**7184** *J. Agric. Food Chem.* **2005,** *53,* 7184–7192

JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

# Sorption and Aging of Corn and Soybean Pesticides in Tropical Soils of Brazil

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The efficacy and fate of pesticides in soil strongly depend on sorption reversibility that is known to decrease with increasing contact time (aging). We elucidated the aging dynamics of eight different pesticides in two contrasting agricultural soils of tropical Brazil (Ustox and Psamments), using batch equilibrium experiments and sequential extractions of field samples. Adsorption was best described by Langmuir isotherms for the entire and by Freundlich equations for the lower concentration range. In field samples, water extractable pesticide fractions mostly dissipated at least twice as fast as did the solvent extractable fractions. Hence, in comparison to 0 days $K_{OC}$ values, measured field $K_{OC}$ values were higher by a factor of 2.6−38 for the clayey Ustox and 2.1−72 for the sandy Psamments toward the end of the experimental period at 80 days after application. The extent of such aging basically increased with increasing polarity of the pesticide. An absolute enrichment of polar pesticides within the final exhaustive acetone−ethyl acetate−water extracts was observed during the experimental period, so that we may deduce that pesticides had redistributed into stronger sorption sites. The time course of the $K_{OC}$ development was well-described using a semiempirical equation, which had been employed for temperate soils before.

**KEYWORDS: Aging; alachlor; atrazine; chlorpyrifos; endosulfan-α; metolachlor; monocrotofos; pesticides; soil; sorption; simazine; trifluralin**

## INTRODUCTION

The sorption of pesticides in soil is a key process influencing the degradation and leaching of these substances in the soil compartment. Consequently, the determination of the partitioning characteristics of these substances between soil and water phase is essential for the assessment of their environmental fate. Sorption of chemicals in soils and sediments is typically measured with the batch equilibrium method (*1*), which is used worldwide as a standard method to investigate the sorption of pesticides in soils (e.g., *2*−*4*). It is a simple and precise method, except for systems with very low sorption capacities for pesticides (*5*).

The soil sorption coefficient of pesticides ($K_D$), as determined in batch equilibrium experiments, is used for the estimation of the leaching potential of pesticides (e.g., *6*, *7*). As the sorption of nonionic pesticides is primarily related to the organic matter content of soils (*5*), sorption coefficients of pesticides are frequently normalized to the organic carbon content of the respective soil ($K_{OC}$). Sorption isotherms of pesticides in topsoil are measured to obtain quantitative relationships between the sorbed amounts and the solution concentrations of pesticides at different total concentrations in soil (*8*). For temperate soils or soil constituents, sorption isotherms of pesticides are commonly described by Freundlich equations, sometimes also by the Langmuir model.

Studies with "aged" pesticide residues in temperate soils demonstrated that the reversibility of adsorption is not constant but decreases with increasing contact time of pesticides in soils (e.g., *9*−*13*). This phenomenon has been attributed to slow diffusion of substances into certain domains of the organic matter structure and retarded diffusion in soil micropores (reviewed by *14*). Aged residues were shown to be less susceptible to desorption and therefore were less bioavailable, toxic, and degradable (*11*, *15*). Also, this effect may significantly reduce pesticide mobility in soils when compared with estimations based on a complete reversibility of pesticide sorption (e.g., *4*, *14*). Thus, for an assessment of pesticide fate under field conditions, such time-dependent changes of pesticide sorption properties and availability need to be considered. The decrease of pesticide availability with time was proven for temperate soils, e.g., using a sequential extraction of soil with increasingly harsh solvents (*16*).

While pesticide sorption properties were extensively studied for temperate soils and climates (reviewed by *5*, *8*), studies of pesticide sorption in tropical soils were limited to relatively few compounds (e.g., metribuzin, trifluralin, endosulfan, and atrazine), mostly investigating their partitioning without consideration of isotherm characteristics (e.g., *17*−*21*). A comprehensive assessment of sorption properties of the investigated eight pesticides is still lacking for agricultural soils of tropical Brazil. The aging of pesticide residues in tropical field soils has until

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10.1021/jf050969c CCC: $30.25

**Table 1.** Basic Properties of the Studied Soils (0–10 cm)

| soil/study | texture (g kg$^{-1}$) clay | silt[b] | sand | organic carbon (g kg$^{-1}$) | pH (1 M KCl) | CEC[a] (cmol$_c$ kg$^{-1}$) |
|---|---|---|---|---|---|---|
| | | | Ustox | | | |
| laboratory | 477 | 68 | 455 | 26.4 | 4.3 | 12.5 |
| field ($n = 3$) | 429–540 | 25–43 | 424–546 | 16.3–30.6 | 4.8–5.6 | 12.1–17.5 |
| | | | Psamments | | | |
| laboratory | 48 | 8 | 944 | 7.3 | 4.0 | 3.2 |
| field ($n = 3$) | 97–144 | 10–18 | 846–885 | 7.1–10.1 | 4.2–4.3 | 3.7–5.1 |

[a] Potential cation exchange capacity determined in 1 M NH$_4$–acetate (Soil Survey Staff, 1997). [b] Silt fraction: 2–20 $\mu$m.

now not been investigated at all, making a forecast of the long-term fate of these substances in the tropical soil environment difficult.

The objective of this study was to elucidate the sorption behavior of eight frequently used soybean and corn pesticides in two contrasting soils of tropical Brazil. To this aim, adsorption isotherms were measured in topsoil samples using the batch equilibrium technique. The change of pesticide availability and desorption properties in field samples with time after application was evaluated by a sequential extraction of topsoil samples with water and two different organic solvent extracts.

## MATERIALS AND METHODS

**Soils.** The studied soils (laboratory experiment) were collected from a farm, 110 km southeast of Cuiabá, in Mato Grosso State, Brazil (15°53′ southern latitude, 55°16′ western longitude, ca. 800 m above sea level). Samples of a fine clayey, mixed, isohyperthermic Typic Haplustox (Soil Survey Staff, 1997; according to Brazilian classification: Latossolo vermelho-amarelo) and an acid, isohyperthermic Ustic Quartzipsamments (Areia Quartzosa) were taken from the 0 to 10 cm layer of soils, homogenized, air-dried, and sieved (2 mm). Whereas Ustox sites had been under a corn−soybean−pasture rotation, Psamments were collected from areas that had been used as pasture (degraded) during the last 5 years. Samples of aged field soils were taken from a field experiment in central Brazil (see above for location), set up on the two soil types described above (samples were stored frozen until analysis). The investigated pesticides had been applied to bare ground (three field replicates per soil), and their topsoil dissipation was monitored for 80 days after application (see ref *22* for more details). The basic properties of laboratory and field soils are shown in **Table 1**.

An analysis of topsoil samples (laboratory soils) by X-ray diffractometry (Siemens D5000, Siemens AG, Karlsruhe, Germany) showed that the mineral fraction of Psamments was dominated by quartz, with minor signals for gibbsite and hematite. The mineral phase of Ustox also contained a substantial fraction of quartz, besides significant portions of gibbsite, goethite, kaolinite, and hematite (data not shown).

**Batch Experiments.** Batch equilibrium sorption experiments were carried out in glass centrifuge tubes with Teflon-lined screw caps using a soil−solution ratio of 1:5 (w/w), according to principles of the OECD guideline for the testing of chemicals (*1*). Pesticide standards with a declared purity greater than 95% were purchased from Promochem (Wesel, Germany). To reduce the number of experiments, pesticides were batched in pairs, grouping pesticides with similar water solubility: monocrotofos (1 000 000 mg/L) and metolachlor (488 mg/L), alachlor (170 mg/L) and atrazine (33 mg/L), simazine (6.2 mg/L) and chlorpyrifos (1.4 mg/L), and endosulfan-α (0.32 mg/L) and trifluralin (0.22 mg/L). Pesticide solutions were set up directly in the batch vessels. For this purpose, an aliquot of pesticide standard solution (acetone) was pipetted into the empty glass tube and the solvent was left to evaporate at room temperature. Thereafter, the aqueous solution of 0.01 M CaCl$_2$ (25 mL) was added and the vessel was sonicated for 2 min in a water bath to enhance the dissolving process of pesticides in the water phase. The weighed soil sample (5 g dry weight) was then added to the water phase, and the batch vessels were tumbled slowly end-over-end (at ca. 40 rpm) for the respective time periods at 22 ± 2 °C in the dark. After they were shaken, the tubes were centrifuged at 3000*g* for 20 min and the clear supernatant was decanted. Pesticide concentrations were determined in the water phase by solid phase extraction and subsequent gas chromatography−mass selective detection (GC-MSD) analysis. The resulting soil concentrations were calculated from the difference between initial concentration and pesticide amount found in the supernatant. For all experiments, new and unscratched glass tubes were used to minimize initial sorption of pesticides on the glass surfaces. The adsorption of pesticides to the Teflon lining of the screw caps was assessed by batch experiments without soil and was found to be negligibly small for all compounds ($<$2% of the spiked amount at 0.2 mg/mL).

The kinetics of pesticide sorption (2−96 h shaking time) were determined for all compounds in preliminary experiments at one initial water phase concentration in three replicates (data not shown). For pesticide adsorption, an equilibrium time of 48 h was considered adequate, as beyond that time period further sorption of pesticides was negligible. A solvent extraction of the soil phase with acetone−ethyl acetate−water (AEW) (2:2:1, v/v) at shaking times longer than 24 h revealed that at shaking times $\geq$3 days a significant degradation/bound residue formation of some pesticides occurred. Therefore, a shaking time of 48 h for adsorption isotherms was chosen, for which pesticide dissipation remained $<$2% of the applied amount, with the exception of monocrotofos and chlorpyrifos for which $<$10% of the applied amount remained unaccounted.

Isotherm experiments were done in duplicate using initial nominal pesticide solutions of 0.04, 0.2, 0.4, 1.0, and 2.0 mg L$^{-1}$ (shaking time, 48 h). Pesticide desorption experiments were also performed but will not be reported, as the above-mentioned incomplete balance for pesticides after desorption cycles did not allow for an unambiguous interpretation of the significant hysteresis effects observed. However, for comparison with desorption coefficients obtained from field samples, the values for the first desorption step (24 h) at the highest isotherm concentration were reported from this laboratory experiment. Before the desorption cycle, batch vessels were centrifuged and the aqueous phase was decanted and analyzed. The decanted liquid was then substituted in the batch vessel with an equal amount of fresh 0.01 M CaCl$_2$ solution, whose exact volume was determined by weighing the centrifuge tubes before and after the decanting. The batch vessel was then again tumbled for 24 h. During the separate adsorption/desorption experiment, 10 mg L$^{-1}$ of HgCl$_2$ was added to the water phase to suppress any microbial activity (*23*) during the 72 h experiment (the resulting microbial activity was not checked).

Freundlich and Langmuir models (eqs 1 and 2, respectively) were fitted to sorption isotherm data using nonlinear regression.

$$C_s = K_F C_e{}^n \tag{1}$$

$$C_s = K_L C_{Smax} C_e (1 + K_L C_e)^{-1} \tag{2}$$

where $C_s$ (in $\mu$g g$^{-1}$) is the amount of sorbed pesticide, $K_F$ and $K_L$ are the respective Freundlich and Langmuir sorption coefficients (mL g$^{-1}$ and mL $\mu$g$^{-1}$, respectively), $C_e$ ($\mu$g mL$^{-1}$) is the equilibrium concentration of pesticides in the water phase, $n$ is the Freundlich coefficient, and $C_{Smax}$ ($\mu$g g$^{-1}$) is the maximum sorption capacity of the adsorbent in the Langmuir equation.

Desorption properties of pesticides in aged field samples were assessed by a sequential extraction of soil samples, which had been generated during a field experiment in central Brazil. Before analysis, soil samples (stored at −20 °C) were thawed and aliquots (equivalent to 10 g of soil dry mass) were weighed into glass centrifuge tubes and extracted sequentially with 50 mL each of 0.01 M CaCl$_2$ (equivalent to the batch desorption for 24 h), methanol, and AEW (2:2:1, v/v). For the two extraction steps with organic solvents, samples were shaken end-over-end for 4 h. After each extraction step, the samples were centrifuged for 20 min at 3000*g* and the clear supernatant was decanted before the next solvent was added. The water phase was extracted and analyzed as described below. The solvent extracts were processed as described in ref *24*. The pesticide amounts in each fraction were

**Table 2.** Model Parameters Estimated for Pesticide Adsorption Isotherms (±Standard Error of Estimation)

| | | Langmuir model | | | Freundlich model | | | Freundlich model (lower end)[a] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| pesticide | soil type[b] | $K_L$[c] (mL $\mu$g$^{-1}$) | $C_{Smax}$[d] ($\mu$g g$^{-1}$) | $R^2$ [e] | $K_F$[f] (mL g$^{-1}$) | $n$[g] | $R^2$ | $K_F$ (mL g$^{-1}$) | $n$ | $R^2$ |
| alachlor | Ox | 1.22 ± 0.36 | 5.50 ± 0.78 | 0.986 | 2.87 ± 0.21 | 0.62 ± 0.10 | 0.960 | 3.90 ± 0.53 | 0.87 ± 0.15 | 0.974 |
| | Ps | 0.33 ± 0.14 | 5.84 ± 1.68 | 0.992 | 1.39 ± 0.08 | 0.82 ± 0.10 | 0.983 | 1.66 ± 0.12 | 1.06 ± 0.13 | 0.988 |
| atrazine | Ox | 0.84 ± 0.06 | 6.89 ± 0.29 | 0.999 | 3.05 ± 0.10 | 0.69 ± 0.05 | 0.992 | 3.62 ± 0.15 | 0.84 ± 0.04 | 0.998 |
| | Ps | 0.35 ± 0.07 | 5.37 ± 0.76 | 0.998 | 1.34 ± 0.05 | 0.80 ± 0.06 | 0.993 | 1.51 ± 0.06 | 0.96 ± 0.06 | 0.996 |
| chlorpyrifos | Ox | 4.95 ± 0.83 | 38.3 ± 5.0 | 0.999 | 98.2 ± 8.9 | 0.86 ± 0.03 | 0.999 | 129 ± 29 | 0.93 ± 0.06 | 0.997 |
| | Ps | 3.95 ± 1.27 | 26.1 ± 5.9 | 0.995 | 46.7 ± 7.6 | 0.81 ± 0.07 | 0.990 | 88.3 ± 4.4 | 1.00 | 0.983[h] |
| endosulfan-α | Ox | NS[i] | NS | | 148 ± 39 | 0.95 ± 0.08 | 0.990 | 187 ± 13 | 1.00 | 0.967[h] |
| | Ps | 4.31 ± 1.36 | 27.5 ± 6.1 | 0.996 | 54.4 ± 9.5 | 0.82 ± 0.07 | 0.990 | 157 ± 16 | 1.12 ± 0.03 | 0.999 |
| metolachlor | Ox | 0.79 ± 0.18 | 5.54 ± 0.72 | 0.994 | 2.34 ± 0.12 | 0.70 ± 0.08 | 0.980 | 3.08 ± 0.04 | 0.95 ± 0.02 | 1.000 |
| | Ps | 0.81 ± 0.24 | 2.49 ± 0.39 | 0.988 | 1.04 ± 0.08 | 0.66 ± 0.11 | 0.964 | 1.33 ± 0.08 | 0.94 ± 0.09 | 0.993 |
| monocrotofos | Ox | NS | NS | | 0.80 ± 0.10 | 0.46 ± 0.14 | 0.811 | 1.25 ± 0.14 | 1.00 | 0.907[h] |
| | Ps | NS | NS | | 0.19 ± 0.01 | 0.78 ± 0.09 | 0.984 | 0.20 ± 0.02 | 1.00 | 0.916[h] |
| simazine | Ox | 0.96 ± 0.07 | 8.14 ± 0.31 | 0.999 | 3.92 ± 0.11 | 0.68 ± 0.04 | 0.995 | 4.48 ± 0.23 | 0.78 ± 0.05 | 0.997 |
| | Ps | 1.06 ± 0.27 | 3.24 ± 0.39 | 0.990 | 1.56 ± 0.11 | 0.61 ± 0.10 | 0.960 | 2.04 ± 0.07 | 0.89 ± 0.04 | 0.998 |
| trifluralin | Ox | 9.68 ± 2.12 | 26.6 ± 4.0 | 0.998 | 94.5 ± 18.2 | 0.80 ± 0.06 | 0.992 | 273 ± 25 | 1.05 ± 0.02 | 1.000 |
| | Ps | 12.2 ± 2.2 | 14.4 ± 1.2 | 0.995 | 30.9 ± 5.8 | 0.63 ±0.08 | 0.977 | 126 ± 7 | 1.00 | 0.981[h] |

[a] Fitted only to the lower concentration range (initial concentrations, 0.04–1 mg L$^{-1}$). [b] Ox, Ustox; Ps, Psamments. [c] Langmuir sorption coefficient. [d] Langmuir maximum sorption capacity of sorbent. [e] Coefficient of determination for nonlinear regression. [f] Freundlich sorption coefficient. [g] Freundlich exponent. [h] $r^2$ of linear fit. [i] NS = parameter estimation not significant at the $p < 0.1$ probability level.

corrected on the basis of the average weight of water/solvent remaining in the soil after centrifugation (5.4−6.4% of water/solvent weight) in order to compensate the carryover of solution from one fraction to the next.

**Pesticide Analysis.** Pesticides were solid phase extracted from water samples onto bonded silica adsorbent (400 mg of C18-phase, Baker Chemicals, Gross-Gerau, Germany). To ensure a complete retention of polar pesticides during extraction, 1.5 g of KCl (analysis grade) was added as a saturated solution to every 50 mL of batch solution. After extraction, the solid phase cartridges were dried in the air stream (10 min) and pesticides were eluted with 8 mL of ethyl acetate and 4 mL of *n*-hexane. The organic phase was then concentrated and analyzed by GC-MSD. Quality control of pesticide analysis was achieved by the means of internal standards (α-HCH, terbuthylazine, and ditalimfos), for which the recovery (usually >80% of the spiked amount) was calculated to evaluate the extraction efficiency. Solvent extracts of soil samples (methanol and AEW [2:2:1, v/v/v]) were analyses as described in ref *24*.

**Statistical Analysis.** Isotherm models were fitted to the data by nonlinear regression using the software package Sigma-Plot for Windows 2004, version 9.01 (Jandel GmbH, Erkrath, Germany), which employs the Marquardt−Levenberg algorithm for parameter estimation. Linear regressions were executed with the same software package, using the least-squares method. Spearman rank correlations were done with the program Statistica for Windows, version 5.1 (Statsoft Inc., Tulsa, OK). Modeling of pesticide fate (compartment model of Richter et al., *25*) was performed with ModelMaker Version 3 (Cherwell Scientific Publishing, Oxford, United Kingdom).

## RESULTS AND DISCUSSION

Batch experiments were conducted with pairs of pesticides to reduce the amount of samples to be processed. Competition between pesticides may influence their sorption properties (e.g., *26*, *27*); however, when pesticides are present at similar concentrations in the water phase, no substantial alteration of pesticide sorption occurs in comparison to monopesticide systems (e.g., *26, 28*). We may therefore assume that competitive effects provoked by using pairs of pesticides with similar solution concentrations were reasonably small in our batch experiments.

During preliminary experiments, the adsorption kinetics of pesticides were assessed (data not shown). While the nonpolar pesticides showed a fast sorption and attained an apparent sorption equilibrium at ≤12 h (trifluralin, endosulfan-α, and chlorpyrifos), the more polar pesticides alachlor, atrazine, metolachlor, monocrotofos, and simazine exhibited an initial phase of high adsorption rates (<12 h), which decreased until the adsorption reached an apparent equilibrium only after 24−48 h in topsoil. Pesticide degradation and/or bound residue formation became significant for shaking times ≥3 days; hence, a shaking period of 48 h was selected for subsequent adsorption experiments.

The highest initial concentrations of pesticides used for the adsorption isotherms (1 and 2 mg L$^{-1}$) exceeded for the nonpolar substances (chlorpyrifos, endosulfan-α, and trifluralin) in part their nominal water solubility. However, the resulting equilibrium concentrations in the water phase after 48 h of soil contact were well below their maximum water solubility. The Freundlich *n* values for the nonpolar substances were in the same range as for the more polar substances ($n \leq 0.95$; **Table 2**), indicating that equilibrium concentrations of nonpolar pesticides at higher nominal concentrations also increased more than proportionately as compared with lower system concentrations. This is also indicated by the better fit of the Langmuir model to sorption data of the least water soluble compound (trifluralin) in Psamments. Obviously, any precipitated and/or weakly sorbed amount of nonpolar pesticides on the glass surface of the centrifuge tubes after spiking redissolved and equilibrated itself within the soil/water system during the 48 h shaking time.

**Adsorption Isotherms.** Sorption isotherms are used to assess the partitioning of pesticides between soil and water phases at different batch system concentrations, and their shapes may characterize the sorption mechanisms involved at higher solution concentrations. The isotherms measured in our experiments were mostly of the H or L type, indicating that sorption site availability decreased as the solution concentrations of pesticides increased (*8*).

The Freundlich model is usually recommended to describe the adsorption of pesticides, such as atrazine, endosulfan-α, and metolachlor in soils (e.g., *4*, *19*, *29*). More seldom, for soil mineral phase constituents with low sorption capacities (e.g., *30*) or for adsorption of pesticides to crop residue ashes (*31*), the Langmuir model has been used to describe pesticide sorption.

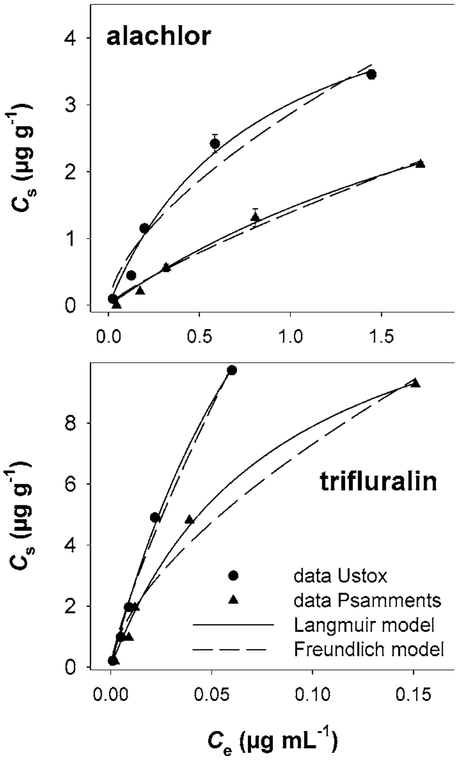

**Figure 1.** Adsorption isotherms of alachlor and trifluralin in topsoil (0–10 cm, $n = 2$); error bars denote standard errors ($C_s$, sorbed amount; $C_e$, equilibrium water phase concentration).

Therefore, the results of a Langmuir and Freundlich modeling of pesticide sorption data are presented in parallel in this study (**Table 2** and **Figure 1**), to allow for a better comparison to published results.

In this study, the Freundlich fit usually explained more than 96% of data variability, as indicated by the coefficients of determination (**Table 2**). The Freundlich $K_F$ values of pesticides for each soil increased with decreasing water solubility (and hence, polarity) of substances (Spearman $R$ of $-0.90$ for Psamments and $-0.93$ for Ustox, $p < 0.05$). For all pesticides, the Freundlich $K_F$ was elevated by a factor of 2 or more in the Ustox as compared to the Psamments, reflecting the higher affinity of the oxidic soil for pesticides. The Freundlich $n$ was slightly higher in Ustox than in Psamments for most pesticides, except for alachlor, atrazine, and monocrotofos, which showed a higher Freundlich $n$ in Psamments. Only trifluralin showed a substantially lower $n$ value in the sandy soil than in the Ustox.

When only the lower four batch concentrations were considered, the Freundlich model described the adsorption data better than for the entire concentration range, as was indicated by a higher $R^2$ (**Table 2**). The Freundlich $n$ values of isotherms for the lower concentration range (0.78−1.12) were always higher than the respective parameters of isotherms for the entire range (0.46−0.95), indicating a more linear shape of isotherms at lower equilibrium concentrations. The Freundlich model was apparently more suitable for describing pesticide adsorption at lower system concentrations, for which the effect of a declining pesticide adsorption at higher equilibrium concentrations was not as pronounced. This finding was frequently observed and has been used to calculate singular soil sorption coefficients ($K_D$) from the "linear part" of sorption isotherms (e.g., *30*). Yet, the tested uppermost isotherm concentration (equivalent to ca. 8 mg/kg soil) in our experiment is of relevance, as it is reached for an application of 1 kg substance/ha when considering the top 1 cm layer of the soil.

$K_F$ values of pesticides increased with their decreasing water solubility for both soils, which corroborated results from other studies comparing the sorption of several substances in one soil (*32*, *33*). The $n$ and $K_F$ values derived from the Freundlich model for the lower concentration range in this study were within the range of the ones reported for the sorption of alachlor, atrazine, endosulfan-α, and metolachlor in a wide spectrum of temperate and tropical soils (e.g., *19*, *34*−*36*). Yet, the Freundlich $n$ pertaining to isotherms of the entire concentration range were mostly lower in our experiment than known from previous publications using similar concentration ranges of these pesticides. We deduce that in the studied tropical soils an increasing saturation of readily available sorption sites led to a decrease of pesticide sorption already at lower equilibrium concentrations than known from many temperate soils.

Consequently, we also tested the Langmuir function to model the adsorption isotherms of pesticides for the entire concentration range. The Langmuir model resulted in better fits for all pesticides as compared to the Freundlich model, which was indicated by a higher $R^2$ relative to that of the Freundlich model and an obvious improvement of curvature description (**Table 2** and **Figure 1**). Especially for the sorption of alachlor, atrazine, metolachlor, simazine, and trifluralin, the Langmuir model better described the nonlinearity of pesticide sorption isotherms at higher system concentrations for both soils. Only for the sorption of endosulfan-α in Ustox and of monocrotofos in both soils, the fitted Langmuir parameters were not statistically significant ($p \geq 0.1$). For endosulfan-α, this was due to a rather linear isotherm shape in the tested concentration range, while for monocrotofos the sorption isotherms suffered from a high variability of the experimental data. For both soils, the maximal sorption capacity $C_{Smax}$ (Spearman $R$ of $-0.89$ for Ustox and $-0.75$ for Psamments, $p < 0.05$) as well as the $K_L$ (Spearman $R$ of $-0.83$ for Ustox and $-0.89$ for Psamments, $p < 0.05$) decreased with increasing water solubility of pesticides. The $C_{Smax}$ of Langmuir isotherms for Ustox exceeded that for Psamments for all pesticides, with the exception of alachlor, which exhibited similar $C_{Smax}$ in both soils.

Although in the literature the fitting of Freundlich isotherms for pesticide adsorption on soils is mostly preferred to the use of the Langmuir model, an inspection of published isotherm data revealed that in some cases the used Freundlich model also did not represent the data well at higher equilibrium concentrations. Because of the nature of the Freundlich isotherm, a too steep decline of pesticide sorption at higher equilibrium concentrations is not well-reproduced by this model and therefore pesticide sorption on mineral constituents or soils with low organic matter content was overestimated at high equilibrium concentrations for moderately polar substances, such as atrazine, hydroxy-atrazine, and metolachlor (e.g., *29*, *37*, *38*). We conclude that the observed isotherm shapes for pesticide adsorption in our experiments were in agreement with a number of previous studies on pesticide sorption onto soils or soil constituents. The smaller sorption capacity of soils for the investigated pesticides in our experiment, as compared to temperate soils of other studies, may be related to a lower affinity of the organic matter of the studied soils for pesticides and for Psamments, additionally, to the overall low organic matter content of this soil.

**Sequential Extraction of Field Samples.** Sorption data derived from batch equilibrium experiments do not account for the dynamic nature of pesticide sorption properties in field samples (*5*). As a result of the aging processes, pesticide availability for leaching may be significantly reduced in the field, in comparison with pesticide leaching predicted from laboratory sorption coefficients. To identify pesticide pools of increasing desorption recalcitrance, we sequentially extracted soil samples after a water desorption step (readily available fraction, equivalent to the determination of $C_e$ of the sorption coefficient) with methanol, commonly judged to extract pesticides in a "slowly" reversible state of sorption (e.g., *16*, *39*). The final extraction was done with AEW, which was shown to be the most efficient solvent for the extraction of the aged pesticides from oxidic soils (*24*). Hence, this solvent mixture may be assumed to extract those pesticide fractions, which are still potentially available for desorption and biouptake but which prevail in an extraction recalcitrant state in soils, not reached by the methanol extraction.

The major portions of pesticides were extracted with the water and methanol fraction for both soils (**Figure 2**). The portion of substance extracted with the water extract was substantial for the more polar pesticides (monocrotofos, metolachlor, alachlor, atrazine, and simazine) at 0 days after application (52−78% in Ustox and 77−92% of the total amount in Psamments). For nonpolar pesticides (chlorpyrifos, endosulfan-α, and trifluralin), this water extractable portion was significantly lower (2.2−3.1% in Ustox and 5.7−7.3% of total amount in Psamments), as to be expected from their higher $K_D$ values. Generally, the relative portion of pesticides in the water extract was for all pesticides higher in Psamments than in Ustox throughout the monitoring period, reflecting the lower affinity of the sandy soil for pesticides.

With increasing time after application, the water extractable pesticide fractions decreased more rapidly than the methanol extractable fractions, leading especially for the polar pesticides to markedly reduced relative water extractable portions toward the end of the monitoring period (3.5−15% in Ustox and 6.0−23% of total amount in Psamments). Consequently, the relative methanol extractable portion of polar pesticides increased from 19 to 43% in Ustox and 6.5 to 22% of total amount in Psamments at 0 days toward 63−69% in Ustox and 50−62% of total amount in Psamments at 80 days after application. For the nonpolar pesticides, the methanol extractable portion accounted already for >90% of total amount in both soils at 0 days after application; hence, the fast decrease of the water extractable pesticide fraction did not lead to a substantial increase of their relative portion in the methanol extract during the field experiment.

The amount of pesticides extracted with AEW was generally low for all pesticides in both soils at the beginning of the field experiment (0.6−4.5% of total amount). However, the relative portion of AEW extractable pesticides increased for all pesticides during the 80 days course of the field experiment in both soils, leading to maximum values of 17−33% of total amount for atrazine, alachlor, metolachlor, and simazine, of 48−61% of total amount for monocrotofos (at 12 days after application), of 12−23% of total amount for chlorpyrifos and endosulfan-α, and of 4.9−11% of total amount for trifluralin. The absolute concentrations of pesticides in the AEW fraction from 0 days until a later time after application increased significantly for alachlor in Psamments (from 17.9 ± 0.5 to 31.2 ± 0.9 $\mu$g/kg, $n = 3$, ±standard error), for atrazine in Ustox (from 56.1 ± 13.7 to 84.0 ± 17.7 $\mu$g/kg) and Psamments (from 16.4 ± 0.5 to 20.1 ± 0.8 $\mu$g/kg), for metolachlor in Ustox (from 84.6 ± 27.5 to 161 ± 28 $\mu$g/kg) and Psamments (from 18.9 ± 0.8 to 53.3 ± 2.6 $\mu$g/kg), for simazine in Ustox (from 70.5 ± 13.9 to 117 ± 21 $\mu$g/kg) and Psamments (from 24.3 ± 0.9 to 38.4 ± 2.5 $\mu$g/kg), and for trifluralin in Psamments (from 5.3 ± 0.1 to 9.7 ± 0.7 $\mu$g/kg). The absolute amounts of pesticides in this least available fraction at 80 days after application were still substantial for alachlor, atrazine, metolachlor, simazine, and trifluralin in Ustox (10−71 $\mu$g/kg) and for metolachlor also in Psamments (20 $\mu$g/kg).

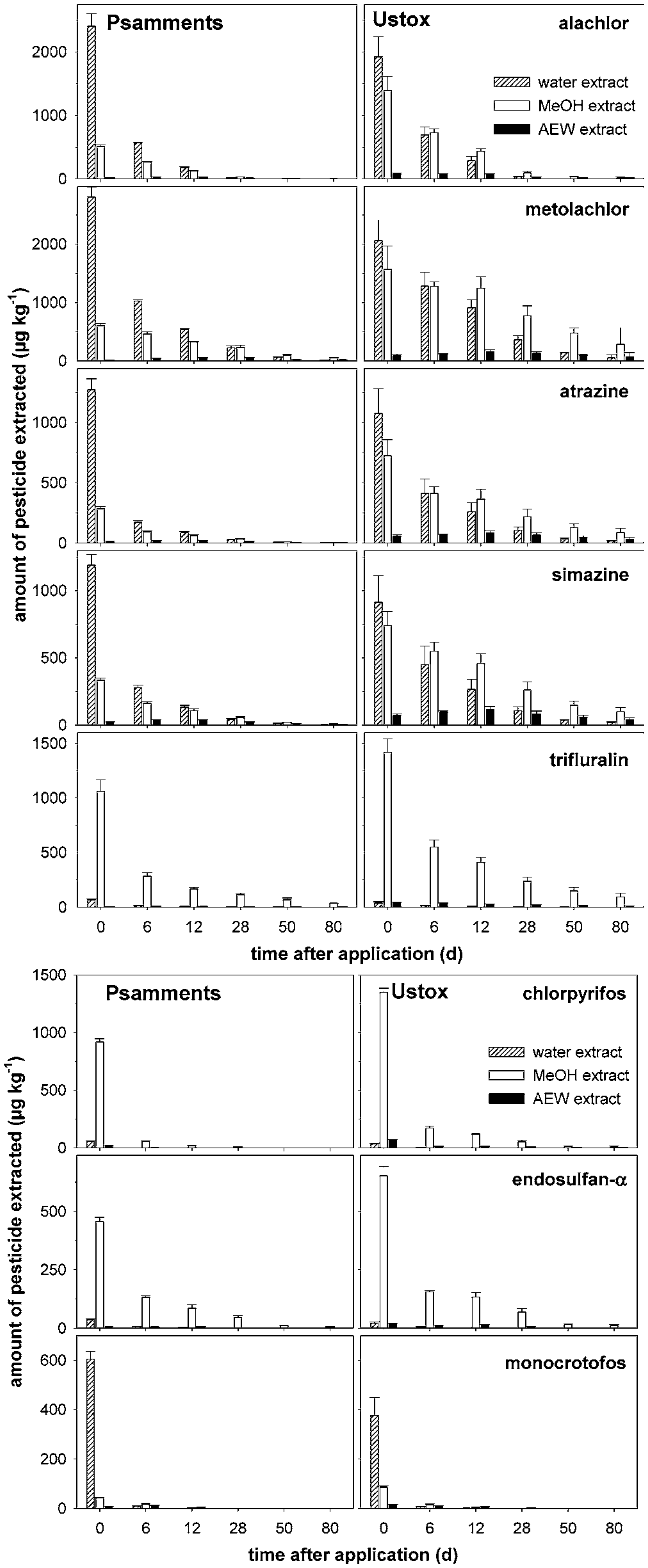

**Figure 2.** Concentrations of pesticides extracted sequentially from topsoil field samples (0–8 cm, $n = 3$; error bars denote standard error) with aqueous 0.01 M $CaCl_2$ (water), methanol (MeOH), and AEW (2:2:1 v/v).

The water extractable pesticide fractions decreased fastest, followed by the methanol and AEW extractable portions (**Figure 2**), reflecting that the availability of pesticides to degradation

**Table 3.** Concentration of Pesticides in Soil Extracts (±Standard Error, $n = 3$) and Modeled Dissipation Times

| | | water extractable fraction (0.01 M $CaCl_2$) | | | | | solvent extractable fraction (MeOH + A/E/W[a]) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | concn ($\mu$g kg$^{-1}$) | | dissipation time (days) | | | concn ($\mu$g kg$^{-1}$) | | dissipation time (days) | | |
| pesticide | soil type[c] | 0 days | 80 days | $DT_{50}$[d] | $DT_{90}$[e] | $R^2$ [b] | 0 days | 80 days | $DT_{50}$ | $DT_{90}$ | $R^2$ |
| alachlor | Ox | 1930 ± 310 | 1.0 ± 0.3 | 4.4 | 14.7 | 0.999[f] | 1470 ± 240 | 28.0 ± 8.3 | 7.2 | 26.1 | 0.999[f] |
| | Ps | 2400 ± 200 | 0.6 ± 0.0 | 3.2 | 10.9 | 0.978[f] | 528 ± 28 | 8.8 ± 0.3 | 7.0 | 25.1 | 1.000[f] |
| atrazine | Ox | 1080 ± 210 | 18.5 ± 4.1 | 5.0 | 23.2 | 0.983[f] | 781 ± 148 | 120 ± 50 | 12.8 | 102.1 | 0.995[f] |
| | Ps | 1270 ± 90 | 2.9 ± 0.2 | 1.9 | 7.7 | 0.978[f] | 300 ± 16 | 9.5 ± 0.4 | 3.9 | 39.1 | 0.990[f] |
| chlorpyrifos | Ox | 31.1 ± 10.1 | <LOQ[h] | 1.3 | 5.4 | 1.000[f] | 1420 ± 40 | 11.2 ± 2.1 | 1.5 | 8.1 | 0.927[f] |
| | Ps | 56.4 ± 5.6 | <LOQ | 1.3 | 4.2 | 1.000[g] | 937 ± 29 | 0.8 ± 0.1 | 1.4 | 4.9 | 0.957[f] |
| endosulfan-α | Ox | 20.9 ± 6.6 | <LOQ | 1.5 | 14.8 | 1.000[f] | 672 ± 42 | 13.6 ± 3.7 | 1.8 | 26.6 | 0.932[f] |
| | Ps | 36.7 ± 3.1 | <LOQ | 2.0 | 14.1 | 1.000[f] | 464 ± 19 | 6.0 ± 0.9 | 2.5 | 27.3 | 1.000[f] |
| metolachlor | Ox | 2060 ± 350 | 52.9 ± 13.2 | 9.9 | 40.0 | 1.000[f] | 1660 ± 420 | 356 ± 112 | 34.5 | 114.6 | 0.998[g] |
| | Ps | 2810 ± 170 | 18.1 ± 0.4 | 3.9 | 21.6 | 0.996[f] | 622 ± 43 | 74.4 ± 1.8 | 22.2 | 73.8 | 0.996[g] |
| monocrotofos | Ox | 377 ± 71 | <LOQ | 1.1 | 3.6 | 1.000[g] | 102 ± 6 | <LOQ | 2.7 | 12.5 | 1.000[f] |
| | Ps | 605 ± 30 | <LOQ | 0.98 | 3.3 | 1.000[g] | 51.5 ± 2.2 | <LOQ | 5.7 | 19.0 | 0.991[g] |
| simazine | Ox | 914 ± 199 | 19.6 ± 3.8 | 6.8 | 27.4 | 0.991[f] | 811 ± 119 | 138 ± 47 | 24.7 | 81.9 | 0.997[g] |
| | Ps | 1190 ± 80 | 4.0 ± 0.1 | 2.8 | 12.1 | 0.995[f] | 358 ± 19 | 15.2 ± 0.6 | 8.1 | 49.8 | 0.997[f] |
| trifluralin | Ox | 37.7 ± 12.1 | 1.2 ± 0.5 | 3.4 | 19.6 | 0.986[f] | 1460 ± 130 | 103 ± 36 | 4.5 | 58.8 | 0.997[f] |
| | Ps | 68.2 ± 5.1 | 1.1 ± 0.0 | 2.2 | 12.5 | 1.000[f] | 1060 ± 110 | 37.8 ± 1.0 | 2.7 | 31.9 | 1.000[f] |

[a] Methanol and AEW extract. [b] Coefficient of determination (nonlinear regression). [c] Ox, Ustox; Ps, Psamments. [d] Time needed for dissipation of 50% of the initial concentration. [e] Time needed for dissipation of 90% of the initial concentration. [f] Biexponential dissipation model. [g] Simple exponential dissipation model. [h] Below limit of quantification.

and leaching processes decreases with time. The differences in persistence among pesticide fractions may be the result of a preferential degradation of the more available pesticide fractions (water and, to a lesser extent, also methanol extractable fraction) and of a redistribution of pesticides from available to less available or stronger sorption sites in the soil, which also would deplete the more available fractions. Barriuso et al. (*9*) also observed that the water and methanol extractable portions of atrazine decreased with time in field samples of a coarse−loamy temperate soil. As besides the water extractable fraction also the methanol extractable fraction showed a continuous decrease of absolute pesticide concentrations (**Figure 2**), a shift of pesticides from the water to the methanol extractable fraction with time cannot be deduced from our experiment. Yet, the absolute increase of pesticide concentrations in the AEW fraction from 0 days until a later time after application for alachlor, atrazine, metolachlor, simazine, and trifluralin in soil can be interpreted as direct evidence of a field aging due to redistribution of pesticides toward less available/stronger sorption sites with time. Our results were corroborated by Lesan and Bhandari (*40*) who also reported an increase of atrazine residues in a sequential ethyl acetate−water (4:1, v/v) soil extract with increasing contact time, conducting long-term batch experiments with two sterilized temperate soils. It remains to be investigated if and at which time scale the AEW and also the methanol extractable portions of pesticides in tropical soils may be mobilized again under natural conditions (i.e., by desorption into aqueous solutions), as these fractions are of importance for the assessment of the long-term fate of pesticides in soils.

Because of their low water solubility, the nonpolar compounds (trifluralin, endosulfan-α, and chlorpyrifos) were found mainly in the methanol fraction of soils until 80 days after application. However, the nonpolar compounds accumulated less than the polar herbicides in the AEW fraction of soils, despite their higher soil sorption coefficients and therefore affinity toward the tested soils. We may deduce from these findings that the time-dependent extraction recalcitrance of polar pesticides was enhanced as compared with nonpolar pesticides. Assuming that the process of aging involves a diffusive redistribution of pesticides in the soil water phase to stronger or less accessible sorption sites (e.g., in soil micropores), it would be faster for substances with higher water phase concentrations than for pesticides with low water solubility. In addition, functional groups of pesticides, in part responsible for their different water solubility, may play a decisive role for the aging process, which might also involve the in situ consolidation of sorption bindings. Evidence of a short-term and compound specific extraction recalcitrance of pesticides (*12*, *41*), which was also observed for our soils, makes it probable that an increased binding to stronger or "more specific" sorption sites was the major cause of progressing aging of polar pesticides seen in our experiments.

The description of dissipation dynamics of pesticides in the water and solvent extractable (methanol + AEW) pools was achieved by biexponential, and in some cases by monoexponential, decay functions (**Table 3**), as indicated by high coefficients of determination for the fitted decay curves ($R^2$ of 0.927−1.00). This finding is in agreement with previous results from our field experiment concerning the dissipation dynamics of total pesticide concentrations, which were also characterized by mostly biexponential dissipation curves (*22*). In general, the dissipation half-life times ($DT_{50}$) of pesticides were shorter for the water extractable fraction ($DT_{50}$ of 1.1−9.9 days in Ustox and 0.98−3.9 days for Psamments) than for the solvent extractable fraction ($DT_{50}$ of 1.5−34.5 days in Ustox and 1.4−22.2 days in Psamments), reflecting the slower dissipation of pesticides in the substance pool defined by solvent extraction. This effect was least pronounced for the nonpolar pesticides trifluralin, chlorpyrifos, and endosulfan-α, for which the $DT_{50}$ of the solvent extractable pool was enheightened by a factor of <1.5 in respect to the $DT_{50}$ of the water extractable pool. In contrast, the $DT_{50}$ of polar substances in the solvent extractable pool was higher by a factor of 1.6−5.8 as compared with the one of the water extractable fractions. This higher persistence of polar pesticides in the less available fraction, as compared with the one of nonpolar pesticides, also indicates a different quality of aging within the soil for these two substance groups.

Field $K_{OC}$ values of pesticides were calculated as the ratio of the concentration of pesticides in the "water" extract ($\mu$g mL$^{-1}$) and the amount of pesticides extracted with the two solvent

**Table 4.** Sorption Coefficients of Pesticides, Normalized to the Organic Carbon Content of Soils ($K_{OC}$), in Laboratory and Field Experiments (±Standard Error), and Model Parameters for $K_{OC}$ Development with Time

| | | laboratory $K_{OC}$ (mL $g_{OC}^{-1}$) | | field $K_{OC}$ (mL $g_{OC}^{-1}$) | | parameters of $K_{OC}$ development model | | | |
|---|---|---|---|---|---|---|---|---|---|
| pesticide | soil type[a] | adsorption[b] | desorption[c] | 0 days[d] | maximum[d] | $K_{OC}$ ($t_0$)[e] | c[f] | d[f] | $R^2$ |
| alachlor | Ox | 173 ± 26 | 129 ± 14 | 183 ± 33 | 6890 ± 815 | 183.2 | 0.1543 | –0.0237 | 0.997 |
| | Ps | 209 ± 24 | 456 ± 19 | 122 ± 4 | 8770 ± 880 | 122.4 | 0.3594 | –0.0200 | 0.996 |
| atrazine | Ox | 209 ± 24 | 139 ± 3 | 171 ± 17 | 1360 ± 100 | 171.0 | 0.1245 | 0.0088[g] | 0.985 |
| | Ps | 217 ± 13 | 400 ± 38 | 131 ± 7 | 1860 ± 250 | 131.0 | 0.2264 | 0.0088 | 0.996 |
| chlorpyrifos | Ox | 7180 ± 600 | 8660 ± 160 | 12 600 ± 2500 | 33 800 ± 4980 | 12 553 | 0.0551 | –0.1015 | 1.00 |
| | Ps | 10 600 ± 1900 | 12 700 ± 200 | 9290 ± 240 | 33 000 ± 4700 | 9289 | 0.0993 | –0.1133 | 1.00 |
| endosulfan-α | Ox | 6280 ± 510 | 4290 ± 80 | 8770 ± 1590 | 26 800 ± 4950 | 8769 | 0.0232 | –0.0708 | 0.994 |
| | Ps | 12 600 ± 570 | 8210 ± 130 | 7050 ± 250 | 17 600 ± 2500 | 7052 | 0.0770 | 0.0284 | 0.999 |
| metolachlor | Ox | 126 ± 4 | 97 ± 16 | 186 ± 32 | 1530 ± 100 | 185.8 | 0.0734 | –0.0050 | 0.997 |
| | Ps | 193 ± 13 | 334 ± 1 | 122 ± 4 | 2320 ± 340 | 122.5 | 0.1329 | –0.0119 | 0.996 |
| monocrotofos | Ox | 35 ± 10 | –[h] | 66.3 ± 2.8 | 1613 ± 302 | 66.3 | 1.693 | –0.0226 | 1.00 |
| | Ps | 31 ± 5 | –[h] | 47.7 ± 4.7 | 2000 ± 150 | 47.7 | –[i] | - | - |
| simazine | Ox | 281 ± 12 | 200 ± 6 | 214 ± 18 | 1550 ± 100 | 214.2 | 0.1308 | 0.0134 | 0.981 |
| | Ps | 304 ± 37 | 460 ± 25 | 195 ± 10 | 2120 ± 280 | 195.2 | 0.1746 | 0.0051[g] | 0.990 |
| trifluralin | Ox | 7770 ± 260 | 6570 ± 20 | 10 800 ± 2400 | 27 900 ± 4700 | 10780 | 0.0639 | 0.0496[g] | 0.821 |
| | Ps | 16 700 ± 2800 | 10 600 ± 300 | 8750 ± 1110 | 18 700 ± 1200 | 8749 | 0.0622 | 0.0597 | 0.954 |

[a] Ox, Ustox; Ps, Psamments. [b] $K_{OC}$ averaged from linear part of adsorption isotherm ($n = 3$). [c] $K_{OC}$ of first desorption step: 24 h shake ($n = 2$). [d] $K_{OC}$ determined by 24 h shake of field sample replicates ($n = 3$). [e] Experimental value: field $K_{OC}$ at 0 days (mL $g_{OC}^{-1}$). [f] Model parameters, see eq 4. [g] Not significant at the $p < 0.1$ level. [h] Not determined in laboratory experiments. [i] No fit performed due to insufficient amount of data.

fractions ($\mu$g g$^{-1}$ soil). The initial field $K_{OC}$ values of pesticides (at 0 days after application) differed by less than a factor of 2 from $K_{OC}$ values determined in laboratory adsorption experiments for most pesticides (**Table 4**). $K_{OC}$ values derived from pesticide desorption experiments in the laboratory were higher than those in field samples (at 0 days) for Psamments, and lower than those of field samples for Ustox (at 0 days). This finding was presumably related to the different degree of sorption hysteresis in the two studied soils and/or to the effects of adjuvants in pesticides solutions applied to soil in the field experiment. As a consequence of the decreasing water extractable fraction of pesticides in the examined soils, the apparent field $K_{OC}$ values of pesticides increased with increasing time after application (**Table 4** and **Figure 3**). The field $K_{OC}$ values for polar pesticides increased more with aging time (factor of 7.3−72) than did those for nonpolar substances (factor of 2.1−3.6) in both soils. Generally, pesticides showed a higher increase of $K_{OC}$ values with time in Psamments, with the exception of trifluralin and endosulfan-α, which showed increased aging in Ustox.

Our findings corroborated results of other studies (*9*, *13*, *28*), in which elevated $K_{OC}$ values of atrazine and metolachlor by a factor of 2−42 were measured in aged laboratory and field samples of temperate soils (aging times up to 12 months), as compared to sorption coefficients determined in short-term laboratory adsorption experiments. In our experiments, the $K_{OC}$ values of atrazine and metolachlor increased by a factor of 8.0−14 and 8.2−19, respectively, within 80 days in the field. Although pesticides showed a slightly different degree of $K_{OC}$ increase in the Ustox and the Psamments, their maximum $K_{OC}$ values attained in the field experiment varied by a factor of ≤1.5 between the soils. Hence, substance properties were more important than soil properties for the extent of aging seen in our experiment with two tropical soils. An inverse correlation between the extent of aging (expressed as quotient of maximum apparent $K_{OC}$ value vs apparent $K_{OC}$ value at 0 days after application) and the $K_{OC}$ value of substances was also observed in our experiments (Spearman $R$ of −0.929, $p < 0.05$, for both soils), as already postulated by Sharer et al. (*12*). The excessive extent of aging seen for alachlor in our study, in comparison with e.g., atrazine or metolachlor, was due to the nearly complete dissipation of its water extractable fraction toward the end of the experimental period, resulting in a steeply increasing apparent $K_{OC}$ value.

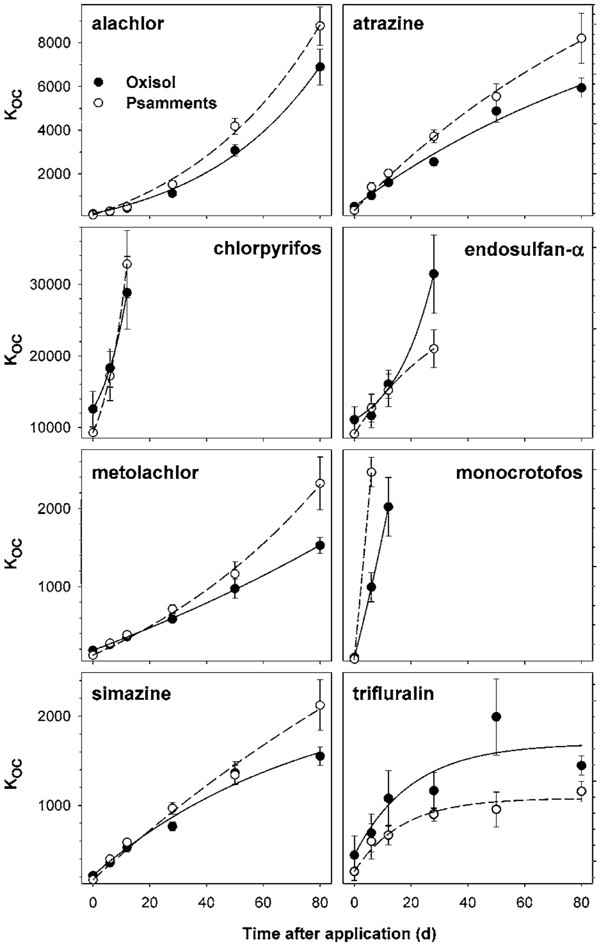

**Figure 3.** Development of the pesticide sorption coefficient ($K_{OC}$, normalized to the organic carbon content of soil) with time in field soil samples (0–8 cm, $n = 3$; error bars denote standard error) and model fit (lines).

For pesticide fate simulation, the development of $K_{OC}$ values with time is of importance for medium- to long-term simulations. Therefore, the time course of the $K_{OC}$ values needs to be described and forecast, if possible. The development of the $K_{OC}$ value with time of all pesticides in our field experiment was adequately described by the following equations:

$$K_{OC}(t) = K_{OC}(t_0) + a*t^b \tag{3}$$

$$K_{OC}(t) = K_{OC}(t_0)*[1 + c/d*(1 - e^{-c*t}] \tag{4}$$

The first equation is similar to the Freundlich function (eq 3), being able to describe increasing ($b > 1$) and decreasing steepness ($b < 1$) of curves without attaining a maximum value with time ($t$); $a$ (mL $g_{OC}^{-1}$) and $b$ (dimensionless) are empirical parameters, and $K_{OC}(t_0)$ is the initial sorption coefficient in field samples (at 0 days). The coefficient of determination for all pesticide $K_{OC}$ curves was acceptable, with values ranging from 0.761 to 1.00 (data not shown). However, the more complicated eq 4 introduced by Richter et al. (*25*) for the development of the "apparent sorption coefficient" (three compartments, three rates fate model) was preferred (see **Table 4**). Model parameters $c$ and $d$ represent transfer/decay rates or combinations thereof [$c$ (days$^{-1}$), rate of transfer from reversible to irreversible sorption site; $d$ (days$^{-1}$), decay rate of amount in water phase minus decay rate of irreversibly bound amount). With this function, a maximum $K_{OC}$ value may be attained, when $d > 0$. Part of our data confirmed this concept (see $K_{OC}$ development of trifluralin in Ustox and Psamments) and also data presented from refs *25* and *42* showed that for simazine, terbuthylazine, and metolachlor the $K_{OC}$ approaches a maximum value with increasing contact time in the studied temperate soils. In our experiment, the $K_{OC}$ development curves of each pesticide showed either increasing ($d < 0$) or decreasing steepness with time ($d > 0$) for both soils (**Figure 3**), with the exception of the one of endosulfan-α, which showed increasing steepness in Ustox and decreasing steepness in Psamments (data only available for 0−28 days after application). All fitted parameters were significant at the $p < 0.1$ level, with the exception of parameter $d$ for atrazine ($p = 0.133$) and trifluralin (0.165) in Ustox, and simazine (0.232) in Psamments (**Table 4**). For monocrotofos in Psamments, no statistically valid fit was achieved, as the number of data pairs was insufficient ($n = 2$).

We tried a simultaneous parameter estimation of all involved singular transfer/decay rates of the Richter et al. model, by fitting the model to our measured experimental data (concentration of water extractable fraction, concentration of solvent extractable fraction, apparent $K_{OC}$). However, an adequate description of all experimental data was not achieved for most pesticides (using ModelMaker), as small absolute deviations of the model from the values of pesticide concentration in fractions toward the end of the experimental period led to excessive errors when calculating the apparent $K_{OC}$ (which is a modified quotient of the solvent and the water extractable concentrations). The use of biexponential functions for a better description of pesticide decay in the two fractions led to an overparametrization of the model (data not shown).

Usually, the soil sorption coefficient of pesticides is determined in short-term laboratory studies and used for many kinds of pesticide fate simulations (e.g., FOCUS groundwater and surface water models of the European Union). Comparing the $K_{OC}$ values from our laboratory and field studies (**Table 4**), we concede that the initial pesticide sorption under field conditions (at 0 days) may be estimated by laboratory $K_{OC}$ values derived from adsorption isotherms. However, our findings underline that the change of pesticide sorption coefficients in tropical field soils with time is significant, especially for polar pesticides, and needs to be considered for a realistic medium- to long-term modeling of pesticide fate. In some pesticide fate models, such as FOCUS PELMO 3.2.2, the sorption coefficient of pesticides may be defined as time-dependent, using a linear function (e.g., *43*). Yet, for a correct implementation of this relation, the change of pesticide $K_D/K_{OC}$ with time has to be investigated for the specific soil properties and climatic conditions, which are to be depicted in the simulation. The nonlinear equation proposed by Richter et al. (*25*) was able to describe all of the $K_{OC}$ functions adequately. It needs to be investigated which environmental key factors (e.g., soil temperature, texture, organic carbon content, pH) influence the aging characteristics of pesticides to forecast the aging of pesticides under different environmental conditions.

**Supporting Information Available:** Set of figures for pesticide adsorption isotherms. Soil properties and singular sorption coefficients ($K_D$ and $K_{OC}$) for three layers (0−10, 40−50, and 90−100 cm depth) of the laboratory soils (data may serve as input for leaching simulations with the described test soils). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Received for review April 27, 2005. Revised manuscript received July 19, 2005. Accepted July 19, 2005. This work was supported by the German BMBF (SHIFT Project ENV54, FKZ 01LT0003/7) and the Brazilian CNPq.**

JF050969C