

Field Aging of Insecticides after Repeated Application to a Northern Thailand Ultisol

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Field aging immobilizes pollutants and reduces their toxicity, but it also boosts their accumulation and holds the risk of future release. We investigated the aging of six insecticides (water solubilities: 0.33 mg L⁻¹—completely miscible) applied five times (10-day intervals) to a tropical fruit orchard under natural weather conditions. After sequential extractions of soil samples with 0.01 M CaCl₂, methanol (MeOH), and acetone/ethylacetate/water (AEW), a conventional ($K_{OC(app)} = [\alpha(MeOH) + \alpha(AEW)]/c(CaCl_2)$, normalized to soil organic carbon) and a newly introduced distribution ratio (MAR = MeOH/AEW ratio; $\alpha(MeOH)/\alpha(AEW)$) were calculated. Field half-lives of the insecticides correlated with $K_{OC(app)}$ but not with MAR, which might reflect that dissipation was significantly affected by abiotic processes. The extent of aging was related to hydrophobicity of the compounds and most pronounced for endosulfan (3-fold increase in $K_{OC(app)}$ within 84 days). For dimethoate, this increase was even steeper (5- to 10-fold within 10 days), which was, however, mostly caused by dissipation from labile pools rather than by aging. The $K_{OC(app)}$ of chlorpyrifos remained constant, but a significant decrease in MAR ($r = -0.78$) revealed that sorption strength increased nevertheless. Results for malathion were ambiguous. Within the time frame of our study, neither $K_{OC(app)}$ nor MAR gave evidence for the aging of mevinphos. The different dynamics of $K_{OC(app)}$ and MAR for the six insecticides studied indicate that different aging mechanisms or rates, or both control the fate of the individual insecticides, which can potentially be revealed by sequential extraction procedures.

KEYWORDS: Aging/ageing; pesticides; sorption coefficient; Ultisol/Acrisol; fruit production

INTRODUCTION

About 50 years ago, Edwards et al. (1) observed for the first time that the toxicity of insecticides in soils decreases over time even when the substances are still extractable in a toxic form. Today, this reduction in bioavailability without chemical alteration of the compound is referred to as aging (2, 3). Aging has been found to be a general phenomenon, but both rate and extent strongly depend on physicochemical properties of the compound (4, 5). In order to study aging processes on a molecular scale, elaborate laboratory studies have been applied (e.g., see refs 6–8). These studies were generally restricted to hydrophobic organic compounds such as PAHs or PCBs, which mainly interact with soil organic matter. Such laboratory studies cannot be applied to explain aging mechanisms of more polar

insecticides, especially not under field conditions. Thus, the degree of field aging of polar pesticides is largely unknown. This is particularly true for soils of the humid tropics (e.g., Ultisols) that are rich in Fe oxides and may have a net anion exchange capacity.

The laboratory reactions involved in the sorption of organic compounds usually start with partitioning reactions into soil organic matter (SOM), which are fast, concentration-independent, and fully reversible. Simple 0.01 M CaCl₂ shake experiments may be sufficient to assess this degree of partitioning. In more rigid parts of SOM, adsorption may occur, which is kinetically hindered (slow sorption (9)). Within these domains, the sorption sites are limited, and desorption hysteresis is observed (10). For efficient re-extraction of organic xenobiotics sequestered in SOM, harsh organic solvents must be used. For tropical soils, Laabs et al. (11, 12) and Amelung et al. (13) suggested a mixture of acetone, ethylacetate, and water (AEW) as an exhaustive extractant. Hence, combining different polar solvents to a sequential extraction procedure may help in identifying the degree of aging for organic xenobiotics, with 0.01 M CaCl₂ serving as the first and AEW as the last extract reagent of choice. In principal, such concepts should be

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Table 1. Vapor Pressures, Hydrolysis Half-Lives (Literature Data Taken from ref 33), Sorption Coefficients, and Field Half-Lives of Pesticides Used for an On-Site Aging Experiment on a Northern Thailand Ultisol

substance	vapor pressure (literature) [mPa]	hydrolysis half-life (literature)	K_{OC} (literature) ^a [mL g(OC) ⁻¹]	$K_{OC(app)}$ (field experiment) ^b [mL g(OC) ⁻¹]		field dissipation half-life ^c [d]	
				minimum	maximum	minimum	maximum
endosulfan- α	0.83 (20 °C)	slow hydrolysis	12400	4713 (1211)	33584 (6460)	2.7	3.5
endosulfan- β				5862 (1599)	46353 (7340)	2.9	5.0
chlorpyrifos	2.7 (25 °C)	1.5–100 d	6070	12477 (1066)	34401 (8451)	2.8	7.2
malathion	5.3 (30 °C)	relatively stable (pH 7)	1800	927 (118)	17620 (12868)	1.4	2.6
dimethoate	0.25 (25 °C)	relatively stable (pH 2–7)	20	200 (3)	2565 (297)	2.2	5.3
mevinphos	17 (20 °C)	120 d (pH6) 35 d (pH 7)	44	152 (41)	1387 (277)	1.4	5.3

^a Sorption coefficients normalized to the OC content of the soil (data from ref 29). ^b $K_{OC(app)}$ was calculated for every sampling day ($n = 26$), and minimum and maximum values of the resulting data set are reported here. ^c Monoexponential decay; minimum and maximum for 5 application cycles (see ref 26 for details).

applicable for both classical hydrophobic organic compounds as well as for more polar pesticides, and for laboratory as well as for field studies.

Polar organic solvents, such as methanol (MeOH), have a higher efficiency of extraction than aqueous solutions. However, MeOH is generally used as an exhaustive extractant only under elevated temperature and increased time of extraction (14) or under supercritical conditions (15). Thus, at atmospheric pressure, cool MeOH obviously extracts a kind of intermediate pool of xenobiotics: This pool is neither freely available nor thoroughly adsorbed; it seems to represent a fraction that is subject to relatively fast kinetic desorption. Although, according to current knowledge, the sorption sites that are accessible by MeOH cannot be characterized exactly, several authors found consistent correlations between the bioavailability of pesticides and their extractability by aqueous MeOH (16–18).

Even though the chemical conditions of the extractions differed slightly between these studies (one or two extraction steps and different water/MeOH ratios), the findings prove that simple, operationally defined pools can be related to ecological functions. Thus, it may be possible to interpret changes in selected extract concentrations in terms of toxicity (in the case of insecticides, that means effectiveness (1)), degradability (feasibility of microbial remediation (19)), leachability (risk of groundwater contamination (20)), and risk of surface runoff (21). It may even be possible to derive apparent partitioning coefficients ($K_{d(app)}$) from sequential extractions and to interpret them as indicators for aging processes (22–24), even if in its strict sense the K_d concept applies to equilibrium conditions only. We therefore propose that MeOH is a suitable intermediate reagent of choice between the first simple 0.01 M CaCl₂ extraction and final AEW extraction for assessing aging processes and different $K_{d(app)}$ values.

We hypothesized that including MeOH into such a sequential procedure will enable us to differentiate between aging reactions of different polar insecticides. This is especially true as pesticides can be expected to dissipate relatively quickly from the aqueous phase, while they should be a bit more persistent in the MeOH extract (compare ref 25). Therefore, the differentiation between the aging processes of different pesticides should be facilitated if the MeOH-extractable fraction is also taken into account.

A field dissipation study we conducted in northern Thailand (26) revealed that ground-applied insecticides, despite half-lives that ranged from 1.4 to max. 7.2 d only (Table 1), accumulated in soil after repeated pesticide treatment. This finding motivated us to investigate the field aging of organochlorine and organophosphorous insecticides with contrasting physicochemical properties after repeated ground application in a northern Thai lychee orchard, as revealed by sequential extraction of samples of the topsoil with 0.01 M CaCl₂, MeOH, and AEW.

MATERIALS AND METHODS

Research Site and Experimental Setup. The fieldwork for our study was conducted in a lychee orchard in northern Thailand previously described by Ciglasch et al. (26), 18°53' N, 98°52'E, ca. 800 m above sea level, facing west, slope ca. 15°, mean annual temperature 21.6 °C, fine kaolinitic thermic Hapludult, 2.89% (S.E. = 0.04%) of organic carbon (OC) in the topsoil (0–10 cm). Pesticides were purchased in typical local formulations and applied five times in 10-day intervals, beginning on 19 June 2002. These insecticides were chlorpyrifos (*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate; water solubility, 2 mg L⁻¹), dimethoate (*O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate; 24 g L⁻¹), endosulfan-(α,β) ((1,4,5,6,7,7-hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylene) sulfite; 0.33 mg L⁻¹), malathion (*S*-1,2-bis(ethoxycarbonyl)ethyl *O,O*-dimethyl phosphorodithioate; 145 mg L⁻¹), and mevinphos (2-methoxycarbonyl-1-methylvinyl dimethyl phosphate; completely miscible with water). The application rate was ca. 2 (mevinphos) to 6 kg ha⁻¹ (endosulfan, chlorpyrifos), and all of them were applied simultaneously in one spraying cocktail directly onto the ground, which was covered with grass and herbs. We collected samples of the topsoil (0–10 cm) with an auger (inner diameter: 3 cm) 1, 2, 5, 7, and 10 days after pesticide application. Soil samples were taken as composite samples that consisted of 5 subsamples. After the sampling on day 10, the next application was carried out and the subsequent sampling cycle started. In total, this was repeated five times (sampling cycles SC1–SC5). In addition to the five regular SCs, we took one final soil sample on September 1st, 34 days after the last application (the period from the end of SC5 to the end of the experiment will be denoted as SC5'). The field-moist soil samples were sequentially extracted in three steps. All of them were carried out in the dark, at room temperature, and at a soil/solution ratio of 1:5. The solvents were (i) 0.01 M CaCl₂ (extraction time = 24 h), (ii) methanol (MeOH; extraction time = 4 h), and (iii) acetone/ethylacetate/water = 3:1:1 (AEW, extraction time = 4 h). Pesticides were quantified on a GC system with electron-impact mass spectrometer (GC/EI-MSD; agilent 6890-N GC with 5972-N MSD). For a detailed description and discussion of the experimental setup, see Ciglasch et al. (26); details on the GC method and its performance were given by Laabs et al. (11) and Amelung et al. (13).

Sorption Coefficients. The concentrations of the different pesticides in the three samples obtained during the sequential extraction of the soil were used to calculate apparent soil/water partitioning coefficients ($K_{d(app)}$ [mL g⁻¹]):

$$K_{d(app)} = \frac{c(\text{MeOH}) + c(\text{AEW})}{c(\text{CaCl}_2)} \quad (1)$$

with $c(\text{CaCl}_2)$ = concentration in the CaCl₂ solution [g L⁻¹]; $c(\text{MeOH})$ = concentration in the MeOH fraction [g (kg dry soil)⁻¹]; and $c(\text{AEW})$ = concentration in the AEW extract [g (kg dry soil)⁻¹]. The index app (apparent) indicates that this partitioning coefficient is not a constant as obtained by batch equilibrium techniques (e.g., see ref 27), but it varies according to the actual field situation and binding strength (24). As the nonionic pesticides used in this study mainly interact with the organic carbon of the soil (28), the $K_{d(app)}$ was normalized to the OC content ($K_{OC(app)}$ [mL gOC⁻¹], eq 2):

$$K_{OC(app)} = \frac{K_{d(app)} \cdot 100}{\% OC} \quad (2)$$

with %OC = % of organic carbon of the sample. To investigate the dynamics of sorption strength within the adsorbed phase, we calculated dimensionless MeOH/AEW ratios (MAR) for each data set as follows:

$$MAR = \frac{c(\text{MeOH})}{c(\text{AEW})} \quad (3)$$

In some samples, no mevinphos could be detected in the MeOH extract. In these cases, we did not calculate the MAR, and the values are missing in the following sections. Furthermore, we had to face the problem of low pesticide concentrations in the CaCl₂ extract. Hence, for the calculations of the $K_{d(app)}$ (eq 1) the concentrations of sorbed pesticides were divided by a very small number, and thus, minor differences in the absolute concentrations in the CaCl₂ extract could have a large influence on the resulting $K_{d(app)}$. Because of analytical problems, dimethoate could not be quantified reliably in aqueous samples from SC1 and SC2 (see ref 26 for details); therefore, $K_{OC(app)}$ values could not be calculated for these sampling cycles. Because this accounted only for the CaCl₂ extracts, the MAR could nevertheless be computed.

RESULTS AND DISCUSSION

Experimental Conditions. The amount of precipitation during our experiment was ca. 25% lower than expected from long-term observations (Kanita Ueangsawat, Chiang Mai University, unpublished data collected from 1993–2000). Especially, the first and the third application cycle were exceptionally dry; (16 and 18 mm of rain within 10 days, respectively; for details, see ref 26). Until mid-August, there were only some distinct rain storms followed by several dry days so that the soil matric potential in 10 cm depth regularly fluctuated between ca. –3 and up to –45 kPa (equivalent to volumetric water contents from 35%–16%). In the last two weeks of the experiment, rain occurred more regularly, and the matric potential of the topsoil did not fall below –10 kPa (ca. 25% vol. water content) any more.

Comparison between Apparent and Tabulated K_{OC} Values and Data Quality. The apparent sorption coefficients calculated according to eq 2 differed substantially from the constants reported in the literature. The lowest $K_{OC(app)}$ for endosulfan- α measured during our experiment was only 38% of the K_{OC} suggested by Hornsby (29), the highest $K_{OC(app)}$ for dimethoate, which was 128-fold greater than the tabulated value (**Table 1**). These deviations demonstrate that differences in soil mineralogy and SOM make it impossible to transfer K_{OC} values from one experiment to another or from the laboratory to the field, although the normalization of sorption data to the OC content of the soil significantly improves the comparability of data sets (28). Relatively high standard errors of our method of pesticide extraction and quantitation with subsequent calculation of $K_{OC(app)}$ (typically 10 to 25%, but up to >70% in few exceptions, e.g., the malathion maximum; **Table 1**) revealed the difficulties associated with exact pesticide analyses of heterogeneous field-fresh samples. It was not possible to further homogenize the samples; because of their high clay content of 35% (30), the field-moist samples were too sticky for sieving (additionally, the risk of cross-contamination would have been too high), but drying of the samples to facilitate sieving would have changed the status of pesticide sorption (31), and harsher homogenization techniques such as pulverization of the samples would expose sorbate entrapped in inner structures of the sorbent to the solvent. This enhances extractability compared with that of undisturbed field fresh samples (32).

Because we took our samples in high temporal resolution, relatively large data sets were available. We therefore observed

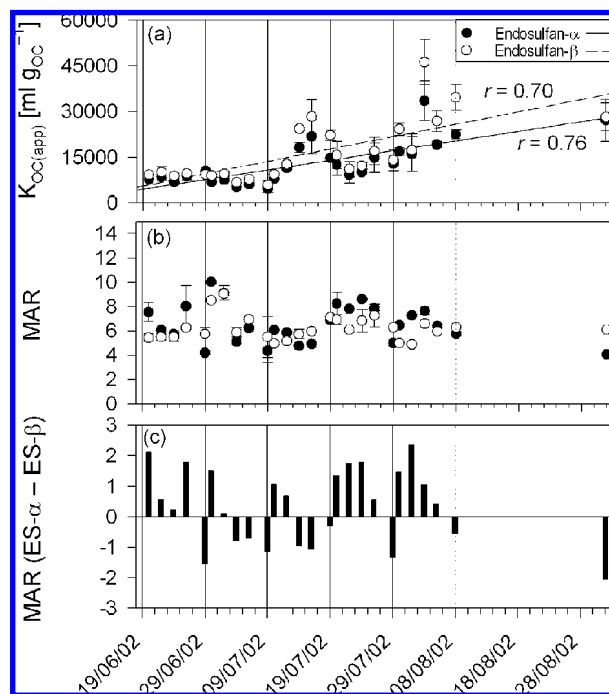


Figure 1. Field aging of endosulfan isomers α and β after application to a tropical Ultisol. (a) Temporal course of apparent sorption coefficients ($K_{OC(app)}$; with linear regressions). (b) Methanol/AEW (acetone/ethylacetate/water; 3:1:1 by volume) ratios (MAR; means and standard errors, $n = 2$). (c) Differences between the MARs of endosulfan- α and - β (data from b) are plotted. Vertical lines mark the application dates.

some clear dynamics in the binding status of the pesticides despite the constraints outlined here. The simultaneous application of six different pesticides enabled us to see whether aging processes are mainly by environmental conditions (such as rainfall/soil moisture) and application mode (repeated input of fresh material due to multiple applications), or whether aging is governed by physicochemical properties of the substances themselves. To present and discuss these results in the next sections, we grouped the substances according to their chemical groups and hydrophobicity.

Endosulfan. Endosulfan is the only organochlorine pesticide among the substances we investigated (all others are organophosphorous compounds). It has the lowest water solubility and is the most hydrophobic compound of our study (**Table 1**). The formulation of endosulfan we applied contained α and β isomers, which we analyzed separately. Their ratio was 2:1 (26), which is typical for technical endosulfan (33). The course of $K_{OC(app)}$ of both isomers looks almost identical (**Figure 1a**), starting at ca. 8000–9000 mL g_{OC}^{-1} at the beginning and raising to just below 30000 mL g_{OC}^{-1} at the end of the experiment. This increase in $K_{OC(app)}$ is very similar to data reported by Laabs et al. for Brazilian Oxisols ((12); 3-fold increase over 4 weeks) and correlates significantly with time ($r = 0.70$ and 0.76 for α and β isomers, respectively), which is a clear indicator of the field aging of endosulfan (24).

Because unaged fresh material was added every 10 days (multiple applications; see Materials and Methods), we assumed that $K_{OC(app)}$ would increase within one SC followed by a drop after the next application to a level somewhat higher than at the beginning of the previous SC, reflecting the coexistence of fresh and aged endosulfan after repeated treatment of the plot. This pattern, however, could only be observed at the transition between SCs 3 and 4 and, less pronounced, between SCs 4 and 5 (**Figure 1a**), but not at the transition from SC1 to 2 and SC

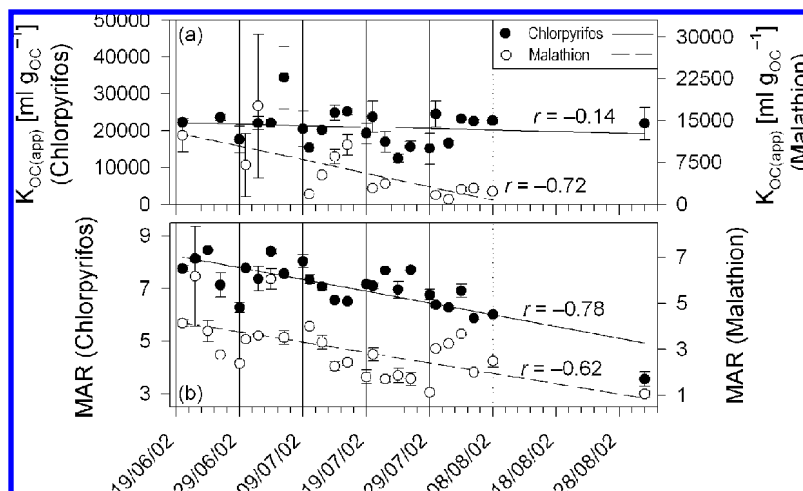


Figure 2. Field aging of chlorpyrifos and malathion after application to a tropical Ultisol. (a) Temporal course of apparent sorption coefficients ($K_{OC(app)}$; with linear regressions). (b) Methanol/AEW (acetone/ethylacetate/water; 3:1:1 by volume) ratios (MAR; means and standard errors, $n = 2$). Vertical lines mark the application dates.

2 to 3. Within SC1, the rise in $K_{OC(app)}$ was almost negligible, and in SC2, $K_{OC(app)}$ even tended to decrease. It is possible that the 10 days of the first sampling interval were too short to obtain any measurable aging of endosulfan because aging is a kinetically hindered process that can last for years (9). However, SC2 had significantly more precipitation than SCs 1 and 3–5 (26). The wetting of the soil organic matter associated with this higher amount of precipitation in SC 2 might lead to an increased release of endosulfan (as described by Altfelder et al. (31) for the herbicide chlorotoluron) thereby lowering the $K_{OC(app)}$ value. We assume that in SC3, the opposite has happened. During the whole SC3, only 25% of the precipitation of SC2 fell (26). Therefore, the organic matter started to dry up, which should lead to an increased adsorption (31). This could explain the steep increase of $K_{OC(app)}$ in the course of SC3. When fresh, unaged pesticide was added with the beginning of SC4, $K_{OC(app)}$ sharply decreased again, especially after the soil was rewetted on July 22nd (Figure 1a).

When discussing $K_{OC(app)}$ as an indicator of aging, however, one has to keep in mind that an increase in $K_{OC(app)}$ cannot exclusively be attributed to stronger sorption, but it may also be the result of a rapid depletion of pesticide concentration in the water-extractable fraction due to leaching (or surface runoff) and degradation (34). Because microbes are able to adapt to the degradation of xenobiotics (35) raising $K_{OC(app)}$ values after repeated applications could reflect a continuously improved efficiency of degradation of the water-extractable pool, which is readily bioavailable (36). However, as endosulfan accumulated in the soil of the research plot, and as the field half-lives of endosulfan values of endosulfan did not shorten significantly from one SC to the next (26), the increase of $K_{OC(app)}$ must, at least partly, be due to an actual increase in binding strength over time, which means true aging. This conclusion is further supported by the fact that within the wettest SC, SC2, where conditions should be best for microbial degradation and thus a degradation-related increase in $K_{OC(app)}$, this coefficient remained unchanged or even decreased (Figure 1a).

Although sorption isotherms were almost linear, and Freundlich coefficients derived from laboratory batch experiments (24 h equilibrium time) were identical for endosulfan- α and - β (data not shown), the two isomers exhibited different affinities to the soil and its organic matter in the field experiment. The $K_{OC(app)}$ of endosulfan- β was systematically higher than that of endosulfan- α (Figure 1a). However, this systematic difference was not

observed in the plot of the MARs of endosulfan- α and - β . We introduced this coefficient to test the hypothesis that partly but not freely available pesticides get increasingly strongly sorbed during aging, which should be reflected by a shift from the MeOH into the AEW fraction (see Introduction). Despite some fluctuations in MAR during the experiment, no correlation between MAR and time of aging could be observed, and the MARs for both isomers seemed to scatter more or less randomly around a value of 6 (Figure 1b; $r = -0.17$ and -0.05 for endosulfan- α and - β , respectively). Thus, the aging of endosulfan during the few weeks of our experiment is mainly characterized by changes in the ratio between dissolved and sorbed endosulfan, but not by a significant refractionation within the sorbed fraction. Plotting the differences between the MARs of endosulfan- α and - β , however, (Figure 1c) we found a clear trend within all SCs: after application, the MAR of endosulfan- α exceeded the MAR of endosulfan- β by ca. 2, whereas at the end of each SC, this had changed to the contrary. This means that at the beginning of the SCs, endosulfan- α appears fresher (easier to desorb) than endosulfan- β , whereas it seems to be older (less extractable) after 10 days of field aging. During microbial degradation, small portions of endosulfan- α can be transferred to endosulfan- β by *Pseudomonas* sp. (37). We therefore speculate that there might be a constant input of MeOH-extractable endosulfan- β , whereas this pool is decreased for endosulfan- α .

Chlorpyrifos and Malathion. Among the substances we investigated, chlorpyrifos and malathion have intermediate hydrophobicities (Table 1). Nevertheless, on the first sampling day, the $K_{OC(app)}$ of both substances was higher than that for endosulfan (Figure 2a), maybe due to faster kinetics of sorption. The $K_{OC(app)}$ of chlorpyrifos remained nearly constant throughout the experiment so that one might conclude that, under our experimental field conditions, chlorpyrifos reaches apparent sorption equilibrium with the soil within 24 h (time span between application and first sample) and, thereafter, is not subject to any form of field aging. Contrastingly, Laabs et al. (12) reported significant aging of chlorpyrifos, expressed by a steep increase of $K_{OC(app)}$ within a very short period after application. However, in our study, the MAR of chlorpyrifos decreased constantly with time (Figure 2b), which we explain as an ongoing sequestration of chlorpyrifos from the MeOH- to the AEW-extractable fraction. Hence, just like endosulfan and like chlorpyrifos in the study of Laabs et al. (12), also in

our experiment chlorpyrifos was subject to field aging processes. It is therefore possible that different structures or domains within the SOM are involved because aging was once exhibited as a reduction in relative water extractability without changes in MAR (endosulfan) and once as a reduction in MAR with unaltered relative water extractability (chlorpyrifos). This observation deserves further process-orientated investigation in the laboratory with well-characterized model sorbents. Furthermore, whether this difference holds up in the long term has to be tested. Our experiment lasted only several weeks, whereas aging processes can evolve and go on for years (38). Thus, it is possible that the differences in aging between endosulfan and chlorpyrifos that we observed in the initial phase might vanish later on.

Malathion seems to show an overall decrease in $K_{OC(app)}$ during our experiment (Figure 2a). However, during SC1 and 2, the concentrations of malathion in the aqueous extract were close to or even below the limit of detection so that only few $K_{OC(app)}$ values could be calculated, and standard errors were high. Yet, even the fact that aqueous concentrations of malathion were sufficient to calculate $K_{OC(app)}$ values at the end of the experiment but not at the beginning can be understood as an indicator that water extractability increased (and not decreased) during our study. Only in the relatively dry SC3, $K_{OC(app)}$ increased steadily, as described for endosulfan. MAR, however, decreased more or less constantly over time, just as described for chlorpyrifos (Figure 2b). Thus, it occurs as if malathion that was associated with the MeOH-extractable domain did not only move to stronger organic binding sites in the course of the experiment but also back to binding sites that were easier to assess in the sequential extraction. This apparent freeing up of malathion from MeOH-extractable binding sites can hardly be explained. Nevertheless, our finding is consistent with the results of Getenga et al. (39) who reported that previously unextractable malathion became biodegradable after ca. 200 h of incubation of their samples. It is possible that malathion was temporarily incorporated by plants or soil biota and then released upon turnover/decay of these organisms. However, information on plant uptake of malathion is lacking (40), and malathion is rather easily degradable by soil microbes (field half-lives = 1.4–2.6 d; Table 1) so that our hypothesis remains speculative. Another explanation for the simultaneous decrease in $K_{OC(app)}$ and MAR is that the MeOH-extractable pool has a higher degradation rate than the water- and the AEW-extractable fractions, possibly due to surface-catalyzed microbial decay (41). Such degradation, however, would not result in the total increase in water-extractable malathion discussed above. Although we cannot explain the observed field aging of malathion in detail, we conclude from our data that the MeOH extract represents a pool of pesticides that is subject to very intense dynamics and that it is reasonable to assume that this dynamics is related to some type of biological activity. Also the microbial conversion of endosulfan- α to - β affected the fraction of methanol-extractable pesticides more than the other two extracts. Thus, our observations seem to be in agreement with the findings of Barriuso et al. (16), who reported that herbicide bioavailability to *Pseudomonas* sp. correlates significantly with extractability by methanolic solvent.

Dimethoate and Mevinphos. Dimethoate and mevinphos have the highest water solubilities of the studied substances (24 g L⁻¹ and completely miscible, respectively (33)). Because of analytical problems, dimethoate could not be measured in the aqueous extract of SC1 and SC2. In SC3, $K_{OC(app)}$ increased sharply during the sampling interval. After the fourth application,

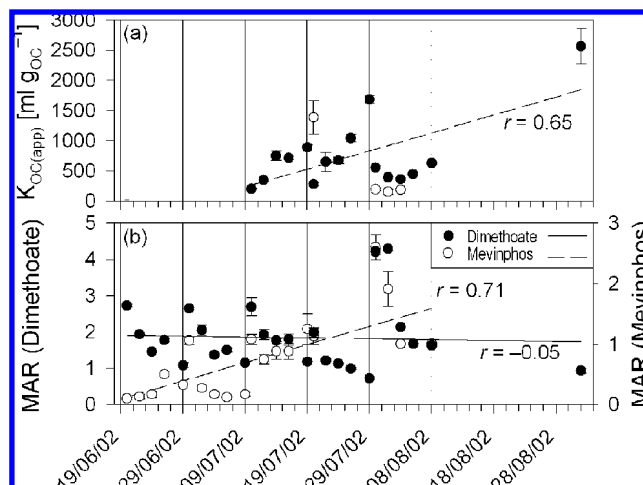


Figure 3. Field aging of dimethoate and mevinphos after repeated application to a tropical Ultisol. (a) Temporal course of apparent sorption coefficients ($K_{OC(app)}$; with linear regressions). (b) Methanol/AEW (acetone/ethylacetate/water; 3:1:1 by volume) ratios (MAR; means and standard errors, $n = 2$). Vertical lines mark the application dates. In SC1–2 no $K_{OC(app)}$ could be determined for dimethoate; see Materials and Methods.

it dropped back to a value just slightly higher than that at the beginning of SC3 and rose again (Figure 3a). Principally, this pattern was repeated once more in SC5. However, it took until the third sampling event of SC5 until the minimum $K_{OC(app)}$ had been reached, and the subsequent rise in $K_{OC(app)}$ was less steep than that in SC 3 and 4. This might be caused by an additional input of fresh dimethoate from plants into the soil by rain or dewfall during the first days of SC5. This wash-off could also be rudimentarily observed for the other pesticides (Figures 2a and 3a); however, it was most pronounced for the highly water-soluble dimethoate. The $K_{OC(app)}$ calculated for the last sampling day (01/09/2002) was the highest of all values and exceeded the tabulated K_{OC} by a factor of 128 (Table 1). Thus, dimethoate clearly shows field aging. Also, Laabs et al. (12) reported the highest relative increase in $K_{OC(app)}$ for the most polar substance they investigated (monocrotophos). However, this observation may most likely be explained by fast dissipation of the labile pool rather than by an increase in sorption strength of the remaining pesticide residues. As a result of the high rate of dissipation, only small amounts of aged dimethoate remain in the soil at the end of each SC. For this reason, the $K_{OC(app)}$ of dimethoate is mainly affected by the residues originating from the respective latest application, and there is only a slight increase in $K_{OC(app)}$ from SC to SC. This contrasts the pattern of aging of endosulfan, where the increase in $K_{OC(app)}$ is more of a constant rise than a repeated pattern. Thus, the relative impact of previous applications on the $K_{OC(app)}$ measured in a later SC is higher for endosulfan than for dimethoate. This finding is in good agreement with the fact that endosulfan accumulates in the studied soil to a greater extent than dimethoate (26).

Like the $K_{OC(app)}$, the MAR of dimethoate also showed a regular pattern for all five SCs. In SC1–3, MAR dropped from ca. 2.7 at the beginning to 1.1 at the end of the sampling cycle; in SC4, it dropped from ca. 2.0 to 0.7; and in SC5 and 5' from 4.2 to 0.9 (Figure 3b). Hence, also in the second coefficient, dimethoate showed aging within each SC. Because of the regular cycles of MAR, there is no overall trend, however, so that MAR does not correlate with time in the long term ($r = -0.05$). Thus, like the $K_{OC(app)}$, the MAR also indicates that dimethoate ages

in soil but that the overall binding state is dominated by freshly added substance, whereas the contribution of residues from former applications seems to be minor ($K_{OC(app)}$) or even negligible (MAR).

Despite its high water solubility, mevinphos was hardly detectable in the aqueous extract so that only four $K_{OC(app)}$ values of mevinphos could be calculated during the experiment (Figure 3a). Obviously, volatilization, leaching, and degradation of the $CaCl_2$ -extractable pool were so fast that it was instantaneously depleted (min. field half-life 1.4 d; Table 1). Consequently, even to a greater extent than that described for dimethoate, the aging of mevinphos must be considered to be an apparent aging, as the $CaCl_2$ -extractable fraction does not sequester continuously into more specific binding sites, but dissipates on other pathways so that only the strongly sorbed fractions remain. The problem of distinguishing dissipation from aging principally applies to all substances investigated in this study, but our data shows that its relevance becomes more pronounced with increasing water-solubility (and thus leaching potential and biodegradability).

In contrast to all other substances studied, the MAR of mevinphos did not drop or remain constant, but it rose (Figure 3b; $r = 0.71$) with time. Despite this increase, the MARs of mevinphos were the lowest of all substances we studied, however. This means that only a small proportion of mevinphos was sorbed to MeOH-extractable domains, whereas the greater part was sorbed to (more stable) AEW-extractable sites. Yet, the relative increase of MeOH-extractable mevinphos (as compared to the AEW-extract) during the experiment might indicate that, in contrast to the other substances, the sorption of mevinphos to the AEW-extractable domain is easily reversible so that the AEW-extractable pool may re-fill the MeOH-pool and keep it on a relatively constant level, although the MeOH- and water-extractable pools are continuously depleted by leaching and degradation. Thus, aging does not appear to be relevant for mevinphos on the time scale we investigated. Nevertheless, if application is constantly repeated over years, even highly soluble and easily degradable pesticides such as carbaryl have been reported to build up unextractable pools (42). That is why mevinphos might also undergo aging processes in the long term, even if the opposite is indicated here in our short-term experiment.

Sorption Coefficients and Pesticide Half-Life. While $K_{OC(app)}$ significantly correlated with pesticide half-lives, no correlation between MAR and half-lives existed ($r = 0.66$ and 0.09 , respectively; Figure 4). We conclude that dissipation mainly affects pesticides that can be extracted by the $CaCl_2$ solution (i.e., dissolved or fully reversible sorption). The distribution of pesticides within stronger binding sites (i.e., the MAR) is irrelevant for dissipation. This might contradict the finding that the MeOH-extractable pesticides represent the biodegradable fraction (17, 18). In a tropical climate, however, not biodegradation, but volatilization seems to be the major pathway of pesticide dissipation (compare refs 26 and 43 and the vapor pressures given in Table 1). Volatilization is, compared with sorption, a relatively fast process that mainly takes place in the first hours or few days after application (44, 45). Hence, after application of pesticides as an aqueous solution, volatilization should mainly occur from the $CaCl_2$ -extractable fraction rather than from the fractions that are extractable by MeOH or AEW. Although the literature data given in Table 1 do not indicate that hydrolysis is a major degradation process for the pesticides we investigated, this dissipation pathway also should mainly

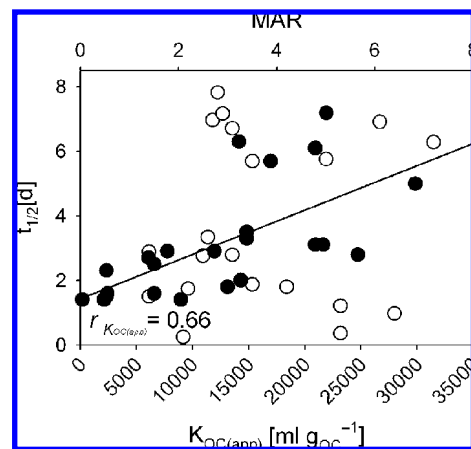


Figure 4. Combined plot of field half-lives ($t_{1/2}$) for all pesticides and all sampling cycles against $K_{OC(app)}$ (●) and MAR (○) values (arithmetic mean of the respective sampling cycle). Field half-lives taken from ref 26. No regression line is drawn for MAR because $r = 0.09$, only.

affect the water-extractable fraction. Thus, both volatilization and hydrolysis result in the observed correlation between $K_{OC(app)}$ and field half-lives.

Overall Discussion and Conclusions. In our study, we observed aging phenomena for all studied substances except mevinphos, although (i) fresh, unaged pesticides were repeatedly applied, (ii) the tropical climate promoted rapid dissipation of the substances, and (iii) the soil was covered by vegetation, which caused pesticide input into the soil to be relatively irregular because of wash-off from the plants (instead of sharp signals of pesticide input upon application, which would be the case if bare soil was treated). The extent of aging, however, was clearly related to polarity of the compounds. Only the organochlorine substance endosulfan, the most hydrophobic compound we investigated, showed aging in the previously described form: $K_{OC(app)}$ rose steadily, and this rise was partly related to the water content of the soil. Also, endosulfan accumulated significantly in soil (26). Aging of organophosphorous pesticides with intermediate hydrophobicity (chlorpyrifos and malathion) was less obvious and could only be revealed by conducting sequential extractions of the soil and introducing the MAR as a new partitioning coefficient. Further research should address the question whether there are general differences in the binding mechanisms of organochlorine and organophosphorous pesticides, which might be hypothesized from our observations. Dimethoate aged within individual SCs, but dissipation was probably so rapid that residual pesticides had no significant influence on the overall binding state after the next application.

Especially when the concentrations of pesticides in the aqueous extract were low, that is, when the denominator of eq 1 was small, the MAR turned out to be more robust (less random fluctuations) than the conventional partitioning coefficient $K_{OC(app)}$. This resulted in smaller standard errors and more complete data sets of the MAR than of the $K_{OC(app)}$. Processes known to be or assumed to be related to microbial activity were reflected by changes of the relative concentrations of pesticides in the MeOH extract. Thus, although microbial activity was not explicitly investigated in our study, our results might support the hypothesis that the MeOH-extractable fraction is bioavailable for microorganisms. Because MAR is nevertheless not suitable to predict field half-lives of pesticides under our experimental conditions, we found an indicator that other processes than microbial breakdown, namely, volatilization, seem to govern pesticide

degradation at our study site (26). It might be interesting to further test whether general relationships between MAR and microbial activity can be derived and which role edaphon plays within the processes of aging.

To improve the understanding of aging processes on the particle or even molecular scale and to identify clear correlations between structural or physicochemical properties of the pesticides and their tendencies to age in soil, further sophisticated laboratory experiments are necessary. Therein, not only the interaction between sorbent and sorbate with model substances should be studied on the microscale, but we also need to know which pools are accessed by the different extractants suggested in the literature. For both questions, modern NMR-techniques (46) might be useful tools.

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