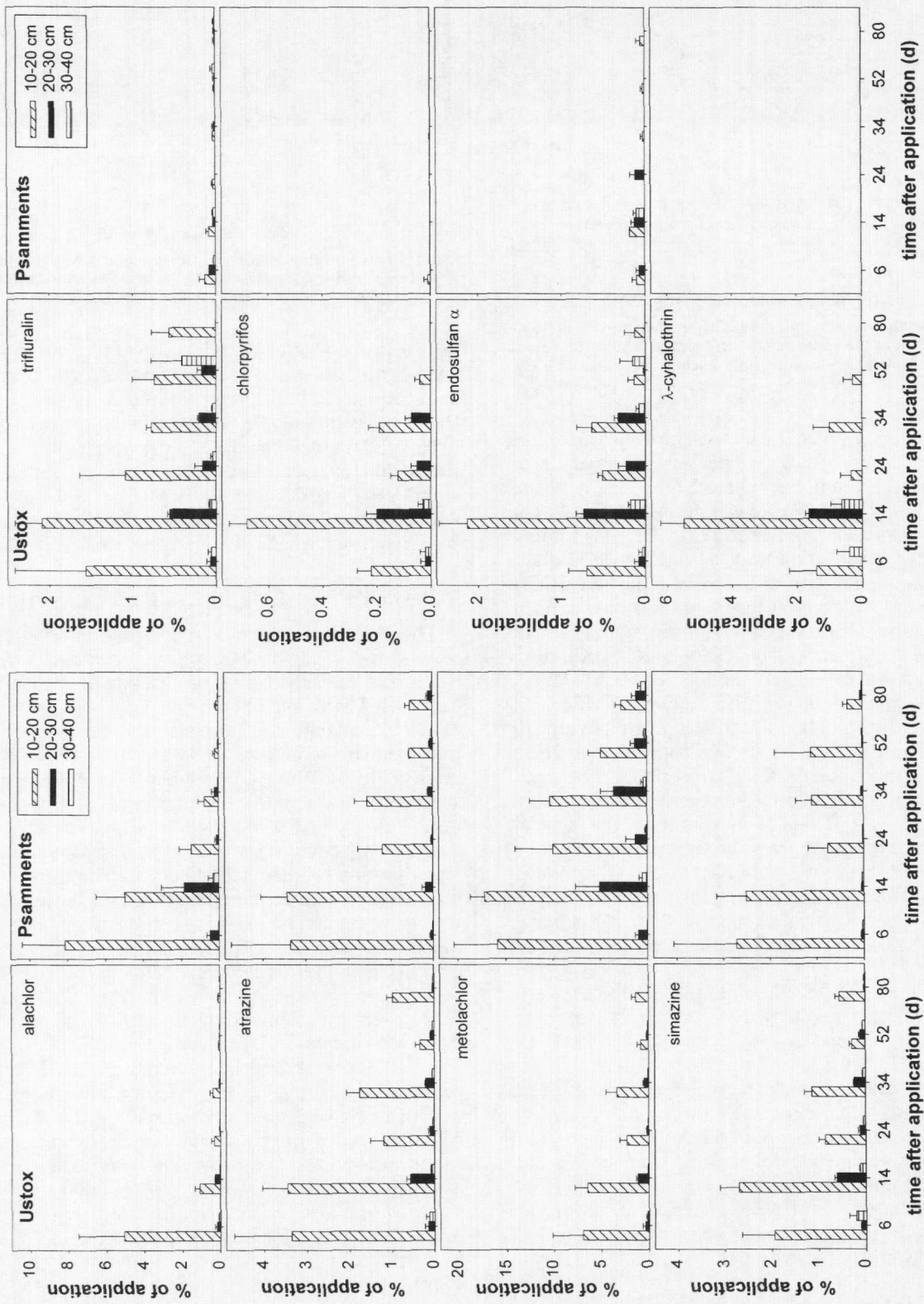
Fig. 3. Leaching of pesticides in the soil profile in percent of the applied amount (error bars denote standard errors, $n = 3$).
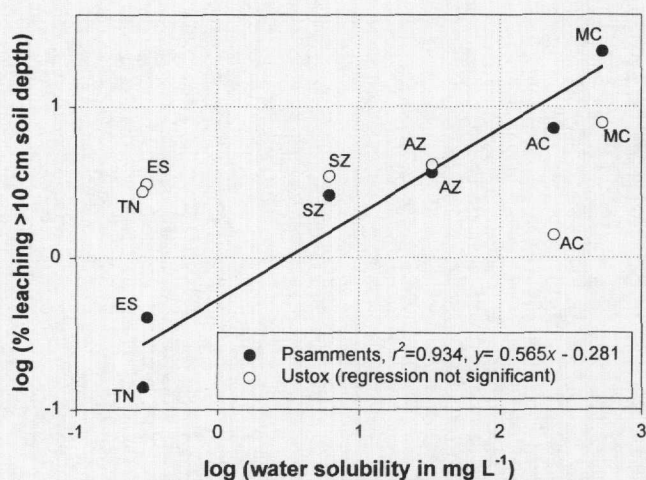
Fig. 4. Relationship between water solubility and the portion of pesticide (in percent of the applied amount) leached beyond 10 cm soil depth at 14 d after application (AC, alachlor; AZ, atrazine; ES, endosulfan α; MC, metolachlor; SZ, simazine; TN, trifluralin).
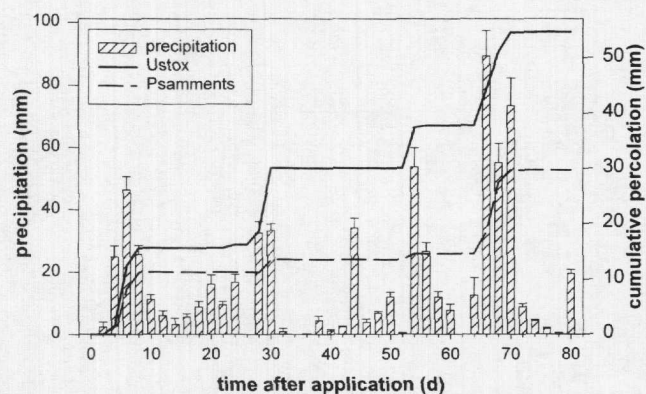

Fig. 5. Mean precipitation ($n = 6$) and cumulative amount of percolate in free-draining lysimeters on Ustox and Psamments soils (35 cm soil depth, $n = 3$), error bars denote standard errors.

Ustox depths. Especially for metolachlor and alachlor, a progressive transport to the deeper soil layers was observed in the Psamments, where 5.6 and 2.2% of the applied amount, respectively, was found below 20 cm soil depth at 14 d after application (Fig. 3). This finding supported the presumption that the faster topsoil dissipation in Psamments than in Ustox of polar herbicides was also related to leaching losses in the sandy soil. In contrast, the apolar pesticides were transported only in low amounts to the subsoil in Psamments (trifluralin, endosulfan α) or not detected at all in deeper soil layers (chlorpyrifos, λ-cyhalothrin). The absence of chlorpyrifos from 14 d after application in soil layers beyond 10 cm was probably caused by its fast topsoil dissipation in Psamments ($t_{0.9} < 2.6$ d). λ-Cyhalothrin did not leach in Psamments despite its relative persistence, due to its insolubility in water (Table 2). In summary, the vertical translocation of pesticides into the subsoil of sandy soils correlated with the water solubility of the compounds (Fig. 4). Pesticides with extremely fast topsoil dissipation ($t_{0.9} < 4$ d) or K_{OC} values greater than 100 000 mL g_{oc}^{-1} could not be detected below the top 10 cm of soil in Psamments.

In contrast to the Psamments, all pesticides were transported to deeper soil layers in substantial amounts in Ustox. Even the apolar pesticides ($K_{OC} > 5000$ mL g_{oc}^{-1}) were leached up to 40 cm soil depth in Ustox, resulting in fractions of 0.03 to 0.63% of the applied amount beyond 30 cm depth at 14 d after application (Fig. 3). As a result, no correlation ($r^2 = 0.04, p > 0.05$) was found between pesticide portions leached beyond 10 cm soil depth in Ustox and their water solubility (Fig. 4). This may be interpreted as a sign of pronounced preferential flow phenomena within this soil: when percolating soil water bypasses much of the soil matrix, a retardation of substances according to their K_{OC} values is prevented (Flury, 1996). For the apolar substances (e.g., λ-cyhalothrin), a particle-facilitated transport in macropores might also contribute to their enhanced vertical translocation in clayey soils (Jacobsen et al., 1997),

as this process is restricted to silty and clayey particles. In experiments with dye tracer on the Ustox soils during the study period the preferential flow of water beyond the plow layer could be observed when soil profiles were excavated (data not shown). We propose, therefore, that pesticide translocation to Ustox subsoils (up to 40 cm soil depth) was dominated by preferential flow events, which led to substantial pesticide concentrations at deeper soil layers regardless of substance polarity.

Pesticide Leaching in Lysimeter Experiments

The detection of pesticides in lysimeter percolate provides direct evidence of pesticide transport in the soil water phase to subsoil regions. In spite of similar precipitation on Ustox and Psamment plots, pan lysimeters in Ustox (35 cm) showed more frequent percolation events and shed substantially more water than those in Psamments (Fig. 5). While pan lysimeters in Psamments only shed water when at least 50 mm of rain fell within 96 h, percolation in Ustox was already induced by smaller rain events. The cumulative amount of leachate collected in free-draining lysimeters at 35 cm soil depth was 4.4 and 8.1% of the cumulative precipitation for Psamments and Ustox, respectively. Although topsoils of Oxisols are mostly well-drained, coarse sandy soil material generally exhibits a higher hydraulic conductivity and a lower water holding capacity in comparison with finer-textured substrate. Thus, only more distinct preferential flow phenomena (e.g., macropore flux) may explain the more frequent and higher percolation in Ustox. As a result a higher portion of precipitation water reached deeper soil layers soon after rainfall in the clayey soils, which agreed with the higher pesticide concentrations found in the Ustox subsoils. This finding corroborates also results of Rao et al. (1974) about fast pesticide leaching in Hawaiian Oxisols. In contrast, the more homogeneous water infiltration in Psamments resulted in less preferential water flow. Apparently, the strong evaporation under the tropical climate caused higher relative water losses from topsoils of sandy soils than from those of Ustox.

The cumulative amounts of pesticides leached (to 35 cm) within the study period were 0.0025 to 0.020% and

Table 4. Lysimeter cumulative efflux and percolate mean concentrations (pan lysimeters, 35-cm soil depth), with standard error in parentheses.

	Ustox ($n = 3$)				Psamments ($n = 3$)			
	Mean leachate concentration		Mean cumulative efflux		Mean leachate concentration		Mean cumulative efflux	
	—— μg L^{-1} ——		—— % of applied ——		—— μg L^{-1} ——		—— % of applied ——	
Alachlor	0.666	(0.249)	0.0147	(0.0077)	0.570	(0.150)	0.0098	(0.0055)
Atrazine	0.276	(0.076)	0.0124	(0.0079)	0.156	(0.045)	0.0049	(0.0033)
Chlorpyrifos	0.050	(0.010)	0.0041	(0.0027)	0.039	(0.022)	0.0027	(0.0023)
Endosulfan α	0.032	(0.011)	0.0077	(0.0022)	0.009	(0.009)	0.0019	(0.0017)
Metolachlor	0.678	(0.300)	0.0204	(0.0141)	19.16	(14.28)	0.1890	(0.0849)
Monocrotofos	0.153	(0.113)	0.0143	(0.0114)	0.044	(0.027)	0.0029	(0.0023)
Simazine	0.264	(0.107)	0.0067	(0.0028)	0.192	(0.015)	0.0039	(0.0020)
Trifluralin	0.063	(0.021)	0.0025	(0.0009)	0.044	(0.017)	0.0026	(0.0021)
			Basic data of percolate sampling					
Number of percolation events	10.0 (1.2)				6.3 (0.6)			
Total percolate volume, L	3.42 (1.53)				1.86 (0.69)			

0.0019 to 0.189% of the applied amounts in Ustox and Psamments, respectively (Table 4). Cumulative leaching of most pesticides was greater in Ustox than in Psamments, although no statistically significant differences were found between the leaching rates ($p > 0.05$). Differences in pesticide concentrations in percolate were small, although concentrations were also consistently higher in Ustox. Metolachlor was an exception, as leaching in Psamments became substantially higher than in Ustox toward the end of the study period (see below). Pesticide concentrations in lysimeter leachate and cumulative efflux were highly variable among the plots of each soil type, which was also reflected by highly variable cumulative percolate volumes within the soil groups (data not shown).

In both soils, all pesticides were detected in water of the first percolation events at 4 and 6 d after application (Fig. 6). Only the pyrethroids (deltamethrin, λ-cyhalothrin) were never detected in soil water, which reflected that they are almost insoluble in water. Cumulative pesticide leaching within the first 30 d after application generally contributed more than 60% to the total amount of leached pesticides in the study period. From 30 d on after application only the polar herbicides still exhibited substantial leaching within both soils. Especially in the sandy soils, metolachlor and alachlor leached in increasing amounts beyond 35 cm soil depth from 60 d on after application. Metolachlor was measured in concentrations up to 47 μg L^{-1} (SE = 13 μg L^{-1}) in lysimeter water during the storm events at 66 to 70 d (Fig. 5) after application in Psamments, suggesting that matrix flow transport of this herbicide was approaching 35 cm soil depth. From 66 d on after application 96% of the total output of metolachlor was recorded in lysimeter percolate. The sudden breakthrough of metolachlor, which was the most polar and persistent of the studied herbicides, suggested that progressive leaching of polar pesticides beyond 35 cm soil depth started in sandy soils toward the end of our study period. However, the lower persistence and polarity of atrazine, simazine, and alachlor in comparison with metolachlor would result in reduced breakthrough intensities of these substances in Psamments. The transport of apolar substances within both soils beyond 35 cm soil depth was mainly due to preferential flow events, occurring

within the first 10 d after application (Fig. 6). Monocrotofos was still detected at 70 d after application in percolate (0.1–0.2 μg L^{-1}) of both soils, in spite of its extremely fast topsoil dissipation and lack of detection in the subsoil layers. For most pesticides (except for metolachlor and alachlor in Psamments), concentrations in percolate of storm events, when high percolation rates occurred (at 8–10, 30, 54, and 66–70 d after application; Fig. 5), decreased with increasing time after application in both soils. This was consistent with findings that preferential flow events led to the highest percolate concentrations of pesticides right after application, due to infiltration of highly contaminated topsoil water (Hall et al., 1989). We conclude that preferential flow events within 30 d after application contributed substantially to cumulative leaching of all pesticides in both soils. Matrix flow transport started to enhance the efflux of polar and/or persistent pesticides in lysimeters at 35 cm soil depth toward the end of our study period in sandy soils.

To investigate pesticide leaching below the main root zone, lysimeters were also installed at 95 cm soil depth. However, in this depth free-draining lysimeters never shed water during the study period, indicating that saturated conditions immediately above the lysimeter pans never existed in both soils. Obviously, storm flow events did not induce fast, saturated water flow up to 95 cm soil depth in both soils.

Capillary-wick lysimeters have been introduced as a means for the sampling of soil pore water under a constant tension, created by a hanging water column in a glass fiber wick (Holder et al., 1991). Therefore, wick lysimeters did not depend on saturated soil conditions to collect water, but sampled percolate against a maximum tension of -50 cm water column (equal to its vertical wick length) in our study. The wick lysimeter design used in our experiment (Fig. 1) should combine the advantages of free-draining and suction lysimeters. As wick lysimeters could be installed only 22 d after the application of pesticides, their data was not useful to report absolute leaching rates within the study period and therefore will not be presented in detail here. However, data from wick lysimeters at 95 cm soil depth provided valuable information concerning the identification of pesticides that migrated beyond the root zone
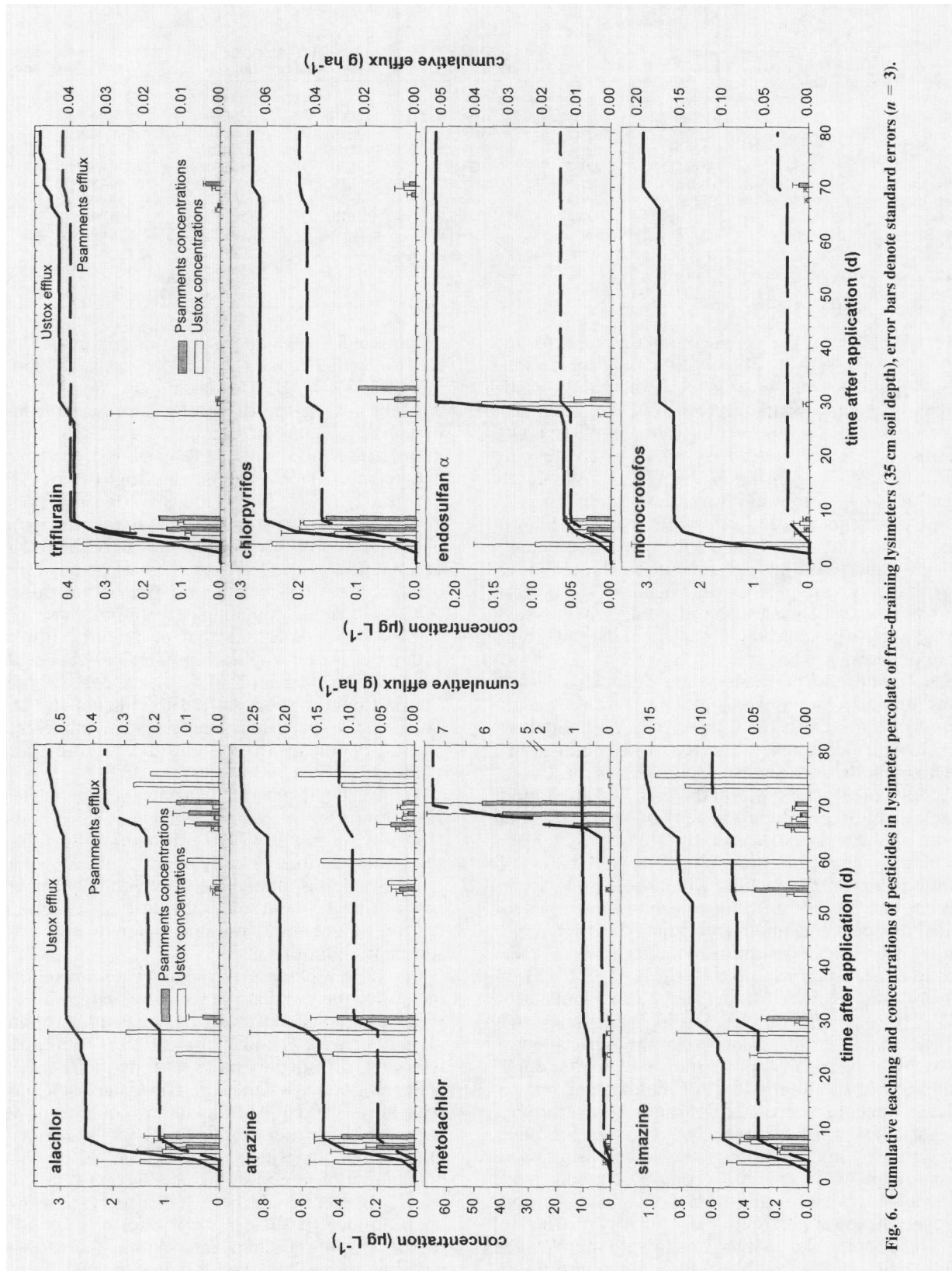
Fig. 6. Cumulative leaching and concentrations of pesticides in lysimeter percolate of free-draining lysimeters (35 cm soil depth), error bars denote standard errors (n = 3).

in our experiments and which therefore are probable contaminants of ground water resources. In addition, wick lysimeter data from 35 cm soil depth was found useful to judge the performance of wick lysimeters in comparison with their free-draining equivalents in different soils, helping to improve the design of lysimeters for future field experiments.

A comparison of percolation data between free-draining and wick lysimeters in 35 cm soil depth since 22 d after application revealed that the wick lysimeters shed water more often and were able to collect a greater amount of percolate (number of percolation events: 17 ± 1.4 [SE], total percolation volume: 3.9 ± 0.7 L [SE]) as compared with pan lysimeters (7.2 ± 0.9 and 2.4 ± 1.3 L, respectively) in Ustox. The substance efflux was not significantly different between pan and wick lysimeters in Ustox for all pesticides, but varied less for the latter lysimeter type (data not shown). In contrast, the 35-cm wick lysimeters in Psamments collected significantly less water (0.04 in comparison with 1.2 L) in fewer percolation events than their free-draining equivalents and consequently exhibited 3 to 100 times lower cumulative pesticide efflux or no efflux at all (data not shown). Obviously, wick lysimeters malfunctioned in the sandy soils at 35 cm soil depth, which might be explained by periodical soil water tensions below −50 cm water column and no subsequent self-priming of the wicks. A high variability of wick lysimeter performance in sandy soils was also reported by Holder et al. (1991).

At 95 cm soil depth, only wick lysimeters were able to collect small volumes of soil water (total amount <100 mL), which derived from few percolation events in both soils ($n = 4$–5). The relatively low percolation rates indicated that at this soil depth continuously high water tensions existed in both soils, in spite of more than 650 mm of rain during the study period. However, metolachlor, alachlor, atrazine, simazine, and trifluralin were detected in substantial amounts in percolate, resulting in the efflux of 11 to 25% and 0.1 to 22% of the amounts recorded in pan lysimeters at 35 cm soil depth in Ustox and Psamments, respectively (since 22 d after application). The detection of trifluralin in leachate may be related to its high vapor pressure, which might have led to a significant vertical translocation of this pesticide within the soil gas phase. An enhanced cotransport of apolar pesticides in soil due to complexation with dissolved organic matter (Nelson et al., 2000) seems unlikely, as other pesticides of similar K_{OC}, such as chlorpyrifos and endosulfan α, were never detected in leachate at 95 cm soil depth. We conclude that all of the herbicides in our study exhibited leaching beyond the root zone in both tropical soils. For future experiments, wick lysimeters with improved wick design (finer glass fibers, thicker braids) need to be tested to enhance their percolation rates.

Comparative Evaluation

It is open to question how pesticide dissipation data from temperate zones can be used to forecast pesticide behavior in the tropics (Racke et al., 1997). In the soils under study, substance half-lives were 5 to 10 times shorter than those reported from temperate zones (Table 3). Exceptions were λ-cyhalothrin, deltamethrin, and alachlor, which exhibited a less reduced soil persistence (factor of 3) under tropical conditions. The more rapid dissipation of pesticides under tropical climates is not necessarily caused by enhanced degradation of pesticides, but can also be due to a higher volatilization of substances from the soil (Racke et al., 1997). Especially for trifluralin, chlorpyrifos, and partly endosulfan α, the substantially shortened half-lives were probably influenced by significant volatilization losses (e.g., Rüdel, 1997). In contrast, the more polar metolachlor and alachlor were less affected by their high vapor pressure, because leaching into deeper soil layers (2–8 cm) during the first rain events presumably reduced further volatilization losses.

The presented data corroborated results reported for the half-life times of metolachlor, alachlor, and endosulfan α in field studies from other tropical regions (Cooper and Zheng, 1994; Ismail and Kalithasan, 1997; Kathpal et al., 1997; Sanyal et al., 2000). Also, the bi-phasic shape of pesticide decay curves had been reported earlier by Kathpal et al. (1997) for endosulfan α. We therefore assume that for most pesticides a fast, bi-exponential dissipation is a general feature of their behavior in tropical soils. Slight differences between pesticide half-life times in comparison with former studies on Ustox (Laabs et al., 2000) may be due to yearly climatic differences and different application dosages.

Studies on the long-term accumulation of persistent pesticides in soils from the tropics are scarce. Ferreira et al. (1988) reported low levels of organochlorine residues in cultivated soils of São Paulo State. However, most of these very persistent insecticides (e.g., DDT, aldrin) have been banned from agricultural use in Brazil in the meantime. Luchini et al. (2000) measured substantial concentrations of trifluralin and endosulfan in cotton-cropped soils in between the cropping seasons. Obviously, at least some presently used pesticides may have the potential for a carryover into the next cropping season in tropical Brazil. Nevertheless, in view of the fast topsoil dissipation of pesticides, a long-term accumulation of the studied pesticides appears to be unlikely in the soil compartment of tropical ecosystems in Brazil.

Compared with Psamments, pesticide translocation due to preferential flow was more pronounced in Ustox during the study period (Fig. 3). As Ustox lacked visible shrinking cracks at the soil surface, due to the kaolinitic–oxidic character of their clay fraction, we attributed the preferential flow phenomena to the granular aggregate/pseudo-sand structure in topsoils. The fast vertical translocation of pesticides in Ustox was also indicated by their presence in lysimeter percolate (Fig. 6). Equally, pesticides were detected in lysimeter percolate at Psamments, but there the soil core results did not show a significant translocation of apolar pesticides to the subsoils (e.g., chlorpyrifos, endosulfan α). This might be attributed to the substantially lower sorption capacity of the sandy soils (low organic carbon content), which resulted in a reduced sorption of pesticides from fast
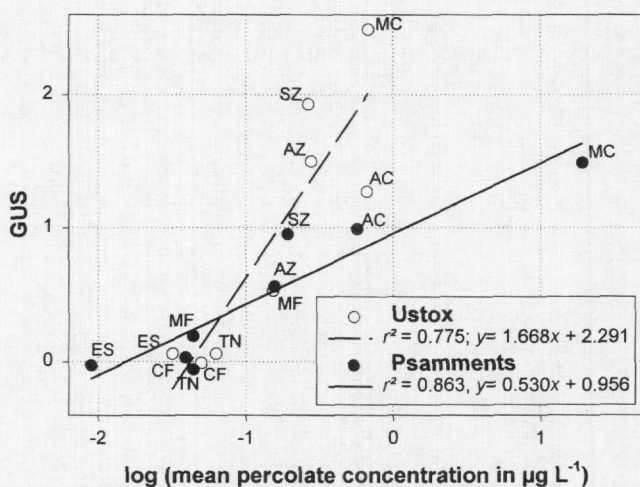
Fig. 7. Relationship between the mean pesticide concentrations in free-draining lysimeters (35 cm soil depth) and the Groundwater Ubiquity Score (GUS = $\log(t_{0.5})[4 - \log(K_{OC})]$), according to Gustafson (1989) (AC, alachlor; AZ, atrazine; CF, chlorpyrifos; ES, endosulfan α; MC, metolachlor; MF, monocrotofos; SZ, simazine; TN, trifluralin); $p < 0.05$ for both regressions.

percolating water, leading to concentrations below the analytical detection limits in the subsoil (Patterson et al., 2000). However, for the polar herbicides (e.g., metolachlor, alachlor) the soil core analysis proved a progressive transport to deeper soil layers in substantial amounts in the sandy soils (Fig. 3), which was reflected by concentrations in lysimeter percolate for metolachlor only toward the end of our study period. Of all pesticides studied, only metolachlor, atrazine, simazine, and, to a lesser degree, alachlor and trifluralin, were detected at all times in all sampled soil layers of the Psamments. We interpreted this as a sign of a continuous downward movement of these pesticides within the soil profile, which eventually would lead to rising leaching rates in lysimeters, too.

Results of our leaching experiments were consistent with data of Nakagawa et al. (1996), who reported mean atrazine concentrations of 0.11 μg L^{-1} (cumulative efflux of 0.025% of application) in lysimeter percolate at 50 cm soil depth within 8 mo after application (Ustox from São Paulo State, Brazil). The low concentrations and leached mass amounts of atrazine in their and our study from the tropics, when compared with soils in temperate regions (e.g., Hall et al., 1989), suggest that leaching of atrazine is reduced in Ustox. It remains to be studied if the fast topsoil dissipation or the low water percolation due to high evaporation losses was more important for reducing atrazine leaching in these studies. In comparison with results of Laabs et al. (2000), leaching rates in Ustox were similar for the apolar pesticides and monocrotofos. However, more than 50 times higher leaching rates within 28 d after application were found in our earlier study for metolachlor, atrazine, and simazine, which we attributed to higher precipitation and artificial irrigation of plots in this study.

To predict the leaching potential of pesticides in soils, various coefficients involving the key parameters $t_{0.5}$ and K_{OC} of pesticides have been proposed (Gustafson, 1989;

Kleveno et al., 1992). In our experiment the simple Groundwater Ubiquity Score (GUS = $\log(t_{0.5})[4 - \log(K_{OC})]$), which has been introduced by Gustafson (1989) to identify and rank leachers according to extensive ground water monitoring studies in the USA, exhibited a good correlation with our cumulative leaching efflux (Spearman $R = 0.79$, $p < 0.05$ and $R = 0.97$, $p < 0.05$ for Ustox and Psamments, respectively). Moreover, the GUS was also closely correlated with the mean concentrations of pesticides in lysimeter percolate as shown in Fig. 7. For our medium-term leaching study the GUS index was therefore useful for the description of the relative leaching potential of pesticides in the studied soils. We conclude that risk-assessment tools developed for temperate environments are also applicable in tropical ones, when parameters for pesticides (K_{OC}, $t_{0.5}$) are determined under the respective climatic conditions. Yet, the absolute GUS values proposed to define leacher (GUS > 2.8), transitional (1.8 < GUS < 2.8), and non-leacher (GUS < 1.8) compounds (Gustafson, 1989) have to be modified according to long-term leaching and ground water monitoring studies in these climates. After the identification of typical leacher and nonleacher chemicals under local conditions a calibration of the used index with these reference chemicals may be conducted (Li et al., 1998). Then, a more meaningful interpretation of index results for other pesticides used in the area under investigation is possible.

The ranking results are in agreement with the findings of many field studies from temperate regions reporting that in spite of preferential flow transport of pesticides, the total amounts leached correlated to mobility characteristics (e.g., soil sorption coefficient, water solubility) of pesticides (Flury, 1996). However, the differences in pesticide persistence and mobility under the given climatic and pedological conditions could lead to increased leaching of some pesticides relative to other compounds in the tropics. In contrast to studies from temperate regions (e.g., Bowman, 1990; Hall et al., 1989), metolachlor, for example, was more mobile in the soil profile than atrazine and simazine, due to its lower K_{OC} and substantially higher persistence in comparison with the triazines in our study. Consequently, the list of priority ground water pollutants in the tropics might differ in some cases from that in temperate zones.

CONCLUSIONS

The evaluation of pesticide dissipation in Brazilian Ustox and Psamments soils demonstrated that their persistence was mostly greater in the clayey than in the sandy soils. In comparison with temperate regions, dissipation of pesticides was 5 to 10 times faster, except for alachlor, deltamethrin, and λ-cyhalothrin, which exhibited a less reduced persistence than under temperate conditions. Leaching of pesticides in the Ustox was thought to be controlled by preferential flow, as indicated by the detection of polar and apolar compounds in lysimeter leachate 4 to 6 d after application and in deeper soil layers. Lysimeter data showed that preferential flow also led to an early detection of many pesticides

in lysimeter percolate in Psamments. However, the soil coring analysis proved that in the sandy soils also a substantial progressive vertical transport of the more polar herbicides took place, which was reflected in steeply increasing concentrations of metolachlor in lysimeter leachate (35 cm depth) from 60 d on after application. Alachlor, atrazine, metolachlor, simazine, and trifluralin were also present in percolate at 95 cm depth in both soils, which indicated their potential for the contamination of aquifer regions under tropical conditions. The GUS was able to describe the relative ranking of pesticides in regard to their leaching properties on basis of the measured dissipation times and K_{OC} values. However, in comparison with ranking lists of pesticides according to their leaching properties in temperate regions, observed leaching rates and computed GUS values of pesticides in our study differed in their relative order and in absolute values.

Long-term leaching studies (2–3 yr) and surveys of ground water contamination in agricultural regions of the tropics are needed to establish a list of priority pollutants for these climates. It still remains to be proven if pesticide leaching in soils under tropical conditions is generally reduced in comparison with temperate regions.

ACKNOWLEDGMENTS

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Photochemistry and Photoinduced Toxicity of Acifluorfen, a Diphenyl-Ether Herbicide

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ABSTRACT

Photochemistry studies can be helpful in assessing the environmental fate of chemicals. Photochemical reactions lead to the formation of by-products that can exhibit different toxicological properties from the original compound. For this reason the photochemical behavior of the herbicide acifluorfen (5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid) in the presence of different solvents was studied. Photochemical reactions were carried out using a high-pressure mercury arc and a solar simulator. Kinetic parameters and quantum yields were determined. The identification of photoproducts was performed by mass spectrometry and [^{1}H] nuclear magnetic resonance (NMR). Nitrofluorfen, hydroxy-nitrofluorfen, 2-chloro-4-(trifluoromethyl)-phenol, 5-trifluoromethyl-5'-nitrodibenzofuran, and other derivatives were identified. The photochemical reactions were also carried out in the presence of either a singlet or a triplet quencher, and in the presence of either a radical initiator or a radical inhibitor. Substances used as inhibitors of the excited levels T_1 and S_1 showed that photodegradation of acifluorfen begins from a singlet state S_1 through a π,π^* transition. The role of free radicals in the photodegradation of acifluorfen was determined and a radical mechanism was proposed. Toxicity tests against *Daphnia magna* Strauss showed that acifluorfen was not toxic at a concentration of 0.1 mM; however, photoproducts formed after 36 h of UV exposure of the herbicide induced a remarkable toxicity to the test organism.

D EGRADATION and transformation reactions of herbicides lead to the formation of by-products that exhibit, in some cases, toxicological properties that are very different from the original compound (Kirkwood, 1986; Scheunert, 1992). With increasing concern and awareness of the fate and effects of these chemicals in the environment, it is important to develop sensitive methods that can characterize the presence and toxicity of residues or reaction by-products at trace levels. This challenge is most evident in the detection of water-soluble and polar compounds, and their degradation products.

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Diphenyl-ethers are highly active herbicides used for the selective control of broadleaf weeds in large-seeded legume crops. Acifluorfen 1, as illustrated in Scheme 1 (Fig. 1), is a nitro-diphenyl ether herbicide (Johnson et al., 1978), acting as protoporphyrinogen oxidase inhibitor, and is used to control monocotyledonous and broad-leaved weeds at rates in the range of 0.38 to 0.6 kg of active ingredient (a.i.) ha^{-1}. Solubility in water is 120 mg L^{-1}. It has acute oral toxicological effects on mammals with oral LD$_{50}$ values between 1370 and 2050 mg kg^{-1} in rats, an acute percutaneus LD$_{50}$ value of 3680 mg kg^{-1} for rabbit, and moderate fish toxicity between 17 and 61 mg L^{-1} (Worthing and Hance, 1994).

Herbicides in this class require light to exhibit phytotoxic activity (Fadayomi and Warren, 1976; Gillham and Dodge, 1987; Vanstone and Stobbe, 1979) and under irradiation they can give rise to several photodegradation products (Scrano et al., 1999). However, the nature of the light-activated mechanism is still unknown.

Photochemical reactions of substituted diphenyl ethers in liquid phases have received attention (Nakagawa and Crosby, 1974; Ruzo et al., 1980), but no information is available on the photochemical behavior of acifluorfen and its photoinduced toxicity. It is only known that in aqueous solutions acifluorfen degraded following first-order kinetics, with loss of the carboxylic acid group (Pusino and Gessa, 1991). Diphenyl ether, 1,4-diphenoxybenzene, and some substituted diaryl ethers (methyl and/or methoxy derivatives) have been irradiated using unfiltered UV light from a high-pressure mercury lamp at 25°C. The reactions observed were cleavage of the ether bond(s), followed by H-abstraction from the solvent yielding phenols and benzene derivatives, and a photo-Claisen type rearrangement yielding 2-and/or 4-hydroxybiphenyl derivatives (Hageman et al., 1970). Another experiment showed that diphenyl ether was converted into *o*-phenylphenol, *p*-phenylphenol, and a small amount of phenol, by UV light in various solvents. *p,p'*-Ditolyl ether was similarly converted into 2-(*p*-tolyl)-4-methylphenol and *p*-cresol, indicating that the photochemical rearrangement proceeds via C–O bond cleavage and recombination of the radical (quinoid) fragments. These reactions were reported as intramolecular and occurred via an excited singlet state or via a short-lived triplet (Ogata et al., 1970).