Insecticide dynamics in the soil environment
of a tropical lychee plantation

– A case study from Northern Thailand –

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Erfahrung ist fast immer eine Parodie auf die Idee.

(Johann Wolfgang von Goethe)

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Abstract

Adverse side-effects of pesticide use are not only controlled by the acute toxicity of the applied substances, but also by their persistence and mobility. Both are hardly investigated for humid tropical climates. The scope of my study was (i) to monitor background concentrations of pesticides in an intensively cultivated Northern Thailand watershed and (ii) to quantify soil-related pathways of pesticide dissipation in a representative lychee plantation under realistic agricultural practice. Therefore, baseflow samples of river-water were analysed for commonly used pesticides. In addition, water and pesticide fluxes were monitored on profile scale during two rainy seasons with a tension-controlled, high-resolution soil solution sampling device and conventional wick-lysimeters, while surface runoff was collected with metal troughs. Pesticide residues in soil were assessed after sequential extractions.

Riverine pesticide concentrations were above European threshold values even in baseflow, so that I found it relevant to study the pathways of pesticide translocation from the plot into ground and surface water in greater detail. A single manual application of various organochlorine and organophosphorous insecticides in the first study year revealed that up to 1% of the applied amount can be leached into 55 cm soil depth over night by preferential flow. Under saturated flow conditions, the preferential flow pathways within the Acrisol were so numerous that sampling devices with a diameter of 9 cm pretended homogeneous flow. Two independent diversity indices showed that, under unsaturated conditions, the flux became increasingly heterogeneous, probably because one flow pathway after the other was "switched off" so that water flux concentrated on distinct fingers.

The pesticide half-lives in the studied Acrisol were among the shortest ever reported (1.4 – 7.2 days, malathion and chlorpyrifos), because the humid tropical climate rather than microbial adaptations promoted both abiotic (leaching, volatilization) and biotic (microbial decay) dissipation processes. Besides climate, also the ground vegetation of the orchard probably enhanced the rate of dissipation, because pesticides on plant surfaces volatilize faster and are more exposed to photodecomposition than pesticides on soil surfaces. Despite this rapid dissipation, all substances except mevinphos (completely miscible with water) accumulated in soil after five repeated applications in the second study year. Using a conventional and a new sorption coefficient ($K_{OC(app)}$ and MAR, the latter calculated from methanol- and acetone:ethylacetate:water-extractable fractions of pesticides), I showed that the accumulation went along with aging processes, which were most evident for endosulfan.

The ground cover and the exceptionally high infiltration capacity of the soil effectively reduced the total amount of surface runoff. Nevertheless pesticide concentrations in surface runoff clearly exceeded tabulated toxicity data for vertebrate and invertebrate aquatic test species. Therefore, I cannot rule out adverse effects on aquatic biota, and the use of pesticides in Northern Thailand fruit cropping requires technical optimization before this form of land-use system can be considered sustainable.

Kurzfassung

Die unerwünschten Nebenwirkungen eines Einsatzes von Pflanzenschutzmitteln (PSM) werden nicht nur durch die akuten Toxizitäten der Wirkstoffe gesteuert, sondern auch von ihrer Persistenz und Mobilität. Beide Größen sind für tropische Klimate kaum erforscht. Das Ziel meiner Studie war, (i) Hintergrundkonzentrationen von PSM in einem intensiv landwirtschaftlich genutzten nordthailändischen Einzugsgebiet zu ermitteln und (ii) Dissiaptionspfade von PSM im Boden für eine repräsentative Litschi-Plantage unter realistischer Bewirtschaftung zu quantifizieren. Hierzu wurden Flusswasser-Proben (Basisabfluss) auf weithin genutzte PSM analysiert. Zusätzlich erfasste ich während zweier Regenzeiten auf der Profil-Skala die Flüsse von Wasser und PSM, und zwar mit einer tensionsgesteuerten, hoch auflösenden Anlage zur Bodenlösungsgewinnung sowie mit konventionellen Dochtlysimetern. Oberflächenabfluss sammelte ich in Metall-Rinnen; PSM-Rückstände im Boden wurden nach sequenzieller Extraktion bestimmt.

Flusswasserkonzentrationen von PSM lagen bereits im Basisabfluss oberhalb europäischer Grenzwerte, sodass ich es für wichtig erachtete, die Transportpfade von PSM vom Feld ins Grund- und Oberflächenwasser detaillierter zu untersuchen. Eine einmalige manuelle Applikation verschiedener Organochlor– und Organophosphat–PSM im ersten Studienjahr offenbarte, dass bis zu 1% der applizierten Menge durch präferenziellen Fluss über Nacht in eine Bodentiefe von über 55 cm verlagert werden kann. Unter gesättigten Flussbedingungen waren die präferenziellen Fließwege im untersuchten Acrisol so zahlreich, dass Probenehmer mit 9 cm Durchmesser ein homogenes Fließfeld vortäuschten. Zwei voneinander unabhängige Diversitäts-Indices zeigten, dass unter ungesättigten Fließbedingungen der Fluss zunehmend heterogener wurde. Wahrscheinlich ist dies darauf zurück zu führen, dass die Fließwege nach und nach „abgeschaltet" wurden und sich der verbleibende Wasserfluss auf einzelne Finger konzentrierte.

Die Halbwertszeiten der PSM im untersuchten Acrisol gehören zu den kürzesten, die jemals berichtet wurden (1,4 – 7,2 Tage, Malathion und Chlorpyrifos), vor allem weil das humide tropische Klima sowohl abiotische (Leaching, Volatilisation) als auch biotische (mikrobieller Abbau) Dissipation fördert. Mikrobielle Anpassung schien keine wesentliche Ursache für die kurzen Halbwertszeiten zu sein. Neben dem Klima wurde die Dissipationsrate wahrscheinlich auch durch den Unterwuchs der Plantage erhöht, weil PSM von Pflanzenoberflächen schneller verdampfen als aus dem Boden und weil sie auf der Vegetation in größerem Maß Photoabbau unterliegen. Trotz der schnellen Dissipation reicherten sich alle Substanzen außer Mevinphos (komplett mit Wasser mischbar) nach fünfmaliger Applikation im zweiten Studienjahr im Boden an. Mit einem konventionellen und einem neu eingeführten Sorptionskoeffizienten (KOC und MAR, letzterer aus Methanol- und Aceton:Ethylacetat:Wasser-extrahierbaren Fraktionen berechnet) konnte ich zeigen, dass die Anreicherung mit Alterungsprozessen einherging, die für Endosulfan am ausgeprägtesten waren.

Der Unterwuchs und die ausgesprochen hohe Infiltrationskapazität des Bodens reduzierten effektiv die Gesamtmenge des Oberflächenabflusses. Dennoch überstiegen die Pestizidkonzentrationen im Oberflächenabfluss deutlich tabellierte Toxizitätsdaten sowohl für aquatische Vertebraten als auch Invertebraten. Deswegen kann ich eine Beeinträchtigung der aquatischen Lebewesen im Untersuchungsgebiet nicht ausschließen, und der Einsatz von PSM im nordthailändischen Obstbau muss technisch optimiert werden, bevor diese Form der Landnutzung als nachhaltig betrachtet werden kann.

1 General introduction

1.1 *Background and motivation of this work*

1.1.1 Sustainable development of mountainous Northern Thailand

About half of the world's population depends either directly on mountain resources (10%) or lives in adjacent medium- and lower-watershed areas (40%). As a result, deterioration of mountain ecosystems is one of our current major environmental problems (UNCED, 1992). This is especially true for the region of Northern Thailand. Ninety percent of this region have been classified as mountainous (UNCED, 2002), and it provides the springs for Thailand's most important rivers. Since the 1960s, the annual growth rate of the rural population of Northern Thailand is around 3 – 3.5 %. With raising needs of a permanent intensification of agriculture (Kunstadter, 1990; Fox et al., 1995), slopes have been continuously deforested (annual rate of forest loss 1961 - 1985: 1.3 %, Hirsch, 1990) and agricultural practice shifted from traditional swidden farming ("slash-and-burn"; subsistence farming) to permanent cropping of cash crops (Kunstadter, 1990). The depletion of drinking water reserves associated with deforestation was accelerated by the additional water demand for irrigation, leading to serious disputes between hilltribes and lowland farmers (Charoenmuang, 1994; Wongbandit, 1994). Besides these social conflicts, the ongoing fragmentation of landscape also causes environmental problems, such as the increasing the risk of erosion-producing overland flow (Ziegler & Giambelluca, 1997; Ziegler *et al.*, 2004). To protect the fragile mountainous ecosystems and to preserve their habitats and genetic diversity, but also their ability to serve as the source of living of upland people, current concepts of land-use have to be refined. Therefore, the sustainable development of mountainous regions is one of the key issues of the Agenda 21 (UNCED, 1992).

1.1.2 Relevance of fruit cropping in Northern Thailand

Fruit cropping is considered to be a sustainable alternative to the cultivation of annual field crops in the uplands of Northern Thailand, because the permanent ground cover, which is common in Thai orchards, effectively prevents erosion. As a result of intensive promotion by the Thai government, the area used for fruit production in Northern Thailand increased by more than 60 % between 1991 and 1999, while the total area of farm land slightly declined (**Table 1.1**) (Center for Agricultural Information, 2000; 2004). In 1999, 10 % of the farm land of Northern Thailand had already been converted to fruit plantations. Yet, as whole villages often specialize on certain farming systems, this proportion can even be larger on local scale. For example, in Mae Sa Mai, an upland village 30 km NW of Chiang Mai inhabited by the Hmong ethnic group, almost 70 % of the farm land is covered by lychee trees (Carsten Riedel, University of

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Hohenheim, unpublished data). Thus, fruit orchards play an increasingly important role in mountainous Northern Thailand.

1.1.3 Agrochemicals in Northern Thai fruit cropping

The sustainability of Northern Thai fruit plantations has never been investigated systematically, although some environmental risks that emanate from this cropping system are obvious: Being produced for national resale and for export, fruits from Northern Thailand must have premium quality. Therefore, and to maintain yields on a high level, regular applications of agrochemicals are common practice (Taylor, 1996; Ecobichon, 2001). In 1999, more than 51300 tons of pesticides were imported into Thailand (Center for Agricultural Information, 2000). Relating this amount to total farm land (ca. 210000 km², Center for Agricultural Information, 2004), I estimate the nation-wide average application rate of the imported pesticides to be as high as 2.4 kg active ingredient per hectare. I am not aware on any data on Thai pesticide production capacities, but it is reasonable to assume that $2.4\,kg\,ha^{-1}$ is a minimum guess (for comparison: average application rates in Germany: $1.9\,kg\,ha^{-1}$ (Bundesministerium für Verbraucherschutz, 2003)). In the uplands with their steep slopes and numerous surface waters, pesticides can be expected to be prone to leaching and wash-off into sensitive non-target ecosystems. Reports in daily newspapers that "Pesticides spread their toxic reach" (Bangkok Post, 06/06/2001) and that "The source of life is poisoned" (Bangkok Post, 27/07/1997) give evidence of an increasing concern among the Thai population. Yet, although relevant concentrations of pesticide residues have been found in Thai food, ground and surface waters, and even in the breast milk of female farmers (Baun *et al.*, 1998; Thapinta & Hudak, 2000; Stuetz *et al.*, 2001), a systematic research on the fate of agrochemicals in the fruit orchards of Northern Thailand is still lacking.

Table 1.1: *Farm land in the region of Northern Thailand and relevance of fruit plantations 1991 – 1999 (Center for Agricultural Information, 2000 (1991 - 1995); 2004 (1996 - 1999))*

Year	Total Farm Land [km²]	Fruit Plantations [km²]	Fruit Plantations [% total]
1991	47031	2806	5.97
1992	46577	3095	6.64
1993	46248	3103	6.71
1994	46470	3134	6.74
1995	46747	3165	6.77
1996	46229	3413	7.38
1997	45763	3758	8.21
1998	45240	4064	8.98
1999	45301	4545	10.03

1.2 State of the art

1.2.1 Pesticide dissipation from soil

Dissipation of pesticides from the treated area reduces the efficiency of the treatment and increases the risk of off-site effects. Detailed knowledge on dissipation pathways is therefore inevitable for the development of sustainable farming systems. Apart from bound residue formation, dissipation may include both transport and transformation processes, which are influenced by numerous biotical and abiotical factors.

Transport

First losses of pesticides from the plot occur upon application itself, namely in the form of spray drift. Spray drift is relevant for the short-range aerial transport and may result in pesticide inputs into adjacent surface waters of up to 30% (3 m from the plot, 95th percentile) of the rate applied in the orchard itself (FOCUS, 2001). However, this point source of pesticide contamination has been systematically investigated earlier (Ganzelmeier *et al.*, 1995), and it can be substantially reduced by an optimization of the technical spraying equipment and by appropriate timing of the application.

The prevailing form of long-range aerial transport is caused by volatilization of pesticides from the treated plot followed by re-deposition in off-target regions (LeNoir *et al.*, 1999). Being promoted by high temperatures, volatilization is especially relevant under tropical climate, and pesticides may be transported into remote regions as far as 75 km away from the closest area of application (Laabs *et al.*, 2002c, study conducted in the Pantanal, Brazil). This is especially true for Northern Thai fruit orchards, which have a permanent ground cover consisting of grasses and herbs. When pesticides are sprayed, they precipitate on the vegetation and not directly onto the soil. This might influence the dissipation pattern because pesticides generally have a lower affinity to plants than to soil (Boehncke *et al.*, 1990) and because the stagnant atmospheric boundary layer at the soil surface is larger than in the plant canopy (Rüdel, 1997). Both these factors promote volatilization, so that pesticides applied to fruit orchards with ground vegetation might be more prone to volatilization than pesticides applied in arable land. Yet, in the humid tropics, pesticides can be expected to be washed into the soil (and thus be protected from volatilization) rather shortly after application. Therefore, and for a better understanding of the dispersion of pesticides into *local* water bodies, *soil processes on the profile and plot scale* should be in the focus of investigation.

On small and medium scales, water is the key factor for pesticide translocation. Because of the high affinity of most pesticides used in Thai fruit production to the soil solid phase (see below), significant transport through the soil (leaching) can only be expected when preferential flow occurs and bypasses the matrix of the soil (Flury, 1996).

Preferential flow can occur in the form macropore flow through animal burrows such as earthworm holes and termite galleries (McGarry *et al.*, 2000). Furthermore, small-scale differences in texture, water content, etc. may lead to heterogeneous infiltration (fingering, Hillel & Baker, 1988; Reichenberger *et al.*, 2002). Thus, an understanding of the flow field of water that reaches beyond predictions based on mean soil physical parameters and accounts for preferential flow is required to understand the leaching of pesticides (Roth *et al.*, 1991).

On the steep slopes of Northern Thailand, pesticides may also be transported laterally. This takes place either above (surface runoff, Wauchope, 1978) or below the surface of the soil (interflow, Johnson *et al.*, 1996). Surface runoff has been demonstrated to be the major pathway of pesticide input from fruit orchards into the Lourens River, South Africa (Schulz, 2001). However, because the Northern Thai fruit orchards have a ground cover that acts like a vegetative filter strip (Krutz *et al.*, 2005) it is unclear whether lateral flow contributes significantly to pesticide discharge from the orchards in my study area.

Transformation

Before, while, and after pesticides are transported they may undergo transformation processes. Abiotical degradation is highly dependent on environmental factors such as soil type, temperature, moisture, UV intensity, etc. These factors also influence the activity of the microbial community and thereby their ability to degrade pesticides. However, microbial breakdown of pesticides depends on additional factors, such as bioavailability of the compound, the adaptation of the microbial community to the agent, or the presence of alternative sources of nutrients (Ragnarsdottir, 2000). Half-lives determined in the laboratory can therefore hardly be used to predict the rates of pesticide degradation under specific field conditions (Vereecken *et al.*, 1995; Beulke *et al.*, 2000). Thus, it is necessary to investigate dissipation rates and degradation products in field trials in order to evaluate the sustainability of pesticide use. This is especially true because degradation may not only eliminate the toxicity of a pesticide, but also harmful metabolites can evolve (for example endosulfan and its sulfate, Wan *et al.*, 2005).

1.2.2 Peculiarities of tropical environments

Among other factors, differences in soil properties and climate make it difficult to transfer data on pesticide dissipation from temperate regions to the tropics. Clayey tropical soils, for example, form microaggregates ("pseudosand") of which the hydraulic conductivities are usually far below average rates of precipitation, so that zones of intra-aggregate bypass flow may evolve even if the soil is not yet saturated with water (Radulovich *et al.*, 1992). Therefore it is possible that pesticides are more

prone to leaching in tropical than in temperate soils. This is especially true under the monsoonal climate of Northern Thailand with its high-intensity rainfalls. By the same time, only small amounts of pesticides should be available for leaching in the tropics because the high temperatures promote other dissipation pathways such as volatilization (Laabs *et al.*, 2002a; 2002c) and microbial breakdown (Racke *et al.*, 1997). Both the higher leaching rate and the temperature-induced degradation are arguments that support the general opinion that pesticides dissipate faster in the tropics than in temperate regions (Cooper & Zheng, 1994; Nakagawa *et al.*, 1996). Nevertheless, the toxicity of pesticides is believed to be higher in the tropics than in temperate regions because high temperatures promote biological uptake and metabolism of xenobiotics (Castillo *et al.*, 1997). Repeated applications generally lead to an adaptation of soil microbes to the respective pesticide, which is reflected by a decrease of half-lives (Araujo *et al.*, 2003; Ismail & Kalithasan, 2003). Yet, if pesticide applications are repeated so frequently that they result in soil concentrations high enough to have direct toxic effects on the microbial community, half-lives may remain unaffected (Piutti *et al.*, 2002) or even increase (de Andrea *et al.*, 2003). To answer the question how repeated applications influence pesticide dissipation rates in Northern Thai fruit orchards realistic field experiments under actual weather conditions of the humid tropics are urgently needed.

1.2.3 Sorption and aging of pesticides

Only the fraction of pesticides dissolved in soil solution is readily bioavailable and prone to leaching. That is why sorption-desorption processes govern pesticide fate in the field (Koskinen *et al.*, 2002), and sorption coefficients are one of the most sensitive input parameters for pesticide fate models (Dubus *et al.*, 2003). Pesticides mainly interact with the soil organic matter (Mader *et al.*, 1997). They can either partition between soil solution and soil organic matter or physically adsorb to the solid phase, for example after entrapment in small pores (Pignatello & Xing, 1996). The latter is a kinetically hindered process, so that sorption strength is not constant, but it increases over time. Increasing binding strength without chemical alteration of the sorbate itself is referred to as "aging" (Alexander, 1995; Gevao *et al.*, 2003). Aging permanently alters the sorption characteristics of pesticides, so that the risk of their release from soil cannot be estimated from tabulated sorption coefficients, but should be assessed by extraction of pesticides from actual field samples.

The vast majority of published studies on pesticide aging is either restricted to comparisons of pesticide extractability of substances aged in the field for years with substances that were freshly added to soil, (Scribner *et al.*, 1992; Weissenfels *et al.*, 1992; Pignatello *et al.*, 1993), the temporal course of extractability during incubation of soil samples spiked with pesticides in the laboratory (Hatzinger & Alexander, 1995; Oi,

1999; Koskinen *et al.*, 2002), or laboratory studies on the process of aging itself (Xing & Pignatello, 1997; Altfelder *et al.*, 1999; Leboeuf & Weber, 2000b; Grathwohl & Rahman, 2002). Field studies on pesticide aging in the first weeks after application under natural weather conditions are rare (e.g. Walker *et al.*, 2005). To my knowledge, the aging of pesticides in tropical fruit plantations has never been investigated. However, this knowledge is essential for the evaluation of environmental risks caused by pesticide use.

1.2.4   Sample collection and analysis

Sample collection

To investigate transport, transformation and aging of pesticides, sound methods for both sample acquisition and analysis are required. While soil samples for pesticide analysis are commonly obtained with simple augers or soil corers (Malone *et al.*, 2000; Laabs *et al.*, 2002a), more sophisticated techniques are needed to assess the movement of water and solutes in soil. The best description of the flow field of water can be derived from high resolution TDR measurements, because this technique works with minimal impact on the studied soil profile (Ritsema *et al.*, 1998; Garrido *et al.*, 2001). However, TDR probes only measure changes in water contents with the help of electromagnetic waves, whereas the simultaneous assessment of water and pesticide fluxes demands for actual sampling of the soil solution. For a quantitative assessment of water and solute fluxes, the samplers must collect water representatively, and they must be inert towards the studied agents. Suction cups fail to account for preferential flow (Brandi-Dohrn *et al.*, 1996; Marques *et al.*, 1996) and may sorb agrochemicals if not made of borosilicate glass (Wessel-Bothe *et al.*, 2000). Free draining lysimeters can be constructed from inert materials such as stainless steel. They catch significant proportions of preferential flow, but underestimate total flux if the soil is not saturated with water (Jemison & Fox, 1992). Laabs *et al*. (2002a) showed that passive lysimeters are nevertheless suitable to assess pesticide fluxes through tropical soils, especially if equipped with glass-fiber wicks that enhance the contact between soil and sampler and which apply (in form of a hanging water column) a small tension to the sampler (Holder *et al.*, 1991). Also passive monitoring boxes seem to collect pesticide fluxes including preferential flow effectively. However, they only provide a low temporal resolution, and water fluxes are not assessed directly, but have to be derived from simulations of the water balance (Bischoff *et al.*, 1999). As an alternative to passive samplers, van Grinsven *et al.* (1988) introduced tension plate lysimeters with adjustable vacuum (suction plates) to collect water and solute fluxes correctly and in virtually any temporal and spatial resolution. By developing suction plates that are completely constructed of inert borosilicate glass, Siemens & Kaupenjohann (2004) made it possible for me to adopt this technique for the analysis of agrochemicals.

Pesticide analysis

For the analysis of pesticide residues, gas chromatography with electron impact mass spectroscopy (GC/EI MS) is widely used because of its high separative power, detector sensitivity, and cost efficiency. Gas chromatography is also adequate for studying the environmental fate of agrochemicals used in Northern Thai fruit orchards, because their majority is non-ionic and thermally stable. However, some of the fungicides used in these cropping systems are ionic organo-metallic compounds (for example mancozeb, $C_4H_6MnN_2S_4$, CAS-No. 8018-01-7) so that GC analysis is not applicable. For this reason, I have confined my study to insecticides commonly used in Northern Thai lychee production.

Soil analysis

Pesticides can be extracted from soil with numerous techniques. Besides the classical Soxhlet extraction (e.g. Mattson *et al.*, 1970), ultrasonic extraction (Babic *et al.*, 1998), supercritical-fluid (Piccolo *et al.*, 1992) and accelerated solvent extraction (Gan *et al.*, 1999), as well as microwave assisted extraction (Padron-Sanz *et al.*, 2005) have been suggested. However, the most common practice to extract pesticides from soil still is a batch approach, that means a shake-extraction of soil with a mixture of solvents. The advantage of this technique is that it does not require any specific apparatus so that it can be easily applied in most laboratories. All methods of extraction share the problem that solvents and experimental parameters must be carefully adapted – both to the soils and the target compounds investigated. For clayey, tropical soils from Brazil Laabs *et al.* (1999) developed such a batch extraction technique, and it was further optimized for Thai soils by Nicolakis *et al.* (1999). Because this approach allows to extract pesticides sequentially from soil (that means that pools of different binding strengths can be identified, Scribner *et al.*, 1992; Laabs & Amelung, 2005), it is the method of choice to investigate the field aging of pesticides used in Thai fruit orchards.

Soil solution analysis

To analyze water samples for pesticides with GC methods, the target compounds must be extracted from the water phase and transferred to an unpolar organic solvent. For this concentration step, solid phase extraction was introduced more than 50 years ago and continuously further developed since then (Liska, 2000). While first reliable results were obtained with *n*-alkylsilicas (for example, C18), graphitized carbon blacks were introduced for pesticide analysis in the early 1980s (reviewed by Hennion, 2000). They have a higher retention potential for polar pesticides than C18, so that they are suitable even for the extraction of pesticides whose solubilities in water exceed 1g l^{-1}. Problems of irreversible sorption to the graphitized carbon black could be overcome by reduction of oxidized functional groups of the solid phase with ascorbic acid solution prior to extraction (Di Corcia & Marchetti, 1991; Nikolakis *et al.*, 1999). Because pesticides are

far better preserved on graphitized carbon black than in aqueous solution (Crescenzi *et al.*, 1995), I believe that pesticide losses that occur in the period between sample collection and sample processing could be minimized if the solid phase extraction was integrated into the soil solution sampling device. Also, this would increase the efficiency of sample acquisition, because solid phase extraction in the laboratory is one of the most time and labor consuming steps of the whole procedure of sample preparation.

1.3 Objectives

This thesis was written within the special research program SFB 564 of the University of Hohenheim, which aims on developing strategies for "Sustainable land-use and rural development in mountainous regions of South-East Asia". My contribution to this program is the basic soil scientific research on processes of pesticide dissipation from a lychee orchard in Mae Sa Mai viallage, Northern Thailand, and on the potential exposure of non-target ecosystems adjacent to the treated area. My findings shall help to evaluate the ecological impact of commercial fruit cropping in Asian uplands. In detail, I investigated the following questions:

⮥ **Are there relevant concentrations of pesticides in the surface waters of the study area? (Chapter 2)**

To testify that surface waters in our study area are affected by the use of agrochemicals in adjacent agricultural land, riverine pesticide concentrations in the study area were monitored for one month. Therefore, daily baseflow samples from three sub-catchments with different forms of land-use were collected and analyzed for 24 commonly used insecticides and fungicides.

⮥ **How does water move through the soil of the studied orchard, and does this flow characteristic bear a specific risk of pesticide leaching? (Chapter 3)**

In this chapter, I suggest an experimental setup to simultaneously assess the small-scale variation of vertical water and pesticide fluxes by coupling an existing soil solution monitoring device (Siemens & Kaupenjohann, 2004) with a solid phase extraction system. It is tested whether this device is suitable to demonstrate the relevance of the "first flush" for pesticide discharge. Observed fluxes are interpreted on the background of preferential flow phenomena, and I parameterize the variation of the water flow pattern with diversity indices. Correlations between these indices with the amount of water moving through the soil should make it possible to derive the occurrence and extent of fingering from percolation rates.

⮫ **At which rates do pesticides dissipate under common lychee farming? (Chapter 4)**

Because studies on the fate of pesticides in tropical ecosystems are rare (Racke *et al.*, 1997) and because results from temperate soils cannot be easily transferred to tropical conditions (Barriuso & Calvet, 1992), I found it necessary to determine the half-lives of pesticides typically used in lychee production under natural weather conditions. In Chapter 4 I focus on the influence of repeated applications on pesticide dissipation rates and discuss possible pathways of pesticide dissipation on the basis of physico-chemical properties of the compounds studied.

⮫ **How do binding strengths between pesticides and soil change with time and repeated applications? (Chapter 5)**

In Chapter 5, I present results of sequential extractions of soil samples I collected after repeated pesticide application. To answer the question whether significant aging occurs despite this repeated input of "fresh" pesticides, the temporal courses of conventional C-normalized soil : solution partitioning coefficients (K_{OC}) and a newly introduced partitioning coefficient are calculated and interpreted.

⮫ **To what extent and on which pathways are pesticides washed off the orchard? (Chapter 6)**

In Chapter 6, I compare leaching through the soil with runoff of pesticides from the plot to elucidate the role of both pathways for pesticide losses from the treated area. Special attention is drawn on the importance of repeated applications for potential contamination of aquatic non-target ecosystems, taking into consideration tabulated data for vertebrate and invertebrate toxicity.

2 River-water contamination with pesticides in mountainous N-Thai farmland

2.1 Introduction

In the last decades, land-use in Northern Thailand has changed from subsistence farming to market-orientated agriculture (Fox *et al.*, 1995; Tonmanee & Kanchanakool, 1999). As a consequence of this change, usage of pesticides increased and pesticide residues have been found in agricultural products, soils and surface water of Thailand (Thapinta & Hudak, 2000). Also in the Mae Sa Noi catchment 30 km NE of Chiang Mai agriculture is intensive, but the level of pesticides contamination in the creeks of this catchment has not yet been quantified. This information, however, decides on the question whether detailed process studies on pesticide fate in this specific area warrant further attention.

Therefore, the objective of this survey was to investigate the current level of pesticide contamination of three subcatchments with different land-use in the Mae Sa Noi watershed. Baseflow samples were collected over one month and analyzed for 24 pesticides which are commonly used in the study area.

2.2 Material and methods

2.2.1 Study area

The study sites were in the Mae Sa valley (18°50' – 18°57' N and 98°47' – 98°57'E), ca. 30 km northwest of Chiang Mai. Three creeks were investigated, all of them tributaries to the Mae Sa River. Referring to the largest villages in the subcatchments, these watersheds were denoted BPK (Ban Pong Krai), BNH (Ban Nong Hoi), and MSM (Mae Sa Mai). Their areas were 146 ha (BPK), 229 ha (BNH), and 1097 ha (MSM), of which 72 %, 92 %, and 79 % were agriculturally used (Carsten Riedel, University of Hohenheim, personal communication). In BPK, equal areas of agricultural land were used for cropping of flowers and vegetables, BNH almost exclusively produced vegetables, and MSM was dominated by lychee production. Because no pesticides are applied in lychee production from May to November, we assume that MSM was the watershed with the lowest rate of pesticide application during the sampling period (09 September 2002 – 11 October 2002).

2.2.2 River water sampling

In BNH and BPK, river water was collected at weirs that had been equipped with mechanical sampling devices described elsewhere (Ballarin, 2004). Briefly, capillary tubes of stainless steel (0.8 mm inner diameter; 0.8 – 1 m length) were inserted through

the weirs so that their inlets were directly in front of the crest. Through these tubes, water was continuously flowing into a container (stainless steel) downstream of the weirs. These containers were carefully protected against the intrusion of water on other ways than through the capillary tube and then placed into the river to keep them at ambient temperature until sampling took place. Increasing discharge raised the water level above the weir and therefore also the water pressure at the entrance of the tube. Hence, higher discharge also resulted in higher flux of water through the tubes. After the beginning of storm events, however, the discharge of the creeks rapidly increased up to the 100 fold of the baseflow and exceeded the capacity of the weirs. By the same time, sediment loads in the water increased and clogged the tube of the sampling unit, which then remained plugged until it was manually cleaned. Thus, the water collected in the stainless steel container represents the baseflow of the creeks before stormflow events. In MSM, we manually collected grab samples of the baseflow. From 09 September 2002 – 11 October 2002, five samples per week (Monday – Friday) of one liter were obtained in all three catchments. The samples were transported to the laboratory in amber glass bottles, where we processed them as described below.

2.2.3   Laboratory analysis

Pesticides were analyzed according to the method of Nikolakis *et al.* (1999), who optimized the method of Laabs *et al.* (1999) for samples from Thailand. Circa 0.5 l of each sample was vacuum filtrated through glass-fibre filters (GF 6; Schleicher & Schuell; Germany). An internal standard (1µg each of terbuthylazine and α-HCH in 10 µl of methanol) was added to the filtrate, which was then concentrated on Carbopack B (solid phase extraction; 300 mg Superclean ENVI-Carb 120/400; Supelco, Bellefonte, PA USA). The cartridges had been pre-conditioned with 5 ml of a mixture of dichloromethane and methanol (9:1, v/v), 2 ml of methanol, and a surplus of ascorbic acid (aqueous solution, pH=2, Di Corcia & Marchetti, 1991). The vacuum during extraction was 80 kPa below atmospheric pressure. After the samples had been sucked through, the cartridges were thoroughly rinsed with de-ionized water and dried in a stream of air. Afterwards, they were wrapped in aluminium foil and stored at –18°C until further processing.

Before elution with 1 ml methanol and 6 ml of dichloromethane/methanol (9:1, v/v) the cartridges were freeze-dried for 1.5 days. We added 50 µl of toluene to the eluate as a keeper to prevent the sample from drying during subsequent concentration by roto-evaporation. The residue was transferred into gas chromatography (GC) vials with ca. 300 µl of toluene. Fluoranthene d_{10} (1µg in 25µl toluene) was added as a recovery standard to quantify losses of pesticides during sample preparation.

Pesticide analyses was performed with an Agilent 6890–N GC (gas chromatograph) with 5972–N MS (mass spectrometer; mode of operation: selective ion monitoring (SIM)). External standards were prepared for 24 substances known to be used in the research area (**Table 2.1**). Pesticide concentrations in the samples were then calculated from a comparison of peak ratios between target substances and internal standards in the samples and in the external standards of known concentrations. The limits of quantification were 250 pg (monocrotophos), 50 pg (dicofol, dimethoate, dicrotophos),

Table 2.1: *Chemical names of pesticides included in a river-water monitoring program conducted in 3 tributaries of the Mae Rim River, Northern Thailand*

Pesticide	Chemical name (IUPAC)
atrazine	1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine
captan	1,2,3,6-tetrahydro-N-(trichloromethylthio)phthalimide
carbofuran	2,2-dimethyl-2,2-dihydrobenzofuranyl-7-N-methylcarbamate
chlorothalonil	1,3-dicyano-2,4,5,6-tetrachlorobenzene
chlorpyrifos	O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioic acid
cyhalothrin	cyano-3-phenoxybenzyl (1S + 1R)-cis-3-(z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl cyclopropanecarboxylate
cypermethrin	(+/-)-alpha-cyano-3-phenoxybenzyl (+/-)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate
DDT	1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane
deltamethrin	(1R-(1alpha(S*),3alpha))-3-(2,2-dibromoethenyl)-2,2-dimethyl-, cyano(3-phenoxyphenyl)methyl cyclopropanecarboxylate
dicofol	1,1-Bis-(p-chlorophenyl)-2,2,2-trichloroethanol
dicrotophos	(E)-dimethyl 1-methyl-3-(N,N-dimethylamino)-3-oxo-1-propenyl phosphate
difenoconazole	1-((2-(2-chloro-4-(4-chlorophenoxy)phenyl)-4-methyl-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole
dimethoate	O,O-Dimethyl methylcarbamoylmethyl phosphorodithioate
ditalimfos	O,O-diethyl (1,3-dihydro-1,3-dioxo-2H-isoindol-2-yl) phosphonothioate
endosulfan-α	(3alpha,5a alpha,6alpha,9alpha,9a alpha)-6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-Methano-2,4,3-benzodioxathiepin 3-oxide
endosulfan-β	(3alpha,5a beta,6beta,9beta,9a beta)-6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-Methano-2,4,3-benzodioxathiepin 3-oxide
EPN	O-ethyl O-p-nitrophenyl benzenephosphonothioate
malathion	1,2-di(ethoxycarbonyl)ethyl O,O-dimethyl phosphorodithioate
metalaxyl	methyl N-(2,6-dimethyl-phenyl)-N-(2'-methoxyacetyl)-DL-alaninate
metribuzin	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one
mevinphos	1-Carbomethoxy-1-propen-2-yl dimethyl phosphate
monocrotophos	Dimethyl 1-methyl-3-(methylamino)-3-oxo-1-propenyl phosphate
parathion-methyl	O,O-dimethyl O-(p-nitrophenyl) thionophosphate
permethrin	3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (3-phenoxyphenyl)methyl ester
profenofos	O-(4-bromo-2-chlorophenyl)-O-ethyl-S-propyl phosphorothioate
Internal standards	
HCH-α	alpha-1,2,3,4,5,6-hexachlorcyclohexane
terbuthylazine	2-(tert-butylamino)-4-chloro-6-(ethylamino)-1,3,5-triazine

30 pg (captan, cyhalothrin, cypermethrin, deltamethrin, difenoconazole) and 10 pg for all other analysed pesticides. This corresponds to concentrations in river water of 0.25, 0.05, 0.03 and 0.01 $\mu g\,l^{-1}$. For details on the GC method, see Nikolakis *et al.* (1999) and Laabs *et al.* (1999).

2.2.4   Determination of blind values

During the sampling period, we collected 7 groundwater samples from a 5 – 10 m deep well in the study area and analyzed it for pesticide residues. Because it is not likely that the well is polluted by pesticides, residues detected within these samples probably go back on contamination during the sample preparation or carry-over by improperly cleaned sampling bottles. We therefore defined the pesticide concentrations apparently detected in groundwater samples as blind values, by which all pesticide concentrations measured in river-water samples were corrected. The blind values were: chlorpyrifos: 0.05 $\mu g\,l^{-1}$, dicofol: 0.13 $\mu g\,l^{-1}$, endosulfan-α: 0.11 $\mu g\,l^{-1}$, endosulfan-β: 0.09 $\mu g\,l^{-1}$, profenofos: 0.15 $\mu g\,l^{-1}$, and DDT: 0.03 $\mu g\,l^{-1}$. If the concentrations were negative or below the limit of quantification after this correction, we set them to zero. Because the possibility that the well-water was contaminated with pesticides cannot be fully excluded, the data presented in the following are a conservative estimation of minimum concentrations of pesticides in river-water.

2.3   *Results and discussion*

In total, we detected 14 of the 24 monitored pesticides. Ten different pesticides were found in BPK, 11 in BNH, and 12 in MSM. Seven substances were detectable in all three watersheds, and only three were exclusively found in one of the watersheds (**Table 2.2**). Thus, the spectrum of pesticides in the baseflow samples was similar despite the differences in land-use.

The insecticide endosulfan was among the most frequently detected pesticides. In all three catchments, the average concentration ($\alpha+\beta$ isomers) was around 0.1 $\mu g\,l^{-1}$, which is the threshold value for surface water valid in the European Union for pesticide registration (FOCUS, 2001). Maximum concentrations of endosulfan found in individual samples were 3 – 4 times higher. Only the maximum concentrations of two of the fungicides we monitored exceeded those of endosulfan: chlorothalonil in BPK and metalaxyl in BNH and MSM. Chlorothalonil was found in 80% of the samples from BPK, metalaxyl in all samples except one from BNH. Also the fungicide difenoconazole was detected in almost all baseflow samples form BNH, although concentrations rarely exceeded the limit of quantification. Contrastingly, fungicides were detected only in less than half the samples from MSM so that average

concentrations were lower than in the other two catchments. This might reflect the fact that, during our monitoring study, pesticides were only applied sporadically in MSM, while regular applications took place in BPK and BNH (see above). Obviously, only endosulfan was sufficiently persistent to prevail in baseflow samples outside the spraying season. Endosulfan is known to sorb strongly to sediment, which protects it from hydrolysis.

Table 2.2: *Concentrations of pesticides detected in samples of baseflow from three tributaries of the Mae Sa River, Ban Pong Krai (BPK, n=25 samples), Ban Nong Hoi (BNH, n=24) and Mae Sa Mai (MSM, n=25). All concentrations in µg l^{-1}*

	——— BPK ———			——— BNH ———			——— MSM ———		
	N (N_T)	AV (90P)	Max	N (N_T)	AV (90P)	Max	N (N_T)	AV (90P)	Max
Insecticides									
chlorpyrifos	11 (0)	0.02 (0.03)	0.11	8 (0)	0.00 (0.02)	0.03	1 (0)	0.00 (0.00)	0.02
DDT	3 (0)	0.00 (0.00)	0.01	8 (0)	0.01 (0.05)	0.05	0		
dicofol	0			6 (0)	0.02 (0.04)	0.17	0		
dicrotophos	0			0			0 (3)	0.00 (0.00)	0.01
endosulfan-α	14 (0)	0.04 (0.15)	0.20	14 (0)	0.06 (0.14)	0.32	11 (0)	0.05 (0.16)	0.22
endosulfan-β	17 (0)	0.04 (0.10)	0.11	16 (0)	0.04 (0.09)	0.13	20 (0)	0.05 (0.10)	0.12
malathion	2 (1)	0.00 (0.00)	0.05	0			5 (1)	0.01 (0.02)	0.03
mevinphos	0			0			1 (0)	0.00 (0.00)	0.03
parathion-methyl	6 (3)	0.01 (0.04)	0.07	1 (6)	0.00 (0.00)	0.06	1 (2)	0.00 (0.00)	0.01
profenofos	2 (0)	0.00 (0.00)	0.04	4 (0)	0.01 (0.02)	0.09	3 (0)	0.01 (0.00)	0.14
Fungicides									
chlorothalonil	20 (0)	0.06 (0.15)	0.41	4 (0)	0.01 (0.02)	0.29	0		
difenoconazole	0 (2)	0.00 (0.00)	0.00	2 (21)	0.03 (0.10)	0.11	2 (2)	0.00 (0.00)	0.07
metalaxyl	11 (3)	0.02 (0.08)	0.10	9 (14)	0.05 (0.18)	0.46	9 (2)	0.03 (0.03)	0.59
metribuzin	0			2 (3)	0.00 (0.01)	0.11	2 (1)	0.00 (0.00)	0.05
Σ		**0.21 (0.42)**	**0.52**		**0.25 (0.47)**	**0.91**		**0.16 (0.30)**	**0.86**

N: number of samples with quantifiable amounts of pesticide (concentration > limit of quantification)

N_T: number of samples with traces of pesticides (concentration < limit of quantitation)

AV: average concentration of all samples (samples that contained only traces were included at lowest quantifiable concentration)

90P: 90th percentile

MAX: maximum concentration detected

However, the sorbed endosulfan may be re-released from the sediment over long periods, thereby maintaining the aqueous concentration on a higher level than predicted from degradation data alone (Peterson & Batley, 1993). For this reason, endosulfan was the only pesticide Dabrowski *et al.* (2002) detected in baseflow samples of an intensively cultivated South African watershed. Especially in small catchments like those we studied, pesticides are mainly transported in direct flow and not in baseflow (Müller *et al.*, 2003). We therefore expect the concentrations we measured to be minimum concentrations that may be exceeded during peak discharge after rainstorms.

All other pesticides studied were detected less regularly than endosulfan and the fungicides. Chlorpyrifos and parathion-methyl were more or less specific for BPK and BNH and occurred in 30 – 50% of the samples. Contrastingly, in MSM a slightly greater variety of pesticides was found than in the other two catchments, but many substances occurred only once or in few samples. Also this is in accordance with the fact that the main crop of MSM, lychee, was not treated during our experiment: The river-water contamination with pesticides in MSM probably results from single treatments of individual plots where vegetables or other crops are cultivated. In BPK and BNH, on the other hand, certain pesticides are probably applied throughout the catchment according to recommendations of the local extension service, resulting in more frequent inputs of pesticides into the rivers. Therefore, average total pesticide concentrations in MSM ($0.16\ \mu g\ l^{-1}$) were lower than in BPK ($0.21\ \mu g\ l^{-1}$) and BNH ($0.25\ \mu g\ l^{-1}$). It needs to be investigated, however, whether this ranking changes during the spraying season for lychee.

2.4 Conclusions

It is remarkable that pesticide residues were found in almost every river-water sample and that European threshold values were exceeded in all three watersheds although only baseflow was analyzed. We conclude that local agricultural practices bear a high risk of water contamination with pesticides. It can be assumed that this contamination will have adverse effects on aquatic biota. To develop effective mitigation strategies, pathways of pesticide entry into surface water should be studied and quantified.

3 Water flow patterns and pesticide fluxes in an upland soil in Northern Thailand

3.1 Summary

Rapid percolation of water through soil facilitates both the recharge and the contamination of groundwater reservoirs. We have studied the variation of water flux and pesticide leaching through a soil in northern Thailand. At a depth of 55 cm, two pits were equipped with tensiometer-controlled glass suction lysimeters that were connected to a novel on-line solid phase extraction device. Nine insecticides varying in water solubility from 10^{-2} to 10^{+6} mg litre^{-1} were applied on the soil surface, and leaching was monitored for eight weeks. Measured water fluxes were compared with simulated values. Total recovery ranged from traces (malathion, triazophos) to 1.3 % (dimethoate) of the applied amount, showing a decreasing retardation with increasing polarity of the substances. All pesticides were detectable in the soil solution during the first precipitation event after application. Due to fingering, 83% of the leachate was transported through 38% of area at leaching rates < 2 mm per day. A new adaptation of the Simpson Index revealed that flow pattern diversity exponentially increased with decreasing rates of seepage water flux (R^2=0.80). No such correlation was found when leaching was faster, indicating that the flow pattern switched from a fingering- to a matric-dominated flux. No long-term leaching of insecticides was observed. The two profiles studied study performed similarly in terms of both water and pesticide transport. Therefore we suggest that the flow pattern is a stable property of the soil that can be accurately described by our combination of novel experimental setup and statistical analysis of the flow field.

3.2 Introduction

In the last four decades, the population in the uplands of Northern Thailand has increased, and farming there has shifted from subsistence to cash crops. One result of this shift has been the loss of approximately half of Thailand's forest. Deforestation of the slopes has led to severe soil erosion, and water supply there was affected by an increased demand for irrigation and by pollution with agrochemicals. To solve the problem of soil erosion and to establish a cropping system that is more sustainable than vegetable farming, fruit orchards such as lychee plantations were introduced. Nevertheless, lychee is a cash crop produced for international markets, and its production requires application of large quantities of agrochemicals. Local lychee farmers were reported to be poisoned by organochlorine pesticides, indicating careless handling of these substances (Stuetz *et al.*, 2001). Although pesticides have also been found in Thai food and ground and surface waters (Baun *et al.*, 1998; Thapinta &

Hudak, 2000), we are not aware of any studies of the flow pathways of water and contaminants in Thai soils.

The soil of the study area swells and shrinks little, it is dominated by microaggregates giving it the structure of sand. Nevertheless flow patterns of soil water and its dissolved agrochemicals may still be highly heterogeneous (Flury, 1996). Most of the preferential flow in the tropics under the typical intense rainstorms passes through animal burrows such as termite galleries (McGarry *et al.*, 2000) and other regions of the soil that are exceptionally conductive (fingering infiltration, Hillel & Baker, 1988; Reichenberger *et al.*, 2002). Preferential flow may contribute to groundwater recharge even when evaporation exceeds precipitation. However, pesticide concentrations also peak in preferential flow, inevitably linking recharge and potential pollution of groundwater reservoirs and thereby bringing about the urgent need for a better understanding of the temporal and spatial variation of water and pesticide fluxes in such soil.

All common approaches to assess water and contaminant fluxes in the field have limitations when preferential flow occurs. In macroporous soils, where water bypasses the soil matrix, pesticide concentrations of the soil solution cannot be estimated from pesticide concentrations of the bulk soil (Malone *et al.*, 2000). Sampling leachate in lysimeters may yield a quantitative estimate of the cumulative leaching efflux (Laabs *et al.*, 2002a), but because of the large surface area of typical lysimeters relevant peak concentrations from preferential flow pathways may be diluted by unloaded adjacent matric flow. In contrast, suction cups reflect the small-scale variation of water and solute concentrations in the field, but they do not sample soil water quantitatively (Magid & Christensen, 1993).

Approaches to take advantage of the strengths of these techniques for sampling the soil solution led to the use of suction plate lysimeters. Van Grinsven *et al.* (1988) introduced tensiometer-controlled suction lysimeters with adjustable vacuums. Recently, this type of extraction system was used with lysimeters that consisted of porous glass plates sintered into glass frames. Those suction plates are free of sealings and glues that might adsorb fractions of the sample or contaminate it (Siemens & Kaupenjohann, 2003). The suction-plate technique has been introduced successfully to analyse seepage water fluxes and chemistry in sandy German soils (Siemens & Kaupenjohann, 2004).

We wanted to establish a novel extraction system so that we could investigate (i) the water flow pattern in a Thai lychee orchard, (ii) its variation during the rainy season, and (iii) its relevance for translocation of organophosphates, organochlorines, carbamates and synthetic pyrethroids. We modelled the flux data and introduced a new adaption of a diversity index. We report our results below.

3.3   *Material and methods*

3.3.1   Study area

The plots for our experiment were established on a ten-year-old lychee orchard 30 km north west of Chiang Mai, Northern Thailand (18°53' N, 98°52'E; ca. 800 m above sea level; facing west; slope ca. 15°; mean annual temperature 21.6° C). Mean annual precipitation is ca. 1600 mm. There are distinct dry (November to April) and wet seasons (May to October). Trees had been planted at 10-m intervals on a grid. The soil surface was covered with grasses and herbs that were mown once in two weeks. The soil contains some termite galleries, but earthworms are rare. It is a Haplic Acrisol in the FAO classification (**Table 3.1**).

3.3.2   Field Experiment

In May 2001, we excavated two soil trenches and equipped them with 17 borosilicate suction lysimeters each (suction plates; 90 mm diameter; ecoTech, Bonn) at the transition between the B1 and B2 horizons at 55 cm below the surface and 50 cm from the trenches (**Figure 3.1**). Following the suggestion of de Rooij & Stagnitti (2000), we installed nests of at least 16 small devices. Combining data from 360 collectors, de Rooij & Stagnitti found 16 collectors sufficient to assess the spatial variation of leaching in a single-grain soil. Also they worked at a depth of 55 cm. We opened a horizontal pit from the main trench, attached suction plates to its ceiling in a narrow zigzag pattern (rows A and B; **Figure 3.1**), then refilled the pit with indigenous soil. Stainless steel tubes were used to connect the suction plates to an on-line solid phase extraction system (on-line SPE) which comprised two vacuum chambers with 3-ml glass SPE cartridges (Mallinckrodt Baker, Phillipsburg, N.J.) at the interface. The cartridges had been filled with 300 mg graphitized non-porous carbon (Carbopack, Supelclean ENVI-Carb SPE Bulk Packing 120/400 mesh; Supelco, Bellefonte, PA) and

Table 3.1: *Properties of the soil. Data on texture were provided by Klaus Spohrer, University of Hohenheim. Standard errors in parentheses (Al and Fe for which n=3). C_{org} is organic carbon*

Horizon	Depth [cm]	pH (KCl)	pH (H_2O)	C_{org} [%]	Texture [%]			Fe_d[a]	Al_o[b]	Fe_o[b]
					Sand	Silt	Clay	——— [g kg^{-1}] ———		
Ah	0–20	4.75	5.67	2.54	39	26	35	23.03 (0.22)	2.72 (0.32)	1.60 (0.12)
Bt$_1$	20–55	4.19	4.90	1.42	29	19	52	29.22 (0.73)	2.64 (0.14)	1.13 (0.15)
Bt$_2$	> 55	4.25	4.92	0.65	31	23	46	32.90 (3.27)	1.61 (0.18)	0.61 (0.09)

[a]determined according to the method of Holmgren (1967)
[b]determined according to the method of Schwertmann (1964)

pre-treated with 5 ml of a 9:1 (by volume) mixture of dichloromethane and methanol, 2 ml of methanol, and 15 ml of 10 g litre^{-1} ascorbic acid (pH adjusted to 2 with M HCl) (Di Corcia & Marchetti, 1991, modified). Computer based, tensiometer-controlled systems (SCS-8, UMS, München) kept the vacuum in the upper chamber at average soil tension (median of four tensiometers).

The suction in the lower chamber was at least 5 kPa greater than that in the upper chamber. Thus, soil solution leached into the extraction system under minimal disturbance of the flow pattern. Then it was sucked through the cartridges, where pesticides were concentrated. The effluent was collected to estimate fluxes for individual plates. An assiduous optimization of the pump parameters turned out to be crucial for successful operation. When the soil was nearly saturated with water after heavy rain (e.g. 21/07/01), the pressure difference of 5 kPa between the two chambers was insufficient to allow complete suction of soil solution from the upper to the lower
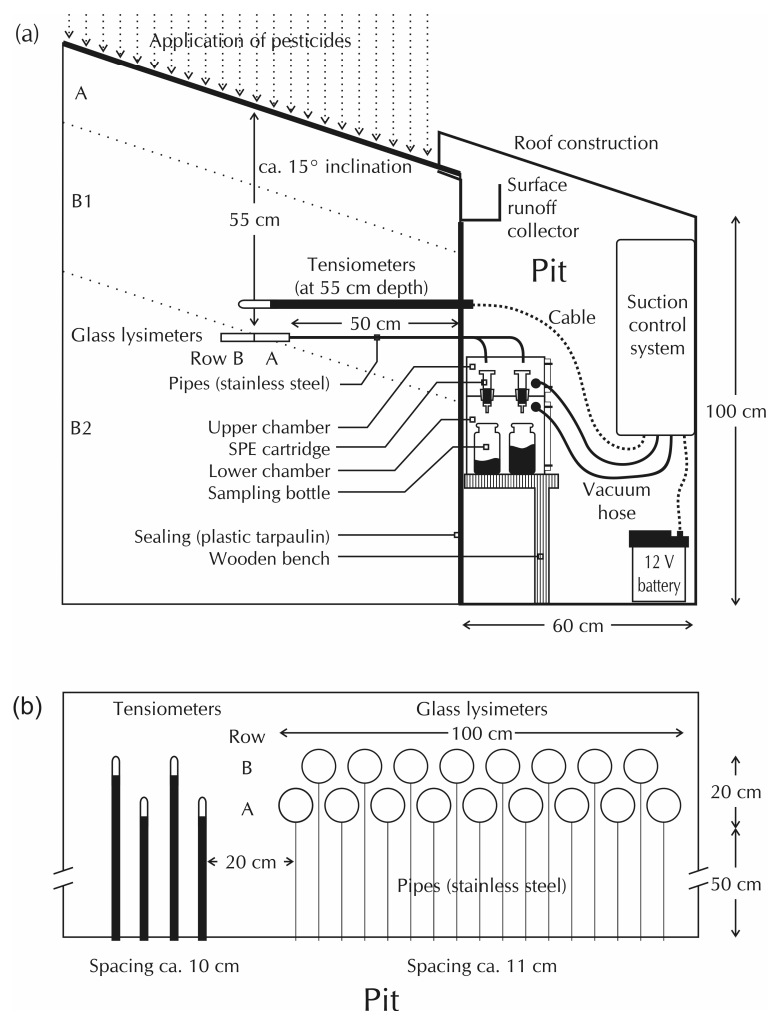
Figure 3.1: *Horizontal (a) and vertical (b) view of soil pit and equipment used to investigate the fluxes of water and pesticides. One plot consisted of 17 suction plates and four tensiometers installed in two rows (A and B) at 55 cm soil depth.*

chamber through the cartridge. To avoid an overflowing of the cartridge, the suction
control system was programmed to increase the vacuum in the lower chamber when the
suction of the soil was less than 3 kPa. This led to a V-shaped relationship between
suction applied to the lower chamber of the extraction system and the suction of the
soil. The suctions in the lower chamber are as follows:

$$S_{LC} = 20 \text{ kPa} - 0.8 \, S_{Soil} \quad \text{if } S_{Soil} < 1.5 \text{ kPa},$$

$$S_{LC} = 8 \text{ kPa} \quad \text{if } 1.5 \text{ kPa} < S_{Soil} < 3 \text{ kPa},$$

$$\text{and } S_{LC} = 5 \text{ kPa} + S_{Soil} \quad \text{if } S_{Soil} > 3 \text{ kPa}.$$

Thus the suction in the lower chamber was greatest when the soil was nearly saturated
(**Figure 3.2**; e.g. on 21/07/01 and 03/08/01). A plastic tarpaulin attached to the open
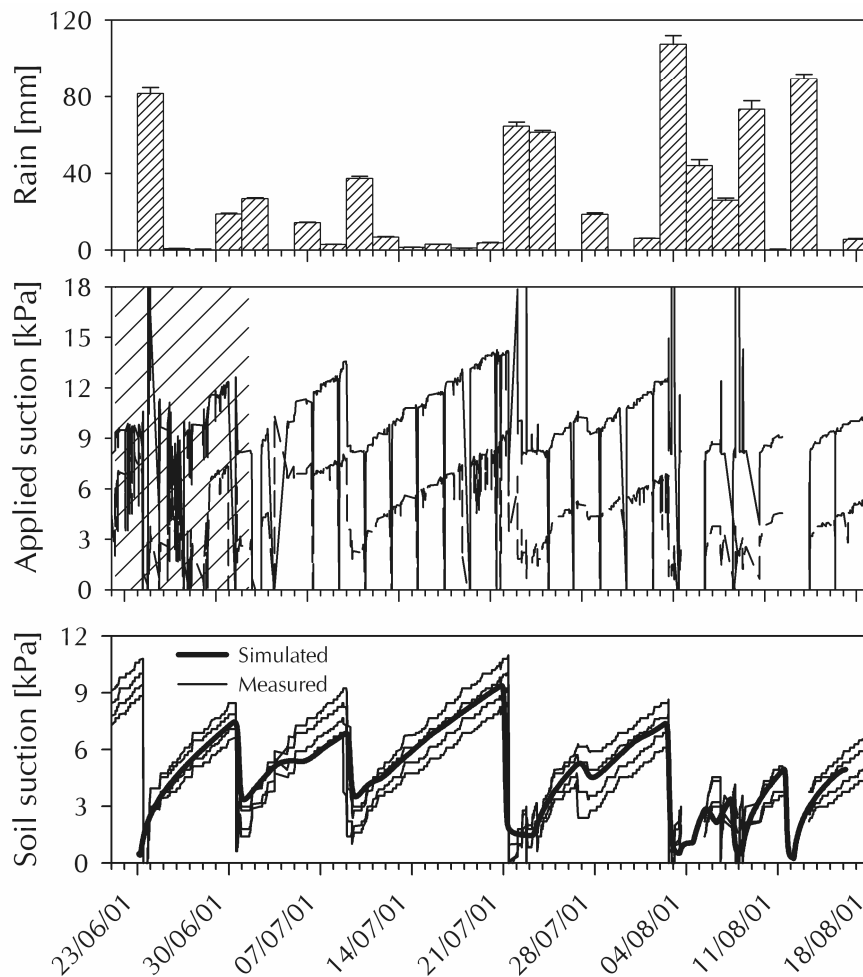
Figure 3.2: *Precipitation (Rain), vacuum (Ψ) applied to the two-chambered extraction system, and*
simulated and measured soil suction. The shaded area marks the period of pump parameter adjustment.
The regular breakdowns of the vacuum reflect the opening the system to exchange the cartridges and
water bottles. The pump failure on 03/07/02 was irrelevant for the soil solution sampling because
almost no water was percolating that day; all pump defects could be rectified on the subsequent
sampling event.

profile wall reduced evaporation through the edges, and a surface runoff collector was installed to prevent erosion of the profile wall. Ten rain collectors were evenly distributed across the sampling site to record amounts of rainfall on each sampling date.

After equilibration of the system, the plot was mown on 20/06/01, and grass residues were removed. A criss-cross grid of strings was tightened across the slope to mark paths for the manual application of pesticide. We equipped a back-pack sprayer with a reducing valve and slit nozzle to promote an even distribution of the pesticide spray. The feed rate of the sprayer was measured to compute the optimal walking speed for application. On 23/06/01, mixtures of commercially available formulations of the following insecticides (all of them commonly used in tropical fruit cultivation) were applied on to the soil surface in two passes (see **Table 3.2** for details):

Chlorpyriphos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate; water

Table 3.2: *Amounts of pesticides applied onto the soil surface, sorption coefficients (K_{OC}; literature data), and field dissipation half-life times (DT_{50}, literature data). Two spray cocktails (denoted C1 and C2 in column 'Amount applied', respectively) were mixed in the field from commercially available formulations and applied with a backpack sprayer in two passes. Each pass took approximately 3 hours*

Substance	Amount applied [g ha^{-1}]	K_{OC}[a] (ml g^{-1} OC)	Half-lives (DT$_{50}$) and references
Monocrotophos	1710 (C2)	1	1.2 days; Brazilian soil (field data, Laabs *et al.*, 2000)
Dimethoate	2860 (C1)	20	11–22 days; cotton crop soil, India (field data, Vig *et al.*, 2001)
Mevinphos	3000 (C1)	44	1 day; Californian foliar vegetable samples taken in June (field data, Spencer *et al.*, 1992)
Dicrotophos	3000 (C2)	75	3 days; sandy loam (laboratory data, Lee *et al.*, 1989)
Triazophos	3000 (C1)	332	10 days; cotton crop soil, India (field data, Vig *et al.*, 2001)
Malathion	3000 (C1)	1800	17 days; soil pH = 6.5 (tropical field conditions simulated in greenhouse, Getenga *et al.*, 2000)
Chlorpyrifos	2860 (C2)	6070	1.1 days; Brazilian soil (field data, Laabs *et al.*, 2000)
Endosulfan	2500 (C2)	12400	2.5 days; Brazilian soil (field data, Laabs *et al.*, 2000)
Cypermethrin	75 (C1)	100000	14 and 28 days; sandy loam and sandy clay, respectively (laboratory data, Roberts & Standen, 1977)

[a] data from Hornsby et al. (1996), except triazophos (Pesticide Safety Directorate (1993), page 19, value for sandy loam)

solubility: 2 mg litre^{-1}), cypermethrin ((RS)-α-cyano-3-phenoxybenzyl (1RS)-cis, $trans$-3-(2,2-dichlorophenyl)2-2-dimethyl-cyclopropanecarboxylate;   0.01   mg litre^{-1}), dicrotophos ((E)-2-dimethylcarbamoyl-1-methylvinyl dimethyl phosphate; completely miscible   with   water),   dimethoate   (O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate;   24 g litre^{-1}),   endosulfan-(α,β)   ((1,4,5,6,7,7-hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylene)   sulfit;   0,33   mg litre^{-1}),   malathion   (S-1,2-bis(ethoxycarbonyl)ethyl O,O-dimethyl   phosphorodithionate;   145   mg litre^{-1}), mevinphos   (2-methoxycarbonyl-1-methylvinyl   dimethyl   phosphate;   completely miscible   with   water),   monocrotophos   (dimethyl   (E)-1-methyl-2-(methylcarbamoyl)vinyl phosphate; 1 kg litre^{-1}), and triazophos (O,O-diethyl O-1-phenyl-1H-1,2,4-triazol-3-yl phosphorothioate; 39 mg litre^{-1}) (Tomlin, 2000). The application rate was 0.075 kg (active ingredient; a.i.) ha^{-1} for the synthetic pyrethroid cypermethrin and approximately 3 kg (a.i.) ha^{-1} for all other substances except monocrotophos, which was available only in a smaller amount on the day pesticides were purchased (**Table 3.2**). To reduce side effects, we treated a total area of approximately 6 m by 30 m (width by length) above the two adjacent sampling units.

Every other day during the eight weeks that followed the pesticide application the SPE cartridges and water collection bottles were collected and replaced. The bottles and cartridges were immediately put on ice and transported within 2 hours to the laboratory where they were frozen and kept at –18 °C until further processing.

3.3.3   Laboratory analyses

Pesticides were eluted from the cartridges with 2 ml of methanol and 6 ml of a 9:1 (by volume) mixture of dichloromethane and methanol (Di Corcia & Marchetti, 1991, modified). The effluent was collected in pear-shaped flasks. After addition of surrogate standards and approximately 150 µl of toluene as a keeper, methanol and dichloromethane were removed with a rotary evaporator. The residue was washed into a gas chromatograph (GC) vial with about 1 ml of toluene. Pesticides were quantified on a GC system with electron-impact mass spectrometer (GC/EI-MSD; HP 6890/5972). For details on the GC method and its performance, see Laabs et $al.$ (1999). Prior to the field experiment, recovery was studied in the laboratory. Pesticide recoveries amounted to > 90% for all substances, and no significant sorption on the suction plates was observed. Pesticide losses can be attributed to degradation or partially irreversible chemisorption on the Carbopack surface (Di Corcia & Marchetti, 1991), or to incomplete pesticide retention on the cartridge. As pesticides are far better preserved on Carbopack than in aqueous solution (Crescenzi et $al.$, 1995), losses in the extraction system should be small compared to conventional soil solution sampling in glass bottles.

3.3.4 Numerical modelling

To evaluate the sampling efficiency of the suction plates, we simulated the water flux with HYDRUS2D, a two-dimensional model based on Richard's equation for water and solvent transport (Simunek *et al.*, 1999). Soil water retention curves for each horizon were parameterized by Klaus Spohrer. The clay content ranged from 35 (topsoil) to 52% (subsoil), and saturated conductivities ranged from 8 (subsoil) to 20 (topsoil) cm day^{-1} (Spohrer, unpublished data). The horizons were parallel to the surface of the land (15° inclination), and hydraulic properties were the same in all directions (no anisotropies). The soil was 1.20 m deep with free drainage at the bottom. To avoid side effects and to allow the formation of interflow, we modelled approximately 10 m of slope, with the suction plates being positioned in the middle of it. Upslope, the vertical boundary condition was no flux, so that water could infiltrate only vertically or laterally downslope. At the vertical boundary downslope, we allowed free drainage, that means interflow, to occur. Precipitation amounts were introduced into the model as measured in the field (atmospheric boundary condition). To estimate realistic precipitation rates we assumed that it rained for 6 hours every late afternoon or evening. Potential evapotranspiration was estimated as 4 mm day^{-1}. The initial moisture conditions of the soil were adjusted by a warm-up phase. According to field observations of the real weather, this warm-up consisted of a 3-fold repetition of several rainstorms (saturation of the profile) that were followed by 4 days without precipitation. The simulation was evaluated by a comparison between the courses of modelled and measured suction of the soil.

3.3.5 Statistical analyses

A previous experiment by Quisenberry *et al*. (1994) had shown that flow pathways vary depending on the amount of water infiltrating the soil. That is why, before statistical analyses, the flux data were sorted by either the total amount of precipitation (Wald–Wolfowitz run test, cluster analyses, see below) or the amount of leachate (beta distribution, Simpson Index, see below) collected during the respective sampling interval. Afterwards, the sets of data for the two profiles were split at their medians, resulting in four subsets of leaching data. Cumulative amounts of leachate for individual plates within all four data subsets were calculated to obtain a first impression of the heterogeneity of the flow field. We elucidated the influence of the soil pit on the flow field by comparing the amounts of water delivered by suction plates in rows A and B (Wald–Wolfowitz Run tests; a non-parametric alternative to the *t*-test for independent samples; STATISTICA for Windows 6.0, StatSoft Inc., 2001). Cluster analyses (tree clustering, Euclidian distance, multiple linkage; STATISTICA for Windows 6.0) (StatSoft Inc., 2001) grouped the suction plates according to the amount of water they delivered. Prior to cluster analysis, the amount of leachate of every sampling day was

standardized. The standardized score was calculated as $(x - \bar{x})/\sigma$, where x is an observed value, and x and σ are the mean and standard deviation of the observations. This was done to avoid biasing the analyses on sampling days with large variances.

Exceptionally rapid leaching (> 40 mm within the two-day sampling intervals) caused an overflowing of the sampling bottles in the lower chamber. This happened once at Plot 1 (26/07/01) and three times at Plot 2 (26/07, 11/08, and 15/08/01). When overflow occurred, we measured its total amount and added equal proportions of it to the volume collected by those bottles that had overflowed. Because this estimated flux data might differ slightly from the true water distribution, the sampling intervals so affected were excluded from statistical analyses. For clarity, calculated data points are marked in figures presented below. The overflowing of bottles in the lower chamber of the extraction system had no influence on the pesticide flux data, because pesticides extraction was completed before the leachate entered the lower chamber (**Figure 3.1**).

We investigated the heterogeneity of the flow by the approach of Stagnitti *et al.* (1999). Flux data of all four subsets of data were sorted in descending order by leachate per plate. Afterwards, the fraction of efflux was plotted against the fraction of the total cross-sectional area, that means the surface area of all suction plates. Following Stagnitti *et al.,* we assumed that the underlying distribution was that of a standard beta function. The probability density of the function is given by

$$p(x; \alpha, \zeta) = \frac{\Gamma(\alpha + \zeta)}{\Gamma(a)\Gamma(\zeta)} x^{\alpha-1} (1-x)^{\zeta-1}$$
$$\text{for } \alpha \geq 0, \zeta \geq 0, 0 \leq x \leq 1;$$

(2.1a)

where Γ is the Gamma function, and its corresponding cumulative density function is the integral:

$$c(x; \alpha, \zeta) = \int_0^x p(t; \alpha, \zeta)\mathrm{d}t$$
$$\text{for } 0 \leq x \leq 1$$

(2.1b)

The function has two free parameters, α and ζ. We obtained estimates for these by fitting the theoretical cumulative distribution function iteratively by non-linear least squares approximation using Microsoft© Excel.

When infiltration is homogeneous, both α and ζ equal 1, and the cdf can be drawn as a straight line with a slope of 1. The more heterogeneous the flow is, the more bent the curve will be. Zones of the curve with slopes > 1 refer to convergent (preferential) flow, whereas ones with slopes < 1 indicate divergent flow. Stagnitti *et al.* (1999) defined the

ratio of the standard deviation (σ) to mean (μ) as measure of dispersion between populations. Scaled to 1 when $\alpha = \zeta = 1$, they defined the heterogeneity index HI,

$$\mathrm{HI}(\alpha, \zeta) = \sqrt{3}\,\frac{\sigma}{\mu} = \sqrt{\frac{3\zeta}{\alpha(\alpha + \zeta + 1)}}\ , \tag{2.2}$$

as a measure of non-uniformity of the distribution, and this allows direct comparison of sets of data. As an independent second measure of diversity, we calculated Simpson Indices (SI) to describe the flow field heterogeneity on the base of the samples obtained once in two days (Simpson, 1949, modified):

$$\mathrm{SI} = \sum_{i=1}^{S} q_i^{\,2}\ , \tag{2.3}$$

where $q_i = n_i/N$. This method is commonly used in biology to describe the diversity of a population, where n_i is the number of the ith species, of which there are S, and N is the total number of individuals observed. We adapted this approach to our needs by considering n_i to be the amount of water delivered by an individual plate, i, and N the total amount of leachate.

3.4   Results and discussion

3.4.1   Numerical modelling

The simulated suction of the soil closely matched the measured one. However, some actual rain intensities might have been estimated wrongly because cumulative precipitation data were recorded only once every two days and then divided into two even parts. Consequently, in a few instances the modelled suction decreased less than observed in the field (e.g. 09–10/07/01; **Figure 3.2**), indicating an underestimation of the real precipitation rate. The course of cumulative leaching simulated with HYDRUS2D accorded with measured fluxes (**Figure 3.3**), but the total amounts sampled in the field were less than predicted by the model, especially in Plot 1. Sensitivity analyses revealed the importance of accurately setting up the collection devices. If the average suction applied to the sampling device is 0.5 kPa too small then the volume of leachate collected with suction plates is ca. 50% less than at ambient soil suction. In Plot 2, there was no spatial trend in the matric suctions obtained by the four tensiometers. Moreover, they seemed to be randomly scattered around the mean value, indicating rather homogenous soil properties within this profile. In Plot 1, however, the suctions systematically decreased with increasing distance from the suction plates (that means the further away from the suction plates, the wetter the soil). Because the vacuum applied to the suction plates was calculated as median of the four tensiometers, suction at Plot 1 probably was too small and thus insufficient to sample percolating soil
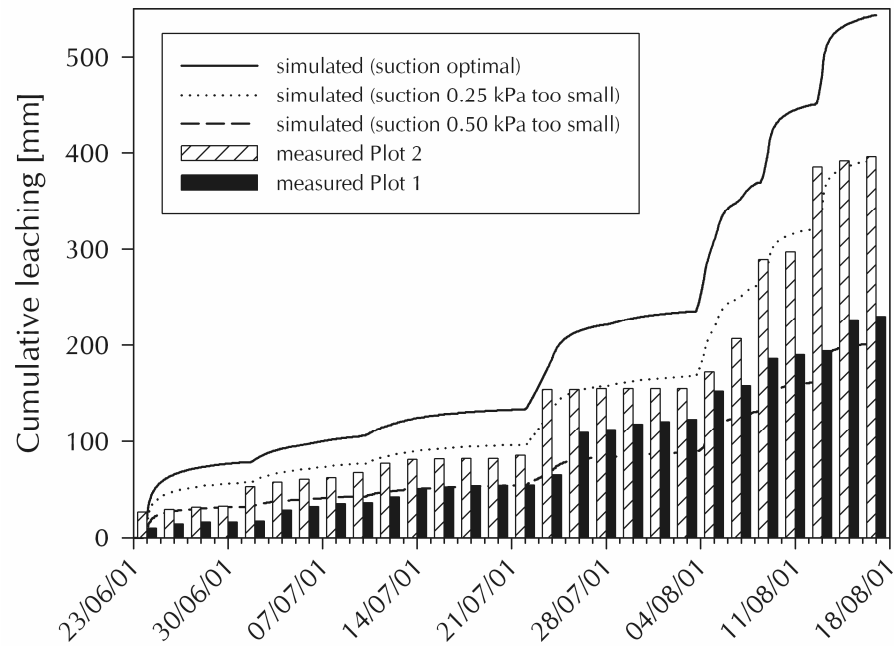
Figure 3.3: *Cumulative water flux through the B1–B2 horizon. The simulated values show the influence of pump adjustment on efficiency of collection as determined by sensitivity analyses.*

water completely. As a result, only 35 % of precipitation was collected by the lysimeters at the B1–B2 horizon transition on Plot 1 and 57 % on Plot 2, although the model predicted that of 73 % of the rainfall should have entered the suction plates. According to our simulation, lateral flux was almost negligible and did not contribute significantly to the water amounts collected by the suction plates.

3.4.2   Soil water collection

The vacuum applied to the suction plates (upper chamber) remained close to the matric suction during the experiment, although the lower chamber was kept at ca. 5 kPa greater suction (**Figure 3.2**). Thus, the SPE cartridge at the interface between upper and lower chambers of the vacuum box was sufficiently air-tight to maintain the pressure difference between the two compartments, but it remained permeable enough for the soil solution to pass. Unfortunately, no heavy rain occurred during the equilibration phase of the system. Thus, when we applied the pesticides, we thought it unnecessary to increase the suction of the lower chamber when the soil was nearly saturated (see Materials and methods). Hence, with an 80 mm rainstorm immediately after the application of pesticides on 23 June, some of the cartridges overflowed. As a result, water and pesticide fluxes were underestimated (see predicted leaching, **Figure 3.2**). By 28/06/01, the appropriate settings had been adjusted. Surface runoff during the storm on 23/06/01 amounted to 0.08 and 0.23 litre m^{-1} length of the

surface runoff gutter (Plot 1 and 2, respectively). During two further sampling intervals, small amounts of surface runoff were collected (22–24/07/01, 03–05/08/01; exclusively on Plot 2).

3.4.3 Water flow pattern

After minor rain events (cumulative precipitation within the sampling interval < median), a large proportion of the total leachate was collected by few suction plates only, whereas more suction plates poured water after heavier rain (**Figure 3.4**). In both profiles, the suction plates farther away from the pit (row B in **Figure 3.4**) delivered significantly more water after light rain than the front plates (row A in **Figure 3.4**). It is possible that small amounts of laterally flowing water arrived in row B, which was slightly higher up the slope than row A. However, no differences in water collection
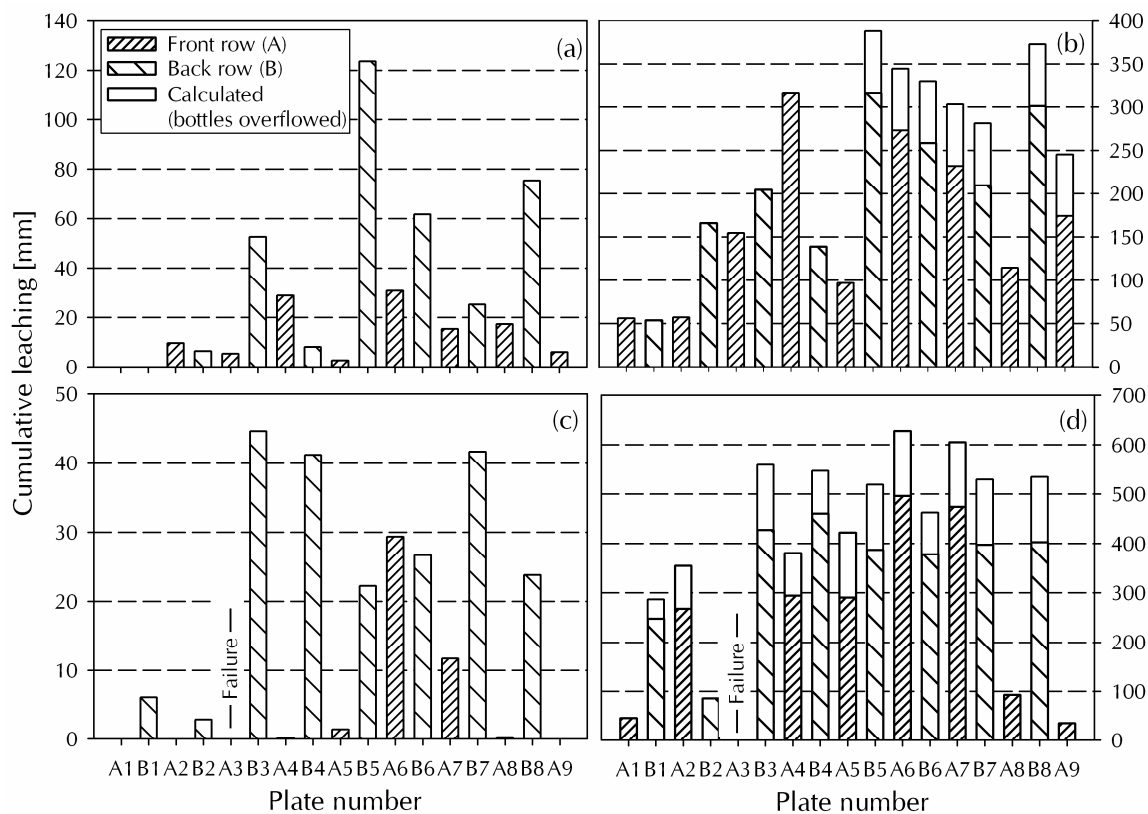
Figure 3.4: Small-scale variation of water fluxes in Plot 1 (a, b) and Plot 2 (c, d). The bars represent cumulative leaching after all rain events with less (a, c) or more (b, d) than median precipitation (note the different scales on the ordinates). The suction plates were arranged in a zigzag pattern; row A was closer to the soil pit than row B (see Figure 3.1). Suction plate A3 in Plot 2 broke during the equilibration of the system and was not replaced to avoid disturbance of the soil profile. As certain sampling bottles overflowed on one sampling event on Plot 1 and three times on Plot 2, the amounts of water collected on those occasions had to be estimated by division the total amount of overflow by the number of bottles that had overflowed. These calculated fluxes are marked as white sections of the bars in (b, d).

between row A and B were observed after heavy rain (p=0.05; Wald–Wolfowitz runs test). Cluster analyses were done for the four data subsets described above in order to group suction plates according to the amount of water they delivered and to show how much these groups vary in relation to precipitation (**Figure 3.5**). All four analyses led to two major clusters of suction plates that contributed either little or much to the total amount of percolate. Only suction plate B5 in Plot 1 (precipitation < median; **Figure 3.5a**) did not fit into these groups and was classified as a suction plate that poured an exceptionally large amount of water even when little rain fell.

The clusters obtained for the two cases (precipitation less than and precipitation > median) were almost identical. In Plot 2, each suction plate remained in its cluster
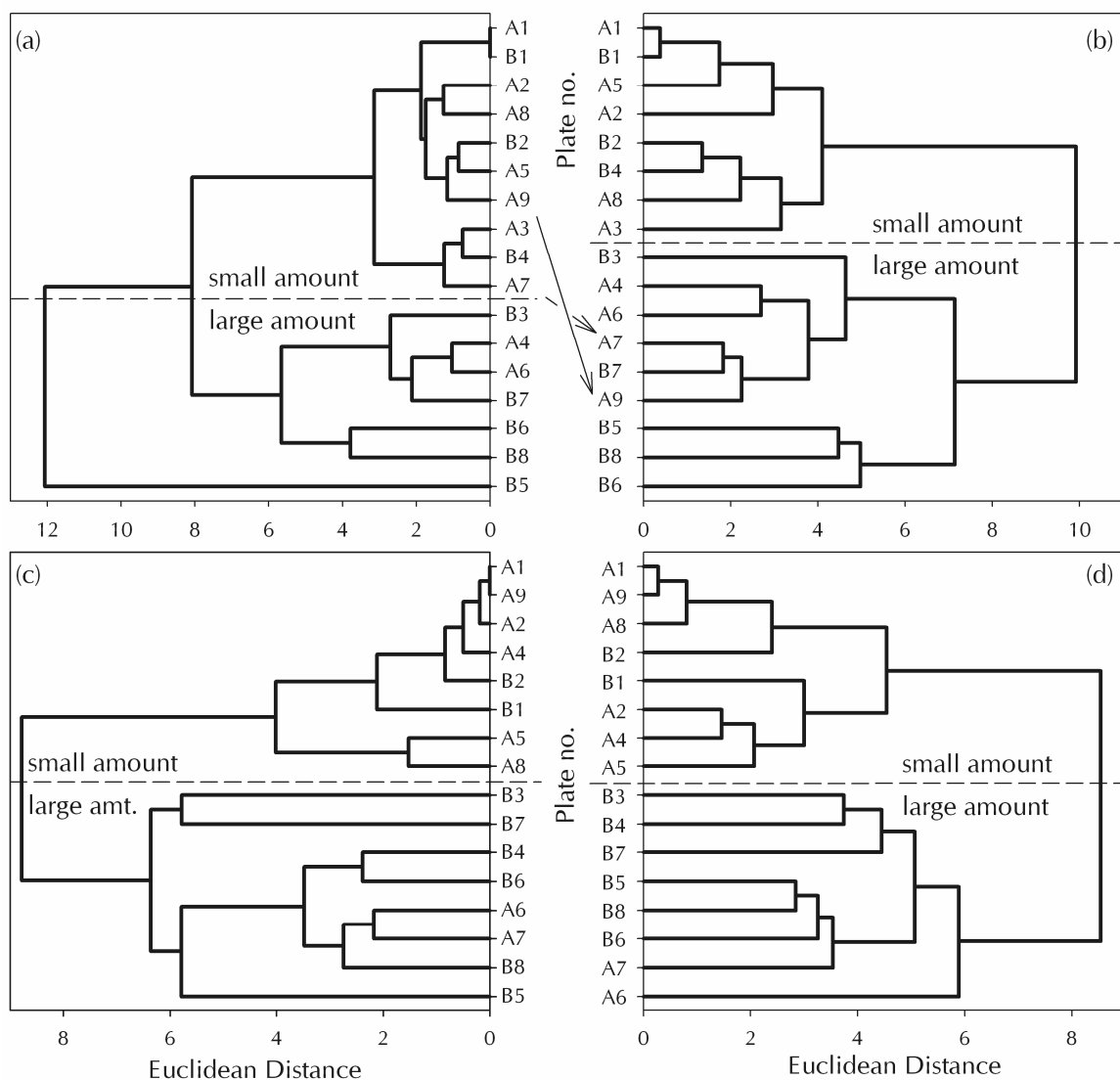
Figure 3.5: *Visualization of cluster analyses for Plots 1 (a, b) and Plot 2 (c, d) to identify groups of suction plates that pour similar amounts of water. For (a) and (c) all sampling events with less than median precipitation were analysed, for (b) and (d) all events exceeding median precipitation. The arrows mark suction plates that switched from the small amount to the large amount group depending on the amount of precipitation (plates number A7 and A9 on Plot 1).*

(small and large volumes of percolate, respectively), independent of the total amount of leachate. Only two of the suction plates from the front row of Plot 1 (A7 and A9; **Figure 3.5a** and **b**) were assigned to the large amount of leachate cluster (rapid percolation) instead of the small amount cluster (slow percolation), which is an indication that the relative contribution of individual suction plates to the total amount of leachate is not triggered by the amount of precipitation. Cluster analyses showed nearly identical results when the data were split at median water flux instead of median precipitation.

We conclude from these analyses that flow patterns in the soils under study are highly stable and rarely influenced by the amount of precipitation or infiltrating water. Similar conclusions have been reported for soils in which biopores remained for several decades (reviewed by Beven & Germann, 1982). However, biopores are rare in our soil, which means that the flow pattern must have been induced by stable local heterogeneities. Reichenberger *et al.* (2002) reported that fingering dominated the preferential flow paths in Brazilian Oxisols. A gravity-driven fingering may also explain the stability of the flow pattern for the soils we studied. Once instabilities of the wetting front have caused fingering infiltration, these flow pathways can persist across a wide range of matric potentials as a result of altered initial moisture contents, and thus hydraulic conductivities, in the soil when the next rain falls (Glass *et al.*, 1989). Ritsema *et al.* (1998) added that the leaching of hydrophobic substances from these fingered pathways into adjacent regions increases their wettability compared with the surrounding soil. As hydrophobicity can be caused by residues and exudates (e.g. waxes) from all kind of plants and soil microbes (Franco *et al.*, 2000) under all kinds of weather (Jaramillo *et al.*, 2000) this amplification of finger stability is also likely to occur at our sampling site.

3.4.4   Characteristics of water flux variation

To test the hypothesis that the diversity of the flow pattern is related to the amount of leachate, we computed heterogeneity indices (HI, Stagnitti *et al.*, 1999) for cumulative water efflux for the four subsets of data (data split at median percolation). The HI was larger at small effluxes than at large ones in both P1 and P2. Thus, slow flux seems to reduce homogeneity and increase fingering. However, the differences in HI for the individual subsets were small, thereby demonstrating that substantially different values for the fitting parameters α and ζ may result in similar HI (**Table 3.3**). In **Figure 3.6**, the number of suction plates involved in sampling (fraction of area, abcissa) increases with an increasing proportion of the total flux (fraction of flux, ordinate). If the flow field was homogeneous, both parameters would be connected by a cdf of the beta distribution with $\alpha = \zeta = 1$ (straight line; slope = 1).

The curvature of the cdf for small effluxes (open symbols; **Figure 3.6**) deviates more from this line than the cdf for large effluxes (closed symbols; **Figure 3.6**). Thus, smaller amounts of percolate induced greater heterogeneity in the flow field, that is, more fingering. In **Figure 3.6**, each area where the slope of the fitted cdf exceeds unity is dominated by preferential flow. This allows us to estimate both the proportion of water flowing along preferential flow paths and the proportion of cross-sectional area contributing to preferential flow by calculating the axis intercepts at the point where the density function (= derivation of the cdf) equals 1 (de Rooij & Stagnitti, 2000). When there was little efflux around 38% of the cross-sectional area delivered 83% of water, whereas when the efflux was large 49% of the area contributed to 76% of water on preferential pathways (mean of data in **Table 3.3**).

The differences in shape of the distributions between the two graphs in **Figure 3.6** were negligible for small and large fluxes, although the fraction of rain that passed our observation level at 55 cm was different in the two profiles as a result of the somewhat incorrect suction in Plot 1 (discussed above). Thus, this error did not qualitatively alter the flux data. Because the variation in flux was nearly identical in the two plots, we consider that these plots are characteristic for the soil we investigated, and we conclude that the interrelationship between the amount of seepage water and the flow field diversity is one of the indigenous properties of the soil.
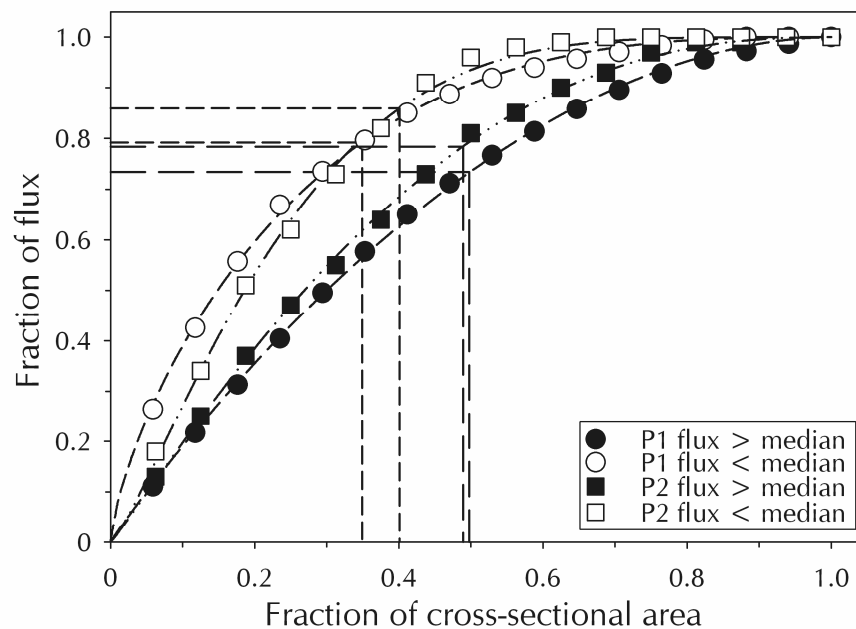
Figure 3.6: *Flow field heterogeneity of Plots 1 and 2 (P1, P2) as indicated from the fitting of the cumulative beta density distributions to relative fluxes (cumulative data for percolation events above and below median) against relative cross-sectional areas of the sampling device. The point where the slope of the fit equals one is marked for every curve with dashed horizontal and vertical lines and indicates where preferential flow switches to divergent flow.*

Table 3.3: Parameters α and ζ of the cumulative beta density distributions fitted to a plot of relative flux (cumulative data for percolation events exceeding and less than median) and relative cross-sectional area of the sampling device (P1, 2 = Plots 1 and 2, respectively)

Data Subset	α	ζ	HI	Contribution to preferential flow[a]	
				Area	Flux
P1; Flux > Median	0.966	1.866	1.230	0.50	0.73
P1; Flux < Median	0.732	2.844	1.596	0.35	0.79
P2; Flux > Median	1.077	2.415	1.224	0.49	0.78
P2; Flux < Median	1.275	4.539	1.252	0.40	0.86

HI: Heterogeneity Index, see equation (2.2). For HI > 1, the significance of fingering increases with increasing HI.

[a] Expressed relative to total cross-sectional area and total leaching amount, respectively. Coordinates of those points of the individually fitted cumulative beta distributions in **Figure 3.6** where the slope = 1, calculated from the associated density distributions.

The approach of Stagnitti *et al.* (1999) is not suitable to characterize flux heterogeneity on any occasion when no water is released from certain suction lysimeters. The fits of the cdf to the data worsen if the total efflux is reached before the total cross-sectional area equals 1. Reducing the cross-sectional area by the surface area of those plates that do not deliver water does not solve this problem, as it pretends that the flow field is less heterogeneous than actually was observed. One can solve this problem by using the Simpson Index (SI), which is a probability measure to predict the relative contribution of individual species (here: suction plates) to the total population (here: amount of leachate). Hence, for the SI, it is a meaningful piece of information if a plate does not pour water, and not a problem, as discussed for the fit of the cdf. To compute the SI, no assumptions about the distribution of the species abundance curve are necessary (Simpson, 1949). Thus, the calculation of SI is possible with our data without any restrictions.

Simpson indices were calculated for every sampling date and correlated with average water volumes per suction plate and sampling date (=two-day intervals; **Figure 3.7**). Average amounts of seepage water varied by four orders of magnitude, ranging from approximately 0.1 to 100 mm per sampling date, whereas the SI ranged from 0.067 to 0.53, only. Generally, smaller amounts of total leachate collected coincided with larger SIs or more diverse flow patterns. We fitted two simple regression lines to the logarithms of water volume, again splitting the data from the events into to two groups the median. The difference in flow characteristics between Plot 1 and Plot 2 was insignificant (**Figure 3.6**), so we pooled the data from the two to increase the sample size. The slope of the regression was fairly steep after rain events that induced average water fluxes of less than 4 mm within two days (–0.088 log(water flux); R^2=0.80;
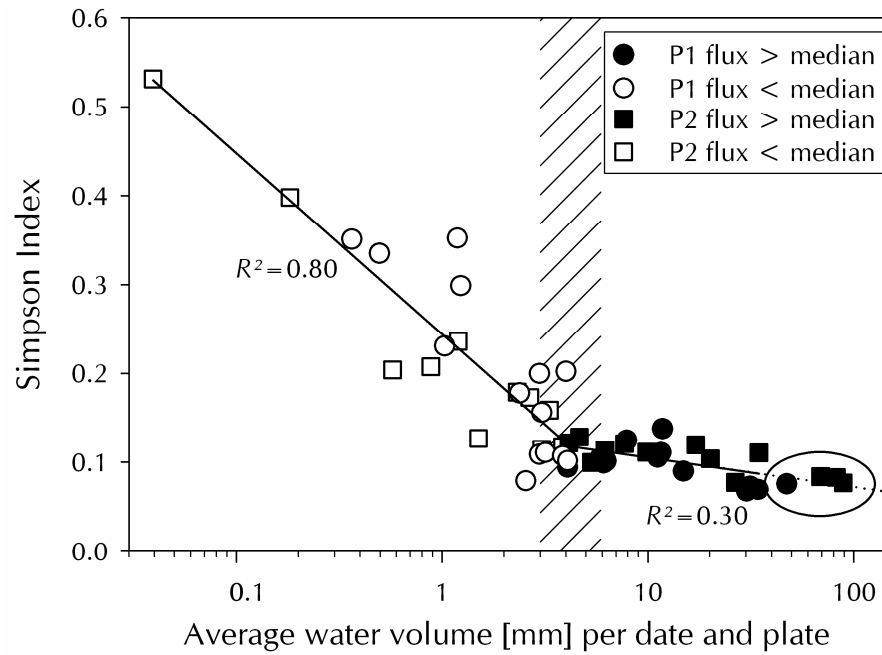
Figure 3.7: *Graph of Simpson Index against the logarithm of water flux of individual sampling events (P1, P2 = Plots 1 and 2, respectively). Large Simpson Indices represent a heterogeneous flow field. The shaded area marks the switching from (homogeneous) matric flux to (heterogeneous) preferential flow. The data points in the ellipse represent the four cases at which sampling bottles overflowed (corrected data; excluded from regression).*

Figure 3.7). Then, as the amount of water decreased, the number of flow pathways that contributed to solute leaching also decreased. We could not tell whether soil solution samples collected on days with little percolation originated from recent precipitation or if it was a plume of an earlier rainfall event. At large average percolation, the slope of the regression curve was only –0.015 log(water flux) and R^2 decreased to 0.30, again confirming that increasing flux significantly reduces the heterogeneity of the flow pattern. Preferential flow was indirectly proportional to the amount of water flowing through the soil. We conclude that there is a critical limit of 2 mm per day: fingering through preferred flow pathways becomes the dominating transport mechanism when the seepage flux is less than this threshold. If leaching is further reduced one flow pathway after another dries and is switched off (see Hillel & Baker, 1988). Percolation rates exceeding 2 mm per day promote matric flow and homogenize the flow pattern. Nevertheless, preferential flow still takes place when percolation is rapid, as indicated by the HI > 1 and by the hardly altered cluster analyses of the flow pattern at large or small amounts of seepage flux as discussed above.

3.4.5   Relevance for pesticide transport

The 80 mm of rain that fell immediately after the application of pesticides (**Figure 3.2**) moved small fractions of all the pesticides (0.001 to 2 % of the amount applied) to a depth of at least 55 cm in one night, i.e. in a single flush. These fractions represented 75 to 100 % of the total amounts translocated, although the sorption coefficients vary by six orders of magnitude. **Figure 3.8** shows both the fractions moved in the first flush (as black discs) and the totals moved (as open circles); evidently there is little difference between them for any compound. From this we can infer that the *relative translocation* of the pesticides in the first flush is independent of sorption coefficients. This fact reflects that preferential flow dominated the pesticide displacement in our soil, as also reported for tropical Oxisols (Laabs *et al.*, 2002a). Nevertheless, a chromatographic effect during leaching was observed: the *total recoveries* of all pesticides we studied except cypermethrin (discussed below) were negatively correlated with their adsorption coefficients ($r = -0.86$; **Figure 3.8**), as described by Elliott *et al.* (2000). Obviously, the time from pesticide application to the beginning of the rainstorm was long enough to allow sorption of part of the pesticides. This sorption was promoted by the fact that the pesticides were applied with only a small amount of water (equivalent to ca 0.1 mm rain), which probably evaporated rapidly after application and left the active ingredients directly on the soil surface. Thus, when preferential flow set in, only small fractions
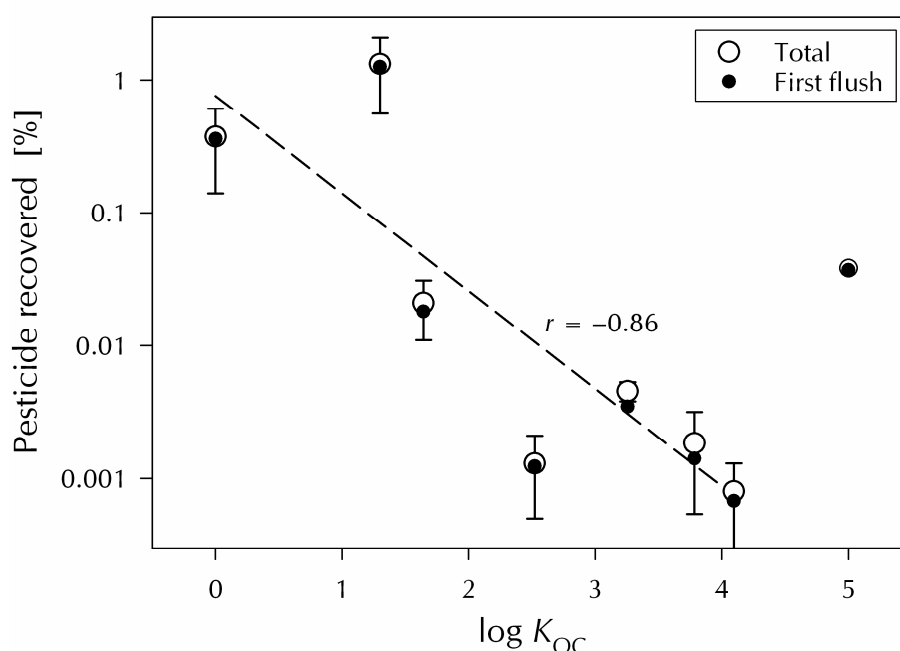
Figure 3.8: Pesticide recoveries in soil solution extracted from two plots at 55 cm depth in relation to the respective sorption coefficients (means and standard errors of Plots 1 and 2 against K_{OC} from Hornsby et al., 1996). The total recoveries are shown by open circles, the recoveries in the first flush by black discs. Cypermethrin (log K_{OC} = 5) was found in samples only from Plot 2 and excluded from the dashed regression line (see text for discussion).

corresponding to the K_{OC} values (= soil–solution partitioning coefficient K; standardized to the content of organic carbon, OC, of the soil) of the pesticides were still available for displacement. An additional explanation for the chromatographic separation of pesticides during the translocation might be sorption to the walls of the preferential flow pathways.

Only two of the pesticides were found in the soil solution for longer than 10 days. Dimethoate was detectable for about 1 month and endosulfan was detectable in individual samples throughout the entire experiment. The highly polar substances (dicrotophos, monocrotophos, and mevinphos) dissipated rapidly. Much longer half-lives have been reported for less polar pesticides (**Table 3.2**). These hydrophobic pesticides, however, sorb strongly to the soil and should not be detected in the percolate. Hence, the recovery of chlorpyrifos in soil solution was not consistent with the results of previous experiments (Armbrust, 2001). Cypermethrin also was reported to be immobile in soil (Kaufman *et al.*, 1981). This is also true for other synthetic pyrethroids such as deltamethrin and λ-cyhalothrin, as they are barely soluble in water (Laabs *et al.*, 2000). However, we clearly identified the unique triple-peak of cypermethrin in several chromatograms of samples from Plot 2. The cypermethrin concentrations found in the soil solution did not exceed its maximum solubility (ca. 1 μg l^{-1} against 10 μg l^{-1}; Tomlin, 2000). Nevertheless, we do not believe that solute transport alone can explain the movement of cypermethrin in our experiment, because of its large sorption coefficient (**Table 3.2**), especially since other more polar and more persistent compounds such as chlorpyrifos, endosulfan, and malathion were leached in smaller proportions. The commercial formulation of cypermethrin we applied probably contained chemical solubilizers that might have hindered immobilization during the short time between pesticide application and the beginning of the rainstorm. Another explanation for the exceptionally large displacement of cypermethrin might be colloidal transport mediated by indigenous dissolved organic matter or particle-bound transport (Magee *et al.*, 1991; de Jonge *et al.*, 1998). All these mechanisms suggest an enhancement of transport specific to pyrethroids, which warrants further attention if detected again. As we cannot explain sufficiently the leaching of cypermethrin we excluded the compound from the regression of pesticide recovered on log K_{OC}. **Figure 3.8** shows the regression line, with the excluded cypermethrin in the extreme right of the graph.

The differences between the seepage flux observed in the field and the flux predicted by the simulation of matric flux could be explained by small differences between the soil tension and the vacuum applied to the extraction system. We therefore conclude that preferential flow contributes little to the total water flux in the soil. However, preferential flow was important for pesticide displacement in the first rainstorm after

pesticide application, as substances which are generally considered to be immobile in soil were detected in soil solution extracted at the B1–B2 horizon transition at 55 cm.

3.5 Conclusions

Two findings were constant throughout the course of our experiment; (i) fingering flow pathways were stable, and (ii) flow-field diversity patterns for the two plots were nearly identical at both large and small average fluxes. We conclude that the flow pattern is an indigenous soil property that can be measured in a reproducible way by the sampling device we developed and the statistics we applied. The amount of water percolating through the soil was the variable that controlled the proportion of water transported by fingering along preferential flow pathways. Fingering always occurred at our study site, but was less pronounced after heavy rain than after light rain. The reason for this pattern was the increasing importance of homogeneous matrix transport with increasing amount of leaching. Preferential flow was sufficient to translocate all the insecticides into the soil to a depth of 55 cm overnight. However, these results might be limited by the fact that we made only a single, short-term field experiment which included an extreme rainstorm. Thus, further experiments under different weather conditions should be done to investigate the range of pesticide dissipation rates and the relationship between water and pesticide fluxes.

Both field equipment and statistical approaches turned out to be suitable for describing the small-scale variation of flow patterns. The combination of water sampling with on-line pesticide extraction improved sampling efficiency. However, the whole range of expected precipitation rates should be tested to optimize pump parameters. One might apply these techniques to other soils and thereby obtain an improved understanding of flow field variability.

4 Insecticide dissipation after repeated field application to a Northern Thailand Acrisol

4.1 Summary

Side-effects of pesticide application are promoted by high persistence of the active ingredients. We determined the half-lives of 6 insecticides commonly used in Thai fruit orchards under tropical field conditions. A mixture of endosulfan-α and -β, chlorpyrifos, malathion, dimethoate, and mevinphos was applied five times in ten-day intervals onto an Acrisol (lychee plantation ground-covered with grass vegetation, Chiang Mai Province, NW Thailand). On days 1,3,5,7, and 10 after each application, composite samples of the topsoil (0-10 cm) were collected and exhaustively extracted. Fitting a first-order model to the datasets revealed rapid initial dissipation (half-lives 2.2±0.4 (malathion) – 5.4±1.3 d (chlorpyrifos)). Volatilization appeared to be a major process of pesticide dissipation, especially for malathion and mevinphos. Because 8% of the applied endosulfan-α and -β had been converted to the sulfate metabolite within one day after the first application, also microbial degradation contributed significantly to pesticide dissipation. Nevertheless, no trend in half-lives over the five application cycles could be observed, which means that microbes apparently did not adapt to pesticide degradation within the experimental period. Precipitation and soil moisture were key parameters of dissipation, but dissipation processes were too manifold to be generalized for all substances studied. Despite their short half-lives, all pesticides except mevinphos accumulated in soil, (up to 656 %; endosulfan-α), and this accumulation correlated significantly with the hydrophobicity of the substances ($r = 0.88$). We interpret this as an aging process and conclude that pesticide aging must be considered relevant also in tropical environments, where it has received very limited attention so far.

4.2 Introduction

In modern farming, agrochemicals are inevitable for the enhancement of agricultural productivity and to fight pest insects (Ecobichon, 2000). This is also true for Thailand, where the cultivation of cash crops is advanced and agricultural products are the most important export goods (Taylor, 1996). Besides their benefits, however, pesticides may also have undesirable side-effects, such as intoxication of humans and adverse effects on quality and diversity of ecosystems (Racke, 2003b). Numerous studies have shown that pesticides can accumulate in soil (Miglioranza *et al.*, 2003), leach through the soil and threaten the ground water (Troiano *et al.*, 2001; Laabs *et al.*, 2002a), and disperse in the environment due to spray drift, surface runoff and volatilization (Steinheimer *et al.*, 2000). Because of the high application rates common in Thai agriculture, pesticide

residues have been detected widely in soils, surface and ground waters, agricultural products, and even in the breast milk of female farmers (Baun *et al.*, 1998; Thapinta & Hudak, 2000; Stuetz *et al.*, 2001). In these studies, organochlorine and organophosphorous pesticides prevailed.

To assess the hazard of ground- and surface-water contamination by a certain pesticide, its persistence and mobility in soil have to be determined (Gupta & Gajbhiye, 2002; Fernandes *et al.*, 2003). These factors are not only influenced by intrinsic physicochemical properties of the pesticide (e.g. octanol-water partitioning-coefficients, Berger *et al.*, 2002; Wauchope *et al.*, 2002), but also by biotic and abiotic degradation, microbial biomass, pH-value and organic carbon content of the soil as well as concentration of the substance itself (e.g. Racke *et al.*, 1996; Rice *et al.*, 2002). Two of the most crucial controls of pesticide dissipation are soil moisture and temperature (Garcia-Valcarcel & Tadeo, 1999). Laboratory studies generally do not adequately represent the specific field situation, for example variable weather conditions, leaching, distinct preferential flow, UV oxidation and volatilization (Beulke *et al.*, 2000). Consequently, Zabik *et al.* (2001) reported higher dissipation rates of pesticides in field than in laboratory studies. To determine realistic effective dissipation rates of pesticides, field studies are therefore necessary (Ismail & Kalithasan, 2003). However, also field studies cannot be transferred from one region to another, especially if differences in climate or pedogenic conditions are as substantial as they are between temperate regions and the tropics. Nevertheless, pesticide fate in the tropics has rarely been studied (reviewed by Racke, 2003b); the vast majority of studies on the environmental behaviour of pesticides focuses exclusively on temperate regions (e.g. Malone *et al.*, 2000; Bedos *et al.*, 2002; Chen *et al.*, 2003). Generally, field dissipation half-lives of pesticides in the semi-arid and semi-humid tropics are shorter than in temperate regions ($t_{1/2} < 15$ d) (Laabs *et al.*, 2000), because the higher temperatures promote degradation and volatilization of pesticides (Laabs *et al.*, 2002c). Data on pesticide dissipation in the humid tropics are almost completely lacking, but dissipation may be, due to better moisture supply, even faster than in dryer tropical environments (comp. Hultgren *et al.*, 2002). However, fast dissipation reduces the efficacy of pesticide treatments, so that greater total amounts or higher spraying frequencies than in temperate regions are needed.

Microbial degradation is a major pathway of pesticide dissipation (e.g. Shelton *et al.*, 1995; Ragnarsdottir, 2000). It is often enhanced after repeated applications (Vig *et al.*, 2001; Ismail & Kalithasan, 2003), because repeated applications may stimulate the growth of microbial populations adapted to the breakdown of specific pesticides (Wada *et al.*, 1989). Yet, if pesticide applications are repeated so frequently that they result in soil concentrations high enough to have direct toxic effects on the microbial community, half-lives may remain unaffected or even increase (Singh *et al.*, 2002; de

Andrea *et al.*, 2003). To our knowledge, it has never been studied how multiple consecutive applications of insecticides affect pesticide dissipation in the soils of tropical orchards, although, in these systems, repeated treatments are common practice during fruit maturing.

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

4.3   Materials and methods

4.3.1   Study area

We conducted our experiment on a lychee orchard in Northern Thailand (18°53' N, 98°52' E). The climate of this region is monsoonal with pronounced dry (November to April) and wet (May to October) seasons. Mean annual precipitation and temperature are 1600 mm and 21.6°C, respectively. The elevation of the research site is 800 m above sea level; overall inclination of the westerly exposed slope is about 15°. Due to former rice cultivation about 30 years ago the surface still was terraced with alternating steep and more even sections ("microslopes" and "microplains"). Lychee trees with an average height of 2.5 metres were planted around 10 years ago in a grid of ca. 10 by 10 metres. The ground was covered with grass vegetation, which was mown biweekly during the experiment. The soil, which developed on strongly weathered Triassic granites (Rhodes *et al.*, 2000), was classified as Haplic Acrisol in FAO classification. A more detailed characterisation of the soil was given in Chapter 3, (**Table 3.1**, page 19).

4.3.2   Set-up of research site

On the orchard, a 6 by 30 meter large area was marked as research site. Soil matric potential was determined both in microplains and microslopes (see above). Therefore, we installed 3 tensiometers each in 10 and 45 cm soil depth (12 tensiometers in total) along one of the 30 m long borders of the research plot (**Figure 4.1**). To monitor the volumetric water content of the topsoil (0–10 cm), we assigned TDR (Time Domain Reflectrometry) measuring points adjacent to the tensiometers (ThetaProbe ML2x, Delta T Devices, Burwell). Additionally, we installed 6 rain collectors (2.5 L-bottles of amber glass with a glass funnel (⌀ 14.5 cm) on top). Each funnel was equipped with a stainless steal mesh to prevent particles from entering the collectors. All instruments were installed adjacent to the area that was to be treated with pesticides, but not on the

treated area itself. This was done to avoid contamination of the instruments by pesticides as well as disturbance of the plot upon reading of the instruments. After this instrumentation, we set up a grid of colored bamboo stacks around the application area to allow orientation during application of pesticides and during soil sampling (**Figure 4.1**).
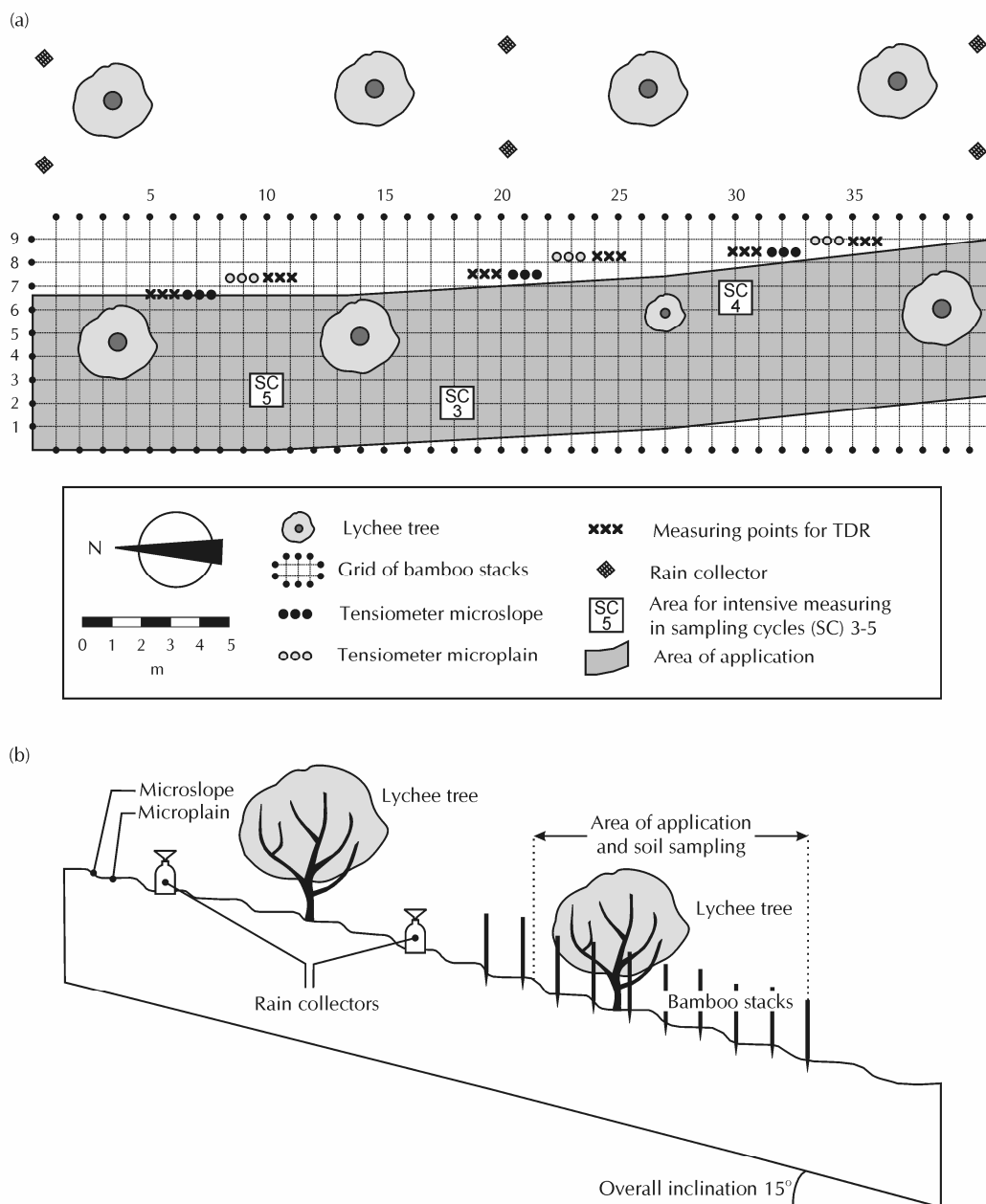
Figure 4.1: Layout (a) top view (drawn to scale) and (b) cross section (sketch) of sloping plot established in a northern Thailand lychee orchard to determine field half-lives of pesticides repeatedly applied to the soil.

4.3.3 Pesticide application and sampling strategy

On 19 June 2002 we used a backpack sprayer to apply six insecticides in one combined "spraying cocktail" of commercially available formulations directly onto the soil surface (**Table 4.1**). This is not according to farmers' practice, as they spray into the crowns of the trees. However, their spraying equipment is simple, so that pesticides are lost in the form of overspray and spray drift. Because these losses precipitate onto the soil, our treatment can nevertheless be considered to be rather representative for lychee cropping. The direct ground application allowed us to spread the pesticides in a reproducible way, especially as straight walking paths for the spraying person had been marked with bamboo stacks (see above). Before spraying, we determined the feed rate of the sprayer and calculated the walking speed needed to achieve the desired rate of application. To evaluate the amount of pesticides actually reaching the soil (that means applied amount less spray drift) and to control the homogeneity of the application, we put six glass-fibre filters (GF 6, Ø = 6 cm, Schleicher and Schuell Microscience, Dassel) randomly onto the grass vegetation before each application. Immediately after application, the filters were wrapped into aluminium foil, placed on ice and brought to the laboratory. There, they were stored at –18°C until they were transported frozen to Germany for further processing.

Table 4.1: IUPAC-names and relevant physicochemical properties of insecticides (Water sol. = water solubility; V.p. = vapour pressure; Tomlin, 2000) that were repeatedly applied to a northern Thai lychee orchard in one combined spraying "cocktail"

Substance	Water sol. [mg l^{-1}]	log K$_{ow}$	V.p. [mPa]
Endosulfan-α ((3α,5aβ,6α,9α,9aβ)- 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide)		4.74	
	0.33		0.83 (20°C)
Endosulfan-β ((3α,5aα,6β,9β,9aα)- 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide)		4.79	
Chlorpyrifos (O,O-diethyl (O-3,5,6-trichloro-2-pyridinyl) phosphorothioate)	2	4.70	2.7 (25°C)
Malathion (S-1,2-bis(ethoxycarbonyl)ethyl O,O-dimethyl phosphorodithioate)	145	2.75	5.3 (30°C)
Dimethoate (O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate)	24000	0.70	0.25 (25°C)
Mevinphos (1-Carbomethoxy-1-propen-2-yl dimethyl phosphate)	c.m.	0.13	17 (20°C)

c.m.: completely miscible

Every 10 days we repeated the application until a total of 5 applications and thus 5 corresponding sampling cycles (SC1–SC5) had been completed. All six insecticides are commonly use by Thai farmers in the study area, and they cover a broad spectrum of physicochemical properties (**Table 4.1**). Although the pesticides usually are not applied together in one spraying cocktail, we chose this practice to investigate the dissipation behaviour of pesticides with contrasting physicochemical properties under the same weather conditions. On our research plot, none of the insecticides had been applied within the last 12 months. The application rates were ca. 2 (mevinphos) to 6 kg ha^{-1} (endosulfan, chlorpyrifos; **Table 4.2**).

Samples of the topsoil (0–10 cm) were taken with an auger (inner diameter: 3 cm) on day 1, 3, 5, 7 and 10 after each application. Only the inner part of the content of the auger was used, and we thoroughly cleaned the auger before every new use. After taking the soil samples on day 10, the subsequent application of pesticides was carried out, and the next SC started. Each soil sample consisted of 5 sub-samples. The composite samples were wrapped into aluminium foil, placed on ice, transported into the laboratory and frozen at –18°C until further processing. In SC1 and 2, the individual sub-samples were taken at randomly chosen grid points. The grid was defined by the bamboo stacks (**Figure 4.1**), and random numbers as coordinates of sampling points were generated in Microsoft Excel. After the first two SCs, however, we did not continue to collect the sub-samples randomly, but took them from "areas of intensive measuring" defined for each sampling cycle SC3 – SC5 (size: 1 m² each; discussed

Table 4.2: *Application rates of 6 insecticides repeatedly sprayed on a lychee orchard in northern Thailand. Dates mark the day of application and thereby the beginning of a new sampling cycle (SC 1–5). Data are arithmetic means with standard errors (n=6 for the individual SCs, n=30 for the overall mean)*

Substance	SC1 19/06/02	SC2 29/06/02	SC3 09/07/02	SC4 19/07/02	SC5 29/07/02	mean
	———————— kg (active ingredient) ha^{-1} ————————					
Endosulfan-α	4.51 (0.26)	5.14 (0.49)	4.41 (0.50)	4.64 (0.45)	4.84 (0.25)	4.71 (0.18)
Endosulfan-β	2.27 (0.13)	2.56 (0.23)	2.14 (0.24)	2.33 (0.22)	2.35 (0.12)	2.33 (0.09)
Chlorpyrifos	5.94 (0.37)	6.83 (0.64)	6.21 (0.76)	6.34 (0.60)	6.76 (0.34)	6.42 (0.25)
Malathion	4.02 (0.21)	4.53 (0.42)	4.11 (0.47)	4.18 (0.40)	4.30 (0.23)	4.23 (0.15)
Dimethoate	4.27 (0.25)	4.88 (0.49)	4.32 (0.39)	4.76 (0.43)	4.02 (0.21)	4.45 (0.17)
Mevinphos	1.79 (0.13)	2.05 (0.27)	1.87 (0.23)	1.99 (0.18)	1.66 (0.10)	1.87 (0.08)

below). On every sampling day we measured soil matric potential as well as soil moisture and determined the amount of rainfall that had fallen since the previous sampling.

4.3.4   Sample preparation and analysis of pesticides

The filters used to control the rate and the homogeneity of the application were freeze-dried and extracted. Therefore, the filters were shaken twice with 20 ml of acetone and twice with 20 ml of ethylacetate (10 minutes each at 140 strokes per minute) in glass vessels with teflon-lined screw caps. The extracts were decanted into pear-shaped flasks through glass funnels with a piece of glass wool in their outflows in order to prevent particles from entering the flasks. After rinsing the funnels with ethylacetate, an internal surrogate standard (5 µg of terbuthylazine (N2-*tert*-butyl-6-chloro N4-ethyl-1,3,5-triazine-2,4-diamine) dissolved in 50 µl of methanol (MeOH) was added into the flasks. Furthermore, we added 150 µl of toluene as keeper to prevent the sample from drying up during the following rotoevaporation of the solvents. Thereafter, we washed the residues with ca. 300 µl toluene into deactivated gas-chromatograph (GC) vials (500 µl). As recovery standard, we added 5 µg of fluoranthen D_{10} dissolved in 50 µl MeOH into the vial. The vials were capped and stored at 4°C until measurement.

Although only total soil concentrations were taken into account for this study, we extracted the soil samples sequentially with three solvents of increasing efficiency (Nikolakis *et al.*, 1999; Laabs, 2002a, modified). This was done to investigate field-aging of the studied pesticides on the same set of samples (**Chapter 5**). Before extraction, however, we thoroughly mixed the soil samples and dried aliquots of all samples to obtain their gravimetric water contents. Then, an aliquot of freshly thawed "field fresh" soil equivalent to 10 g of dry soil was weighed into centrifuge vials with teflon-linded screw caps. The vials were filled with 50 ml of 0.01 M $CaCl_2$ and shaken end over end at room temperature for 24 h in the dark. Afterwards, we centrifuged the vessels at 1000 *g* for 10 minutes to obtain a clear supernatant, which was then decanted through a paper filter (fluted filter 597 ½, Schleicher and Schuell) into a solid-phase extraction system (SPE). This system was composed of 3 ml glass SPE cartridges (Mallinckrodt Baker, Phillipsburg, N.J.) with 100 ml reservoirs (amber glass) mounted on top. The solid phase was 300 mg graphitized nonporous carbon (Carbopack, Supelclean ENVI-Carb SPE Bulk Packing 120/140 mesh particles; Supelco, Bellefonte, PA). The cartridges were pre-treated with 5 ml of a mixture of dichloromethane (DCM) and MeOH (9:1 v/v), 2 ml of MeOH and 15 ml ascorbic acid (10 mg L^{-1}, pH=2, adjusted with 1 M HCl (Dicorcia & Marchetti, 1991)). After adding an internal surrogate standard (5 µg of terbuthylazine dissolved in 50 µl MeOH) into the reservoir glasses and rinsing the filter with a surplus of 0.01 M $CaCl_2$, the solution was sucked through the cartridges with a vacuum pump (suction with circa 20 kPa below atmospheric

pressure, drying of the cartridges with highest vacuum possible). The dried cartridges were wrapped into aluminium foil and kept at –18°C until further processing. For re-extraction, we freeze-dried the cartridges and eluted them with 1 ml MeOH and 6 ml of a mixture of DCM and MeOH (9:1, v/v, Dicorcia & Marchetti, 1991). The eluate was collected in a pear-shaped flask and spiked with 150 µl toluene as a keeper. The other solvents were rotoevaporated. To exclude residual water from the samples, we inserted an additional drying step. Therefore, we put a plug of glass wool into the outflows of glass funnels, filled the funnels with anhydrous Na_2SO_4 and rinsed them with DCM. Afterwards, the eluate was transferred onto the salt and thoroughly washed through with DCM. The effluent was collected in pear-shaped flasks, of which the DCM was rotoevaporated once more. The extract was transferred into a GC vial with circa 300 µl toluene, and the recovery standard (5 µg flouranthen D_{10}, dissolved in 50 µl MeOH) was added. Until measurement, the capped vials were stored at 4°C.

While the SPE was running, we added 50 ml MeOH to the centrifuge glasses with the $CaCl_2$-extracted soil samples. The soil pellets that had formed upon centrifugation were re-suspended by vigorous manual shaking. Then, the vials were automatically shaken end over end for four hours in the dark. After centrifugation at 1000 g for 10 minutes the supernatant was filtered through a paper filter into a pear-shaped flask, and the centrifuge vials with remaining soil were put into a refrigerator (4°C) overnight until further processing. The filters were then washed with MeOH. Afterwards, we added the internal surrogate standard (5 µg of terbuthylazine dissolved in 50 µl MeOH) and 150 µl toluene as keeper into the flask and rotoevaporated the MeOH. To conduct a liquid-liquid-extraction (LLE), we transferred the remaining solution into a separatory funnel, which already contained 5 ml of a saturated KCl solution (ca. 1.5 g KCl) to promote the transfer of pesticides into the organic phase. Afterwards, the flasks were rinsed with 25 ml DCM, which were also poured into the separatory funnel. The funnels were closed with glass stoppers and shaken horizontally for 10 minutes before the two phases were allowed to separate for another 10 minutes. Afterwards the organic (lower) phase was let off into a funnel filled with Na_2SO_4 as a drying agent; the effluent was collected in a pear-shaped flask. This LLE procedure was repeated twice. Having washed the Na_2SO_4-containing funnels with additional DCM, we rotoevaporated the solvent and pipetted the extract into GC-vials. Then we added the recovery standard directly into the vials as described above, capped them and kept them at 4°C until measurement. The centrifuge vials containing MeOH-extracted soil were filled with 50 ml of a mixture of acetone: ethylacetate: water (AEW, 9:1:1, v/v/v) on the next day. Further steps of the extraction were carried out analogously to the extraction with MeOH.

Pesticides were analysed on a GC system with electron-impact mass spectrometer (GC/EI-MSD; agilent 6890–N GC with 5973–N MSD). Measuring and quantification were performed according to Laabs *et al.* (1999).

4.3.5 Calculation of field half lives

We summed up the pesticide concentrations of all three extracts and standardised them to the dry weight of the soil to obtain data on pesticide dissipation with time. First order kinetics were then calculated for all pesticides and sampling cycles. This was done by a least-squares fit of Eq. 4.1 to concentration vs. time data using the Sigma Plot for Windows Software package, version 7.0 (Jandel GmbH, Erkrath).

$$c(t) = c_o \cdot e^{-k \cdot t} \qquad (4.1)$$

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

$$t_{1/2} = \ln(2) \cdot k^{-1} \qquad (4.2)$$

4.4 Results and discussion

4.4.1 Climatic conditions and soil moisture

Total rainfall in the sampling period (19 June – 8 August 2002) was 171 ± 0.6 mm, which was only ca. 25% of the amount collected in the same period one year before (693 mm, **Chapter 3**). Median daily precipitation was 2.7 mm, whereas the arithmetic mean was 6.3 mm, demonstrating the importance of singular heavy rain events. Generally, these heavy rainfalls were separated from each other by several dry days with low or no precipitation. This precipitation pattern resulted in fluctuations of the soil matric potential Ψ from –30 to –5 kPa and volumetric water contents from < 20 to almost 40% in 0–10 cm soil depth (**Figure 4.2**).

4.4.2 Variability of data and initial concentration of pesticides

The field conditions under which our experiment was conducted may lead to two different kinds of variability: (i) variability of the initial concentration due to heterogeneous application (ii) spatial variability in pesticide dissipation kinetics. Although heterogeneities in ground vegetation may lead to non-uniform pesticide applications (Hill & Inaba, 1991), the controls that were placed on the soil surface during applications revealed that the manual spraying was homogeneous and reproducible (S.E. within one application was max. 13.3%, S.E. between applications was below 5%, **Table 4.2**).

To cope with the problem of spatial heterogeneity, we took combined samples from randomly chosen sampling points (see above). In the course of the experiment, however, we observed that the micro-relief lead to systematic differences in soil moisture: due to higher exposure to sunlight and lower input of rain per area, the microslopes were generally drier than the microplains (**Figure 4.2**). This should directly influence the dissipation of pesticides, because soil moisture is a key parameter for the activity of pesticide-degrading microbes (Hultgren *et al.*, 2002), pesticide volatilization (Bedos *et al.*, 2002), and sorption (Kottler *et al.*, 2001). After two sampling cycles, we therefore decided to assign distinct areas of intensive measuring on a microplain for each of the following three sampling cycles (size: ca. 1 m²; **Figure 4.1**). The microplains were chosen for intensive measuring because they covered a much larger area than the microslopes and because pesticide application on an even surface of the microplains can be expected to be more regular than on the microslopes. The concentration of soil sampling onto smaller areas improves the comparability of samples taken on different sampling days within a sampling cycle; moving the sampling area from sampling cycle to sampling cycle increases representativeness of the experiment for the whole plot and reduces the risk of influencing the experiment by taking the samples (soil compaction during sampling, creation of artificial "macropores" with the auger).

On the first day after application, the concentrations of the different pesticides in the topsoil (0–10 cm) varied widely: While ca. 25 to 40 % of the applied dimethoate,
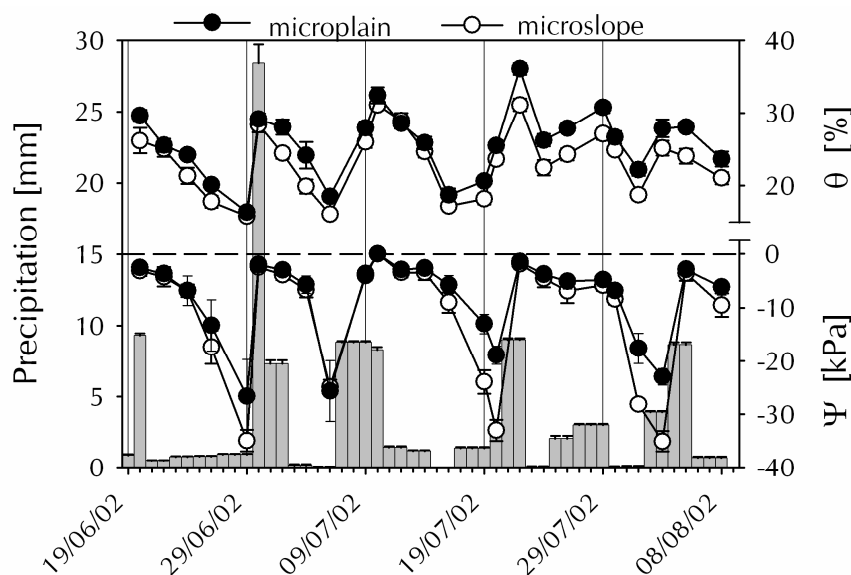
Figure 4.2: *Precipitation and course of matric potential ψ and volumetric water content θ in the topsoil (0–10 cm) of an acrisol in northern Thailand during a study of field dissipation of pesticides. Means and standard errors (precipitation n=6, soil matric potential n=3, volumetric water content n=9); vertical lines mark the days of pesticide application.*

chlorpyrifos and endosulfan (α and β) could be recovered from soil, this fraction was 10 to 20 times smaller for malathion and mevinphos (**Table 4.3**). Because the latter two substances have much higher vapour pressure than the other four pesticides studied (**Table 4.1**), this difference in recovery probably goes back on rapid (= within 24 h) volatilization of large fractions of the applied malathion and mevinphos. High volatilization rates were favoured by the tropical weather conditions under which our experiment was conducted: Volatilization increases with increasing temperature (Bedos *et al.*, 2002) and relative humidity (Grass *et al.*, 1994), which typically were around 25°C and 80% during application (Klaus Spohrer, University of Hohenheim, unpublished data). Furthermore the ground vegetation of our research plot promoted volatilization because pesticides generally have a lower affinity to plants than to soil (Boehncke *et al.*, 1990) and because the stagnant atmospheric boundary layer at the soil surface is thicker than in the plant canopy (Rüdel, 1997).

The recovery of the less volatile substances on the first day after application was within the expected range: Racke (2003a) reported that initial concentrations of pesticides in soil are ca. 50 % of the applied amount. However, according to FOCUS (2000), only 10 % will be recovered if the soil surface is densely covered with vegetation. Because

Table 4.3: *Relative recovery (% of applied) and concentrations of repeatedly applied insecticides on the first day of each sampling cycle (SC) in an Acrisol in northern Thailand (0–10 cm). Means and standard errors (n=2)*

Substance	——— SC1 ——— ——19/06/2002 —— μg (kg soil)$^{-1}$	% of applied[a]	SC2 29/06/2002	SC3 09/07/2002 ——————— μg (kg soil)$^{-1}$ ———————	SC4 19/07/2002	SC5 29/07/2002
Endosulfan-α	2010 (452)	35.7	5094 (136)	3251 (110)	1951 (942)	2023 (8)
Endosulfan-β	1076 (168)	38.0	3147 (96)	2658 (171)	1939 (703)	2472 (140)
ES-sulfate	732 (14)	8.3[b]	1181 (24)	2202 (250)	2095 (611)	2173 (133)
ES-lactone	7 (1)	0.1[b]	42 (3)	26 (1)	39 (10)	113 (1)
Chlorpyrifos	1735 (239)	23.6	3793 (107)	4090 (147)	2230 (857)	2891 (62)
Malathion	107 (11)	2.1	246 (21)	240 (7)	159 (92)	419 (6)
Dimethoate	1527 (9)	28.6	1853 (226)	3722 (116)	2393 (732)	2778 (42)
Mevinphos	37 (9)	1.6	19 (2)	13 (1)	9 (2)	34 (2)

[a] bulk density of topsoil: 0.8 g cm^{-3} (field estimation); calculated for first SC only because of carryover of pesticides from SC to SC occurred (see **Figure 4.3**)

[b] based on the sum of applied endosulfan-α + -β

the rainy season had not yet reached its climax when we conducted our experiments, the ground cover of our research plot was not yet fully developed, so that initial recoveries of pesticides were between the values suggested by Racke (2003a) and FOCUS (2000). The relative recoveries varied from sampling cycle to sampling cycle, which might partly go back on carry-over effects and on differences in precipitation within the first 24 h after application (discussed below).

4.4.3 Dissipation of pesticides

After each application of the pesticides soil pesticide concentrations sharply increased, but decreased again in the course of the subsequent sampling cycle. The dissipation patterns of the different pesticides showed two common characteristics: (i) the highest concentrations of pesticides were not always measured on the first day after application but sometimes after the third day only, and (ii) despite their wide range of physicochemical properties, differences in dissipation from soil were small for the various pesticides we investigated (**Figure 4.3**, illustrated for endosulfan-α and dimethoate).

Ad (i): The time-lag between application and highest soil concentrations again demonstrates the role of the ground vegetation as a buffer of pesticide input to soil. Obviously, precipitation was needed to wash the pesticides from the plant surfaces into the soil. This buffer-function of the plant cover is relevant for pesticide fate because volatilization from plants is usually higher than from soil (Boehncke *et al.*, 1990; Rüdel, 1997). Hence, the precipitation pattern after application influences the scale on which the pesticides affect the environment: If it rains soon after application, the compounds are rapidly washed into the soil. This means that they will mainly act on plot scale, while the probability of (air-mediated long-range) transport into remote off-target areas (LeNoir *et al.*, 1999; Laabs *et al.*, 2002c) will increase with increasing time between application and wash-off from the plants. It is remarkable, however, that the delayed input of pesticides from plants into the soil did not always coincide with rainfall, which can most clearly be seen at the beginning of sampling cycle 5 (**Figure 4.3**). Obviously, dewfall was sufficient to transfer pesticides from plants onto the soil, as described by Thompson *et al.* (2000). Yet, because our experiment focused on pesticide dissipation from soil, processes on the plant-soil interface were not studied in detail and are suggested as a topic of upcoming research. The delay between pesticide application and highest concentration in soil had a direct influence on our calculations of field half-lives: whenever we observed this lag, the dissipation kinetics were not fitted from the first, but from the second to the last sampling day within each application cycle.
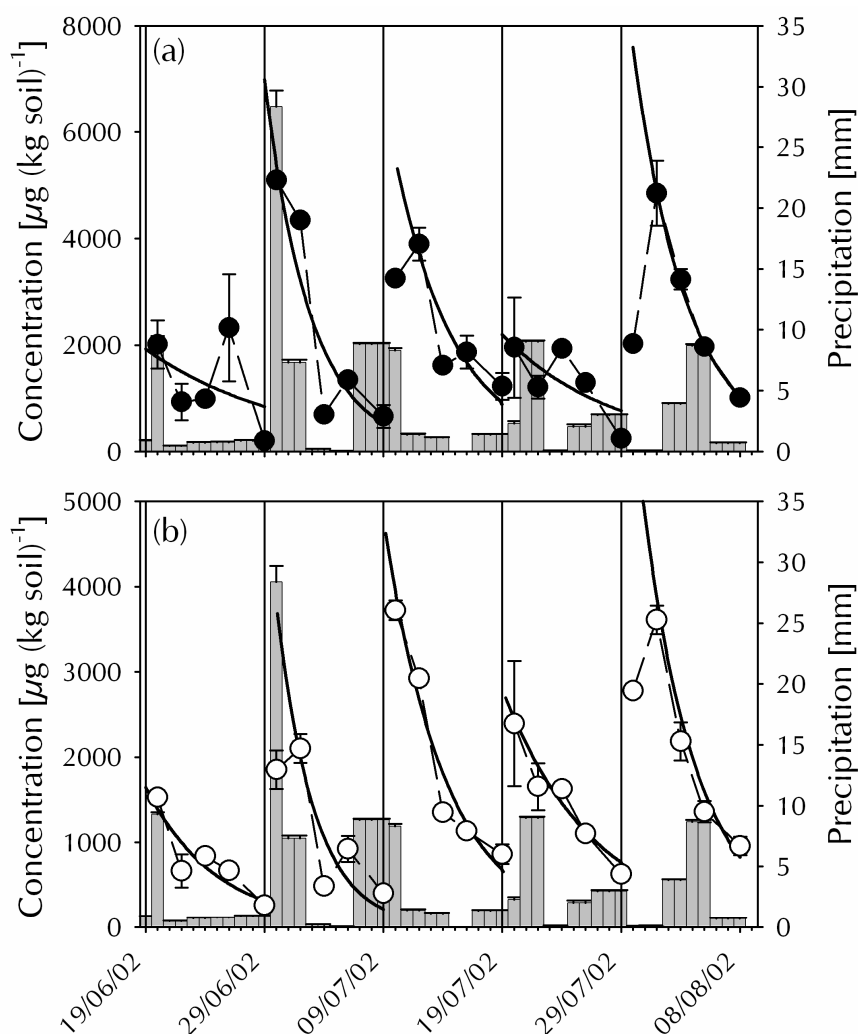
Figure 4.3: *Temporal course of concentrations of (a) endosulfan-α and (b) dimethoate in the topsoil (0–10 cm) of a northern Thailand Acrisol after repeated applications. Vertical lines mark the application dates, solid curves mono-exponential dissipation-kinetics. Grey bars show the precipitation during the experiment.*

Ad (ii): The dissipation rates of all pesticides in the soil studied were similar despite of their physicochemical properties, as indicated by variations in mean field half-life that were small compared with previous reports in literature ($t_{1/2}$ = 1.4 – 7.2 d). Also, the absolute half-lives were among the shortest reported in literature (**Table 4.4**). We attribute these findings to the humid tropical climate at the experimental site, which increases the probability of rainfall soon after application as well as the total amount of rain. Yet, rainfall may affect pesticide concentrations in soil in various ways: Wash-off from plants increases concentrations in topsoil. At the same time microbial activity in moist soil is generally higher than in dry soil, which promotes pesticide degradation (Garcia-Valcarcel & Tadeo, 1999). Excessive rainfall may lead to pesticide leaching or surface runoff (Ciglasch *et al.*, 2005), which also reduces their concentrations in topsoil.

Table 4.4: *Field half-lives ($t_{1/2}$) of insecticides in a repeatedly treated tropical Acrisol (sampling cycles SC1–5; the dates refer to the day of application). The $t_{1/2}$ were calculated by fitting mono-exponential decay curves to measured soil concentrations. Data was considered to be reliable and is reported here only if the R^2 (given in parentheses for SC 1–5) of the fit exceeded 0.60. For comparison, half-lives reported in literature for field experiments under tropical and subtropical climates are given*

Substance	SC1 19/06/02	SC2 29/06/02	SC3 09/07/02	SC4 19/07/02	SC5 29/07/02	mean ± S.E. SC1–5	Literature	Reference and description
			$t_{1/2}$ [d]					
Endosulfan-α	n.r.	2.7 (0.84)	3.5 (0.75)	n.r.	3.1 (0.95)	3.1 ± 0.2	1.7	(Laabs et al., 2002a, Brazil, Ustox)
Endosulfan-β	n.r.	2.9 (0.61)	n.r.	n.r.	5.0 (0.84)	4.0 ± 1.1	5.4 [a] / 9.7–12.2 [a]	(Kathpal et al., 1997, India, sandy loam) (Vig et al., 2001, India, cotton crop soil)
Chlorpyrifos	n.r.	2.8 (0.64)	6.1 (0.63)	n.r.	7.2 (0.82)	5.4 ± 1.3	0.8 / 12.3	(Laabs et al., 2002a, Brazil, Ustox) (Menon et al., 2004, India, loamy sand)
Malathion	n.r.	2.6 (0.85)	2.5 (0.93)	n.r.	1.4 (0.99)	2.2 ± 0.4	17	(Getenga et al., 2000, tropical conditions simulated in greenhouse, soil pH = 6.5)
Dimethoate	4.2 (0.76)	2.2 (0.71)	3.5 (0.94)	5.3 (0.70)	3.1 (0.96)	3.7 ± 0.5	5.1–7.1 / 6.7 / 11–22	(Wu & Fan, 1997, China, loam) (Suzuki, 2000, Japan, Andosol) (Vig et al., 2001, India, cotton crop soil)
Mevinphos	2.1 (0.81)	5.3 (0.78)	6.4 (0.89)	1.4 (0.93)	1.4 (0.83)	3.3 ± 1.1	1	(Spencer et al., 1992, California, vegetables)

Furthermore, moist soils can (depending on various other boundary conditions and properties of the pesticides) either reduce or enhance the rates of pesticide volatilization (Reichman *et al.*, 2000). Probably, these contrasting effects of rainfall on pesticide dissipation levelled out the differences in dissipation rates between the studied compounds, which probably would have existed under stationary climatic conditions.

An example for the effects of precipitation on the soil concentration of different pesticides presented in **Figure 4.3**: while the rainstorm of 28.4 mm on 30/06/02 right after application caused substantial wash-off of the hydrophobic endosulfan-α from plants into the topsoil, the same amount of rain was probably sufficient to leach the more polar dimethoate into deeper soil horizons than investigated in our study. This resulted in a steeper "apparent" increase in the soil concentration of endosulfan-α than of dimethoate. Contrastingly, the much lighter rainfall that occurred after the third application (10/07/02) probably washed relatively high amounts of dimethoate into the topsoil, while a larger fraction of endosulfan-α than in the second sampling cycle may have still remained on the plants.

Due to the high relevance of precipitation and other environmental conditions for pesticide dissipation, the effect of microbial adaptation to the degradation of pesticides reported in literature (e.g. Ismail & Kalithasan, 2003) was completely masked and could not be quantified. Nevertheless, our data clearly indicates that microbial degradation contributed significantly to pesticide dissipation: both metabolites of endosulfan that we investigated were detectable in the topsoil. Only one day after the first application, 8.3 % of endosulfan had been converted to endosulfan-sulfate, and 0.1 % to endosulfate-lactone (**Table 4.3**). While the sulfate is a typical microbial metabolite (Goebel *et al.*, 1982), the lactone may also form by photolysis (Archer *et al.*, 1972). The concentrations of both substances in topsoil increased over time, but the increase was steeper and concentrations fluctuated less for the lactone than for the sulfate (**Figure 4.4**). Obviously, the lactone was much more persistent than the sulfate, which only is an intermediate product that underlies further dissipation itself. However, also the half-life of endosulfan-sulfate must be higher than of the parent compound, because otherwise, it would not accumulate in soil. This is in accordance with the findings of Ghadiri & Rose (2001), who reported an accumulation of endosulfan-sulfate in Australian clay soils, and Leonard *et al.* (2001), who found that toxicity effects of endosulfan-sulfate in rivers prevail longer than those of the parent compounds.

4.4.4 Half-lives and accumulation of pesticides

Because of the multitude of pathways of pesticide dissipation, spatial and temporal variability of environmental conditions and because of the small range in field half-lives, we did not observe any correlation between mean dissipation rates of pesticides
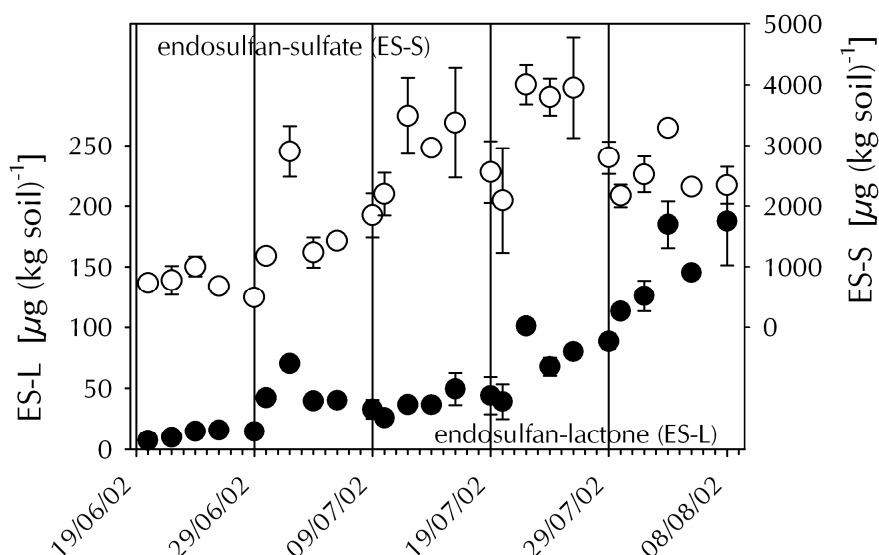
Figure 4.4: *Formation of two metabolites of endosulfan, endsulfan sulfate and endosulfan lactone in the topsoil (0–10 cm) of a northern Thailand Acrisol. Vertical lines mark the application dates of the parent compound.*

from topsoil and their physicochemical properties (r (half-life vs. log K_{OW}) = 0.33; r (half-life vs. vapour pressure) = 0.26; not shown).

Therefore, one might come to the conclusion that any pesticide applied to the lychee orchard we worked on will dissipate so rapidly that it will have no adverse effect on off-target ecosystems at all. Yet, a comparison between simulated and measured soil concentrations after repeated applications reveals that this conclusion over-simplifies the field situation: If we assumed the field half-live of two certain pesticides to be 1.4 and 7.2 days, and if these pesticides were applied five times in 10-day intervals, 1 and 61 % of one application would be present in soil after 50 days (**Figure 4.5**). **Figure 4.5** also reveals that the accumulation factor, expressed as concentration on the end of the last sampling cycle divided by the concentration on the end of the first sampling cycle should be 1.01 and 1.60 for pesticides with field half-lives of 1.4 and 7.2 days. Yet, the accumulation factors we calculated were much higher (up to 6.5, endosulfan-β) for all substances except mevinphos, which fully dissipated in the last sampling cycle, resulting in an accumulation factor of 0 (**Figure 4.6**). This means that the mono-exponential decay model does not adequately describe the actual pesticide dissipation. Obviously, not the total amount of pesticides in soil was readily available for dissipation processes. This is in agreement with literature, where different dissipation kinetics have been suggested for pesticides in different compartments of the soil (e.g. sorbed and in soil solution, Scow *et al.*, 1986), or for abiotic dissipation and microbial degradation (Hill & Schaalje, 1985). However, due to the relatively short observation period (five values per sampling cycle), we did not find it reasonable to fit a bi-exponential dissipation model with four or five free parameters to our data.
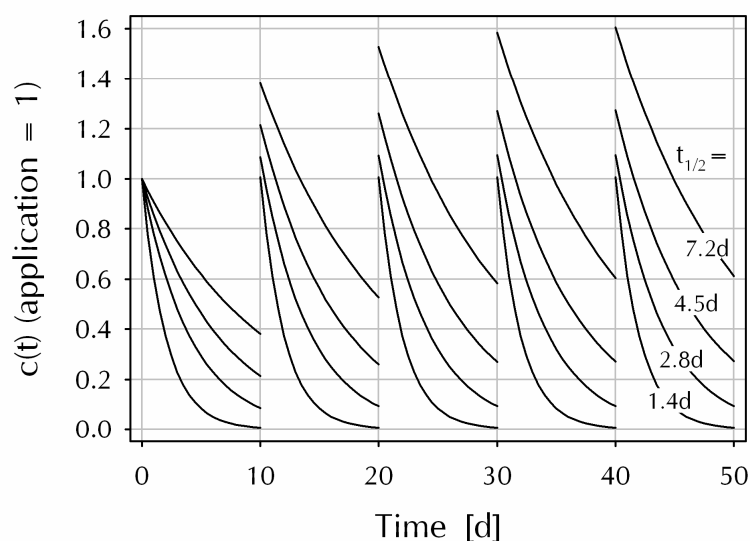
Figure 4.5: *Simulation of soil concentrations of pesticides with hypothesized half-lives of 1 to 7 days after repeated applications in 10-day intervals under the assumption of ideal mono-exponential decay.*
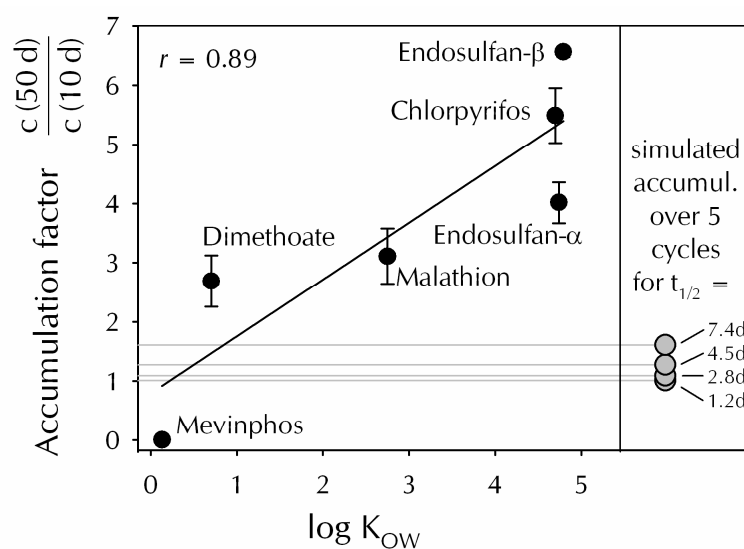
Figure 4.6: *Plot of accumulation of six pesticides in a Northern Thailand Acrisol against their logarithmized octanol-water partitioning coefficients after five applications (calculated as conc. at the end of the 5th sampling cycle divided by conc. at the end of the 1st cycle). For comparison, simulated accumulation factors for pesticides with ideal mono-exponential dissipation and half-lives from 1 to 7 days were added in grey color (data from **Figure 4.5**).*

The accumulation factors of the individual pesticides closely correlated with their polarities ($r = 0.89$; **Figure 4.6**). This means that the deviation from ideal mono-exponential decay increased with increasing hydrophobicity of the pesticides. Because hydrophobicity is directly related to binding strength (Wauchope *et al.*, 2002), sorption

appears to be the major process that determines pesticide accumulation in the studied Acrisol and deserves further attention (**Chapter 5**).

4.5   Conclusions

The humid tropical climate promoted pesticide dissipation from the studied Acrisol, so that half-lives were among the shortest published. Pesticide dissipation was influenced by numerous different factors and processes. All of these had different relevance for the various substances we studied, so that in total, no differences in dissipation kinetics were observed. Volitilization appeared to be a major pathway of pesticide dissipation, especially for mevinphos and malathion, and it was promoted not only by the high temperatures and relative humidities, but also by the ground vegetation. Repeated applications did not affect dissipation rates. Obviously, the weather conditions within the different sampling cycles had a higher influence on pesticide dissipation than microbial adaptation to pesticide degradation, or the microbes already were adapted to pesticde degradation as a result of applications in previous years. However, dissipation was not complete, but increasing accumulation occurred with increasing hydrophobicity of the substances.

5 Field aging of pesticides after repeated application to tropical Ultisol, N-Thailand

5.1 Summary

Field aging immobilizes pollutants and reduces their toxicity, but it also boosts their accumulation and holds the risk of future release. We have investigated the aging of insecticides repeatedly applied to a tropical fruit orchard under natural weather conditions. A combined mixture of endosulfan (α and β), chlorpyrifos, malathion, dimethoate and mevinphos was sprayed every 10 days onto the soil surface (5 repetitions). Within 11 weeks after the first application, we took 26 composite samples of the topsoil, which were extracted sequentially with 0.01 M $CaCl_2$, methanol, and a mixture of acetone, ethylacetate and water. We analysed all extracts for pesticide residues by GC/MS. A conventional and a newly introduced sorption coefficient ($K_{OC(app)}$ and MAR) were calculated and interpreted against the background of aging. Endosulfan exhibited pronounced aging (increase in $K_{OC(app)}$ from below 10000 to almost 30000 ml g_{OC}^{-1}). For dimethoate, the raise in $K_{OC(app)}$ was even steeper (5- to 10fold within one sampling cycle), however, this was mostly caused by dissipation from labile pools rather than by aging. The $K_{OC(app)}$ of chlorpyrifos remained constant (22000 ml g_{OC}^{-1} throughout the experiment), but a significant decrease in MAR ($r = -0.78$) revealed that sorption strength increased over time. After pronounced initial sorption, malathion was more and more released during the study, probably due to microbial activity. For mevinphos, no aging was observable under our experimental conditions. Combining the information of $K_{OC(app)}$ and MAR we demonstrated that, even if fresh material is repeatedly added, aging is a relevant process that may explain accumulation of hydrophobic pesticides in the studied orchard.

5.2 Introduction

About 50 years ago, Edwards *et al.* (1957) observed 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 (Alexander, 1995; Gevao *et al.*, 2003). Aging has been found to be a general phenomenon, but both rate and extent strongly depend on physicochemical properties of the compound (Northcott & Jones, 2001; Mordaunt *et al.*, 2005). When hydrophobic organic compounds (HOCs; a collective term for pollutants such as PAHs, PCBs and non-ionic pesticides) interact with the soil matrix, two major processes occur: (i) partitioning of the HOC between the soil water and the soil matrix and (ii) adsorption to specific binding sites. Partitioning is fast, concentration-independent and fully reversible. Contrastingly, adsorption is kinetically hindered ("slow sorption", Pignatello

& Xing, 1996), the sorption sites are limited, and desorption hysteresis is observed (Kan *et al.*, 1998). Although HOCs can adsorb to mineral surfaces (Huang et al., 1996) this is considered to be negligible compared with sorption to soil organic matter (SOM) if the content of organic carbon (OC) of the sorbent exceeds 0.01% (Mader *et al.*, 1997).

The fractions of the SOM involved in partitioning and adsorption have contrasting properties. In analogy to polymer theory, organic substance is divided into soft, "rubbery" and rigid, "glassy" domains ("distributed reactivity model" (DRM), Leboeuf & Weber, 1997; Xing & Pignatello, 1997). Rubbery, gel-like material, which is involved in partitioning processes, is relatively fresh organic matter. It is characterized by high O/C-ratios, indicating a low degree of humification. The "older" the organic matter gets, the more hydrophobic and condensed (and thus rigid) it will be (Huang & Weber, 1997). The surface of this glassy fraction is characterized by micropores that are able to entrap HOCs, causing specific adsorption ("hole-filling", Xing & Pignatello, 1997). This adsorption is considered the main reason for aging phenomena.

According to their differences in structure, the two domains where partitioning and adsorption take place have different accessibility for solvents. Aqueous solutions, for example 0.01 M CaCl$_2$, can easily penetrate the layer of fresh organic material, and HOCs dissolved therein will re-partition between the organic phase and the added aqueous solution. To access HOCs entrapped in rigid structures, harsh organic solvents must be used. For tropical soils, Laabs *et al.* (1999) suggested a mixture of acetone, ethylacetate and water (AEW) as an exhaustive extractant. Polar organic solvents, such as methanol (MeOH), have a higher efficiency of extraction than aqueous solutions, but they are not able to access the hydrophobic condensed organic matter and the pesticides entrapped therein, except under elevated temperature and increased time of extraction (Huang & Pignatello, 1990) or if supercritical MeOH is used (Piccolo *et al.*, 1992). Thus, at amospheric pressure, cool MeOH obviously extracts a kind of "intermediate" pool of HOCs (HOCs that are neither freely available nor completely entrapped in micropores). There have been attempts to correlate the MeOH extract with the bioavailable portion of HOCs, but it has been found that chemical desorption can mimic bioavailabilty only after thorough calibration (specific for both the HOC and test organism, Kelsey *et al.*, 1997). Despite this constraint, operationally defined pools of different binding strengths for HOCs are of high ecological importance, because extractability directly controls toxicity (in the case of insecticides, that means effectiveness, Edwards *et al.*, 1957), degradability (feasability of microbial remedation, Weissenfels *et al.*, 1992) and leachability (risk of groundwater contamination, Walker *et al.*, 2005). If HOCs or their metabolites become an unextractable part of the SOM due to manifold processes of incorporation (both chemical and physical) and degradation, so-called bound residues form (Burauel & Führ, 2000, and references therein). However, even these bound residues are not necessarily an eternal sink for HOCs, but

remobilization may occur, for example in the course of microbial turnover of SOM (Burauel & Bassmann, 2005). Unexpected release of bound residues is postulated to be particularly high after repeated inputs of multiple chemicals (Barraclough *et al.*, 2005), which is the case, for example, for pesticides in Thai lychee production.

In 1996, Thailand imported more than $4.5 \; 10^7$ kg of pesticides that are mainly applied to fruits and vegetables (Thapinta & Hudak, 2000). Although pesticides dissipate faster in the tropics than in temperate regions (Laabs *et al.*, 2002a), the environmental risk of pesticide application in the tropics must not be underestimated because the hot, humid climate requires high doses and repeated treatments for an effective pest management. Furthermore, the handling of pesticides in less developed tropical countries such as Thailand is not done as carefully as in western industry nations. Consequently, relevant concentrations of pesticide residues have been found in Thai food, ground and surface waters, and even in the breast milk of female farmers (Baun *et al.*, 1998; Thapinta & Hudak, 2000; Stuetz *et al.*, 2001).

A field dissipation study we conducted in Northern Thailand (**Chapter 4**) revealed that soil-applied insecticides, despite of half-lives that ranged from 1.4 to max. 7.2d only (**Table 5.1**), accumulated in soil after repeated pesticide treatment. It is well-known that pesticide sorption to tropical soils differs from temperate soils (Barriuso & Calvet, 1992), but aging phenomena have not yet been investigated systematically in tropical

Table 5.1: *Field half-lives (DT$_{50}$) of insecticides in a repeatedly treated N-Thai Acrisol (Sampling cycles SC1–5; the dates refer to the respective day of application). The DT$_{50}$s were calculated by fitting monoexponential decay curves to measured soil concentrations taken on five sampling days within each SC. Data was considered to be reliable and is reported here only if the R² (given in parentheses) of the fit exceeded 0.6 (see **Chapter 4** for details)*

Substance	SC1 19.06. 02	SC2 29.06. 02	SC3 09.07. 02	SC4 19.07. 02	SC5 29.07. 02
			DT$_{50}$ [d]		
Endosulfan-α	n.r.	2.7 (0.84)	3.5 (0.75)	n.r.	3.1 (0.95)
Endosulfan-β	n.r.	2.9 (0.61)	n.r.	n.r.	5.0 (0.84)
Chlorpyrifos	n.r.	2.8 (0.64)	6.1 (0.63)	n.r.	7.2 (0.82)
Malathion	n.r.	2.6 (0.85)	2.5 (0.93)	n.r.	1.4 (0.99)
Dimethoate	4.2 (0.76)	2.2 (0.71)	3.5 (0.94)	5.3 (0.70)	3.1 (0.96)
Mevinphos	2.1 (0.81)	5.3 (0.78)	6.4 (0.89)	1.4 (0.93)	1.4 (0.83)

n.r.: not reliable (R^2 of the monoexponential fitting curve $<$ 0.6)

ecosystems. Therefore, to explain our observations, we found it necessary to conduct further studies on the temporal dynamics of pesticide fractionation into different domains of the soil. Consequently, the objective of the work presented in this paper was 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 $CaCl_2$, MeOH and AEW.

5.3 Materials and methods

5.3.1 Research site and experimental plot

The fieldwork for our study was conducted on a lychee orchard in Northern Thailand previously described by Ciglasch *et al.* (2005, 18°53' N, 98°52'E, ca. 800 m above sea level, facing west, slope ca. 15°, mean annual temperature 21.6°C). Mean annual precipitation is 1600 mm with distinct dry (November to April) and wet seasons (May to October). Trees are growing in a grid of 10 by 10 meters; their height is 2–3 m. The soil surface is covered with grasses and herbs. The soil type is a Haplic Acrisol in FAO classification. The average content of organic carbon (OC) in the topsoil (0–10 cm) is 2.89% (S.E.=0.04%). On the orchard, a research plot was established on which the pesticide application and soil sampling took place (ca. 6m by 30m). This plot was mown bi-weekly with a motorised scythe and the plant residues were removed. Along one of the 30 m long sides of the plot, we set up 6 rain collectors and 3 tensiometers (installation depth: 10 cm) to monitor precipitation and the tension of the studied soil layer. These devices were not installed within the treated area to prevent them from contamination with pesticides and to minimize disturbance of the experimental plot.

5.3.2 Pesticide application and soil sampling

Pesticides were purchased in typical local formulations and applied five times in 10-day intervals, beginning on 19 June 2002. This frequency is in accordance with local practice and simulates the treatment of lychee trees during fruit ripening. However, farmers do not apply the pesticides onto the soil, but into the crown of the trees. Thus, our treatment reflects a worst-case scenario for the area between the trees, but it might be representative for the soil close to the trunks where spray-drift and overspray precipitate onto the soil surface. The insecticides we applied are common for tropical fruit production, but we only used substances that had not been used on our plot in the last growing season. Furthermore, we selected substances with a wide range of physicochemical properties. 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" (**Table 5.2**).

Both the plot and a manual backpack sprayer were thoroughly prepared for application. A reducing valve that kept the spraying pressure on a constant level and a special slit nozzle for ground applications guaranteed an even, 40 cm wide spray. We marked the border of the experimental plot with bamboo stacks installed in even distances of 80 cm, so that we had to do exactly two passes per stack when spraying. After pressure adjustment and calibration of the backpack sprayer we calculated the optimal walking speed to apply the desired rate of pesticides. During application, which was done in a criss-cross pattern, an assistant permanently supervised the walking speed of the spraying person with a stopwatch. Six glass-fibre filters (GF6, 60 mm diameter, Schleicher & Schuell Microscience, Dassel) were randomly placed on the plot before each application to control uniformity of deposition. The filters were collected immediately after application and wrapped into aluminium foil, put on ice and transported to the laboratory. There, they were stored at –18 °C until further processing.

5.3.3 Soil sampling

We collected samples of the topsoil (0–10 cm) with an auger (inner diameter: 3 cm) 1, 3, 5, 7 and 10 days after pesticide application. Soil samples were taken as composite samples that consisted of 5 sub-samples. These were carefully mixed, wrapped in

Table 5.2: *Application rates of pesticides for the five application events (SC=sampling cycle; means and standard errors, n=6) and average application rate (mean and standard error of all data)*

Substance	SC1 19.06. 02	SC2 29.06. 02	SC3 09.07. 02	SC4 19.07. 02	SC5 29.07. 02	mean
	———————— [kg (active ingredient) ha^{-1}] ————————					
Endosulfan-α	4.51 (0.26)	5.14 (0.49)	4.41 (0.5)	4.64 (0.45)	4.84 (0.25)	4.71 (0.18)
Endosulfan-β	2.27 (0.13)	2.56 (0.23)	2.14 (0.24)	2.33 (0.22)	2.35 (0.12)	2.33 (0.09)
Chlorpyrifos	5.94 (0.37)	6.83 (0.64)	6.21 (0.76)	6.34 (0.60)	6.76 (0.34)	6.42 (0.25)
Malathion	4.02 (0.21)	4.53 (0.42)	4.11 (0.47)	4.18 (0.40)	4.3 (0.23)	4.23 (0.15)
Dimethoate	4.27 (0.25)	4.88 (0.49)	4.32 (0.39)	4.76 (0.43)	4.02 (0.21)	4.45 (0.17)
Mevinphos	1.79 (0.13)	2.05 (0.27)	1.87 (0.23)	1.99 (0.18)	1.66 (0.10)	1.87 (0.08)

aluminium foil and stored at –18 °C as described for the glass-fibre filters. 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 1 September, 34 days after the last application (the period from the end of SC5 to the end of the experiment will be denoted as SC5'). On every sampling day, soil tensions and the amount of precipitation that had fallen in the meantime were recorded.

5.3.4   Sample preparation and analysis

The filters from the application control were freeze-dried and extracted by rigorous subsequent shaking with acetone and ethylacetate (20 ml, 10 minutes, two times with each solvent) in glass vials with teflon-lined screw caps. After addition of the first solvent to the filters, we spiked 5 µg of terbuthylazine dissolved in 50 µl of MeOH into the vials (internal surrogate standard). After each step of extraction, the solution was decanted into a pear-shaped flask (one combined sample per filter). To exclude floating organic matter or residues of the extracted filter, decanting was done through glass funnels that had a plug of glasswool in their outflows. We rinsed these funnels with ethylacetate and added ca. 150 µl of toluene to the sample. This "keeper" prevented the sample from drying during rotoevaporation of the other solvents. The residues were washed into a gas-chromatograph (GC) vial with ca. 300 µl of toluene. Before capping of the vial and storing it at 4°C until measurement, a recovery standard was added (5 µg of fluoranthene D_{10} in 50 µl of toluene).

Soil samples were sequentially extracted in three steps (Nikolakis *et al.*, 1999; Laabs, 2002b, modified). Before the extraction, we homogenized the samples once more with a stainless steel spatula and dried aliquots of them in the oven (105°C). Loss of weight upon drying was measured to obtain the gravimetric water contents of the samples. The dried aliquots were ground and the OC content of each individual sample was determined with a Carlo Erba NS 1500 C/N analyser (Thermo Electron Corporation, Milan). An amount of well-mixed, freshly thawed moist soil equivalent to 10 g of dry soil was weighed out into glass centrifuge vials (all samples in duplicate). We added 50 ml of a 0.01 M $CaCl_2$ solution before capping the vials with teflon-lined lids and shaking them end over end in the dark for 24 hours (room temperature (21±2 °C)). Then, the glasses were centrifuged at 1000 *g* for 10 minutes. This was sufficient to obtain a clear supernatant, which we transferred through a paper filter (cellulose filter 595½, Schleicher & Schuell) directly into a solid-phase extraction (SPE) system. This system consisted of 3 ml glass SPE cartridges (Mallinckrodt Baker, Phillipsburg, N.J.) with 100 ml storage tanks (amber glass) mounted on top. The solid phase was 300 mg graphitized non-porous carbon (Carbopack, Supelclean ENVI-Carb SPE Bulk Packing 120/400 mesh; Supelco, Bellefonte, PA), pre-treated with 5 ml of a 9:1 (by volume)

mixture of dichloromethane (DCM) and MeOH, 2 ml of MeOH, and 15 ml of 10 g l^{-1} ascorbic acid (pH adjusted to 2 with 1 M HCl, Di Corcia & Marchetti, 1991, modified). After rinsing the filter with further 0.01 M CaCl$_2$ solution we added the surrogate standard (5 µg of terbuthylazine in 50 µl of MeOH, see above). Then, the solution was sucked through the cartridges with a vacuum pump (suction ca. 30 kPa; drying of the cartriges at 80 kPa below atmospheric pressure). The cartridges were stored at –18 °C until they were freeze-dried and eluted with 2 ml of MeOH and 6 ml of a 9:1 (by volume) mixture of DCM and MeOH (Di Corcia & Marchetti, 1991). The effluent was collected in pear-shaped flasks, the keeper was added (150 µl of toluene, see above), and DCM and MeOH were rotoevaporated. Although no water could be observed in the toluene phase, it turned out to be necessary to eliminate residual traces from the samples before pesticide measurement on the GC. Therefore, a glass funnel was plugged with a small amount of glass wool and filled with anhydrous Na$_2$SO$_4$ (oven-dried at 300 °C overnight). After rinsing of this water-absorbing chemical with DCM, the sample was pipetted onto the Na$_2$SO$_4$ and washed through with a surplus of DCM. The effluent was collected in a pear-shaped flask of which the DCM was rotoevaporated. We washed the residue into a GC vial with ca. 300 µl of toluene, spiked 5 µg of a recovery standard (fluoranthene D$_{10}$, see above) directly into the vial and capped it. The samples were stored at 4 °C until measurement.

While the SPE of the aqueous solution was running, we added 50 ml of MeOH to the soil in the centrifuge vials. Because the soil was still wet from the previous extraction step with CaCl$_2$-solution, the extractant was not pure methanol, but an aqueous methanol solution (containing 5–10% of water by volume). We capped the vials again and shook them manually until the pellet that had formed during centrifugation was completely re-suspended. Afterwards, the vials were shaken automatically end over end for four hours and centrifuged as described above. The supernatant was filtered into a pear-shaped flask and the soil samples in the centrifuge vials were stored in the refrigerator at 4 °C overnight until further processing (described below). After thorough rinsing of the filter with further MeOH, the internal surrogate standard and ca. 150 µl of toluene were added into the flask, and the MeOH was rotoevaporated. The remaining solution was poured from the flask into a separatory funnel that already contained 5 ml of a saturated KCl solution (ca. 1.5 g KCl). We rinsed the flask with 25 ml of DCM which was then also transferred into the separatory funnel. Closed with a glass stopper, we shook the funnel at a frequency of 140 strokes per minute for 10 minutes on a horizontal shaker (liquid-liquid extraction, LLE; KCl promotes the passage of pesticides from the aqueous to the organic phase). After we had allowed the two phases to separate for another 10 minutes, the (lower) organic phase was let off into a funnel filled with anhydrous Na$_2$SO$_4$ that had been pre-rinsed with DCM. The effluent of this drying unit was collected in another pear-shaped flask. We repeated the LLE procedure twice.

Then, the Na$_2$SO$_4$ in the funnel was washed with additional DCM, which was rotoevaporated from the flask. As described above, we transferred the residue into a GC vial, added the recovery standard and stored the samples at 4 °C until measurement. On the following day, we gave 50 ml of a mixture of acetone : ethylacetate : water = 3:1:1 (by volume; AEW) into the centrifuge vials with the soil samples and repeated all steps exactly as described above for the MeOH extraction.

Pesticides were quantified on a GC system with electron-impact mass spectrometer (GC/EI-MSD; agilent 6890–N GC with 5972–N MSD). The quantitation was done by comparing the ratios of the peak area between terbuthylazine and the target compounds in the samples with those of standards with known concentrations. For details on the GC method and its performance, see Laabs *et al.* (1999).

5.3.5 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}]):

$$K_{D(app)} = \frac{c(MeOH) + c(AEW)}{c(CaCl_2)}$$

(5.1)

with: $c(CaCl_2)$ = concentration in the CaCl$_2$ solution [g l^{-1}], $c(MeOH)$ = concentration in the MeOH fraction [g (kg dry soil)$^{-1}$], and $c(AEW)$ = concentration in the AEW extract [g (kg dry soil)$^{-1}$]. The index "apparent" indicates that this partitioning coefficient is not a constant as obtained by batch equilibrium techniques (for example OECD, 2000), but it varies according to the actual field situation and binding strength (Pignatello & Huang, 1991). As the non-ionic pesticides used in this study mainly interact with the organic carbon of the soil (Wauchope *et al.*, 2002), the $K_{D(app)}$ was normalized to the OC content ($K_{OC(app)}$ [ml g$_{OC}^{-1}$]):

$$K_{OC(app)} = \frac{K_D \cdot 100}{\%OC}$$

(5.2)

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 dataset:

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

(5. 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 subsequent chapters.

5.4   Results and discussion

5.4.1 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 18mm of rain within 10 days, respectively; **Figure 5.1**). Until Mid-August, there were only some distinct rain storms followed by several dry days so that the soil matric potential in 10cm depth regularly fluctuated between ca. –3 and up to –45kPa. In the last two weeks of the experiment rain occurred more regularly, and the matric potential of the topsoil did not fall below –10kPa any more.

5.4.2 Data quality and comparison with tabulated K_{oc} values

Analysis of the glass fibre filters revealed that the spatial variation of pesticide input within one treatment was ±5 % (SC5) to maximal ±13% (SC2; calculated from the standard errors in **Table 5.2**); the variation between the five subsequent treatments was below 5% for all Table substances (**Table 5.2**). Thus, we consider the application as uniform and reproducible.

The apparent sorption coefficients calculated according to Eq. 5.2 differed substantially
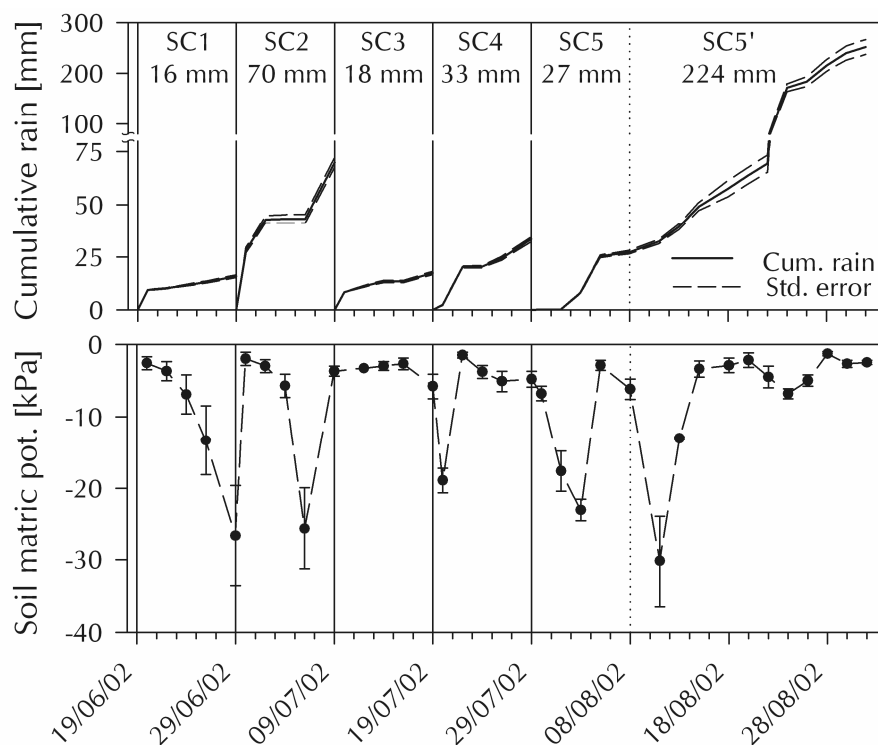
Figure 5.1: *Cumulative precipitation during the five sampling cycles (SC1–5) and matric potential of the topsoil (0.1m depth). Means and standard errors (precipitation: n=6; matric potential: n=3).*

from the "constants" reported in literature. The lowest $K_{OC(app)}$ for endosulfan-α measured during our experiment was only 38% of the K_{OC} suggested by Hornsby (1996), the highest $K_{OC(app)}$ for dimethoate was the 128fold of the tabulated value (**Table 5.3**). 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 datasets (Wauchope *et al.*, 2002). The 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. malathion maximum; **Table 5.3**) reveal the difficulties associated with exact pesticide analyses of heterogeneous field-fresh samples. It was not possible to further homogenize the samples: Due to their high clay content of 35% (Ciglasch *et al.*, 2005) 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 (Altfelder *et al.*, 1999), and harsher homogeneization 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 undisturbed field fresh samples (Ball & Roberts, 1991).

Besides the problem of sample heterogeneity, we had to face the problem of low pesticide concentrations in the CaCl$_2$-extract. Hence, for the calculations of the $K_{D(app)}$ (Eq. 5.1) the concentrations of sorbed pesticides were divided by a very small number, and thus, minor differences in the absolute concentrations in the CaCl$_2$-extract could

Table 5.3 Sorption coefficients (normalized to the OC content of the soil, K_{OC}) of pesticides reported in literature (Hornsby et al., 1996) and range of apparent K_{OC} values ($K_{OC(app)}$) observed in our experiment. Standard errors (n=2) in parantheses

Substance	K_{OC} (literature)	$K_{OC(app)}$ (field experiment)	
		minimum	maximum
	———————— [ml g(OC)$^{-1}$] ————————		
Endosulfan-α	12400	4713 (1211)	33584 (6460)
Endosulfan-β		5862 (1599)	46353 (7340)
Chlorpyrifos	6070	12477 (1066)	34401 (8451)
Malathion	1800	927 (118)	17620 (12868)
Dimethoate	20	200 (3)	2565 (297)
Mevinphos	44	152 (41)	1387 (277)

have a large influence on the resulting $K_{D(app)}$. In the aqueous extracts of the first two sampling cycles (SC1 and SC2), the effluent from the SPE cartridge was not dried over Na_2SO_4 (see Materials and methods). Most likely because of traces of residual water, dimethoate could not be quantified reliably in these samples, and $K_{OC(app)}$ values could not be calculated. Because this accounts only for the $CaCl_2$-extracts, the MAR could nevertheless be computed. The problem was solved by the additional drying step (recovery of dimethoate from a spiked sample: 104.8%±0.1% (mean and standard error, n=2); data not shown). Because we took our samples in high temporal resolution relatively large datasets were available. That is why we could observe some clear dynamics in the binding status of the pesticides despite all constraints outlined in this subchapter. To present and discuss these results in the next chapters, we grouped the substances according to their chemical groups and hydrophobicity.

5.4.3 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 5.3**). The formulation of endosulfan we applied contained α and β isomers, which we analysed separately. Their ratio was 2:1 (**Table 5.2**), which is typical for technical endosulfan (Tomlin, 2000). The course of $K_{OC(app)}$ of both isomers looks almost identical (**Figure 5.2a**), 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. The increase of $K_{OC(app)}$ significantly correlates 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 (Pignatello & Huang, 1991).

As un-aged fresh material was added every ten days (multiple applications; see **Chapter 5.3.2**), we assumed that $K_{OC(app)}$ would increase within one SC followed by a drop after the next application on a level somewhat higher than at the beginning of the previous SC, reflecting the co-existence 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 5.2a**), but not at the transition from SC1 to 2 and SC 2 to 3: Within SC1, the raise 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 (Pignatello & Xing, 1996). SC2 was significantly wetter than SCs 1 and 3–5 (**Figure 5.1**). The resulting higher soil matric potential in SC2 might have helped to keep the endosulfan in an easily extractable state. As rigid domains are considered to be surrounded by fresh, gel-like organic matter (Pignatello, 1998) it is possible that the length of the diffusion path to the rigid zones is simply longer under wet than under dry

conditions, because the outer layer of the organic substance is fully swollen (and thus thicker) when wet. Thus, the relative importance of partitioning might be enhanced simply due to a reduced accessibility of the (glassy) adsorption sites for this apolar compound. Although we cannot test explicitly whether the dual reactivity model (DRM) described in the introduction fully applies to the sorption of endosulfan under our experimental conditions, this model suggests another explanation for the enhanced aging in SC3 compared with SC2: An increase in water content of the organic matter significantly reduces the glass transition temperature (T_g), that means the temperature where organic substances transcends from the glassy to the rubbery state (Schaumann & Leboeuf, 2005).

Leboeuf & Weber (1997) showed that the linearity of sorption isotherms (and thus
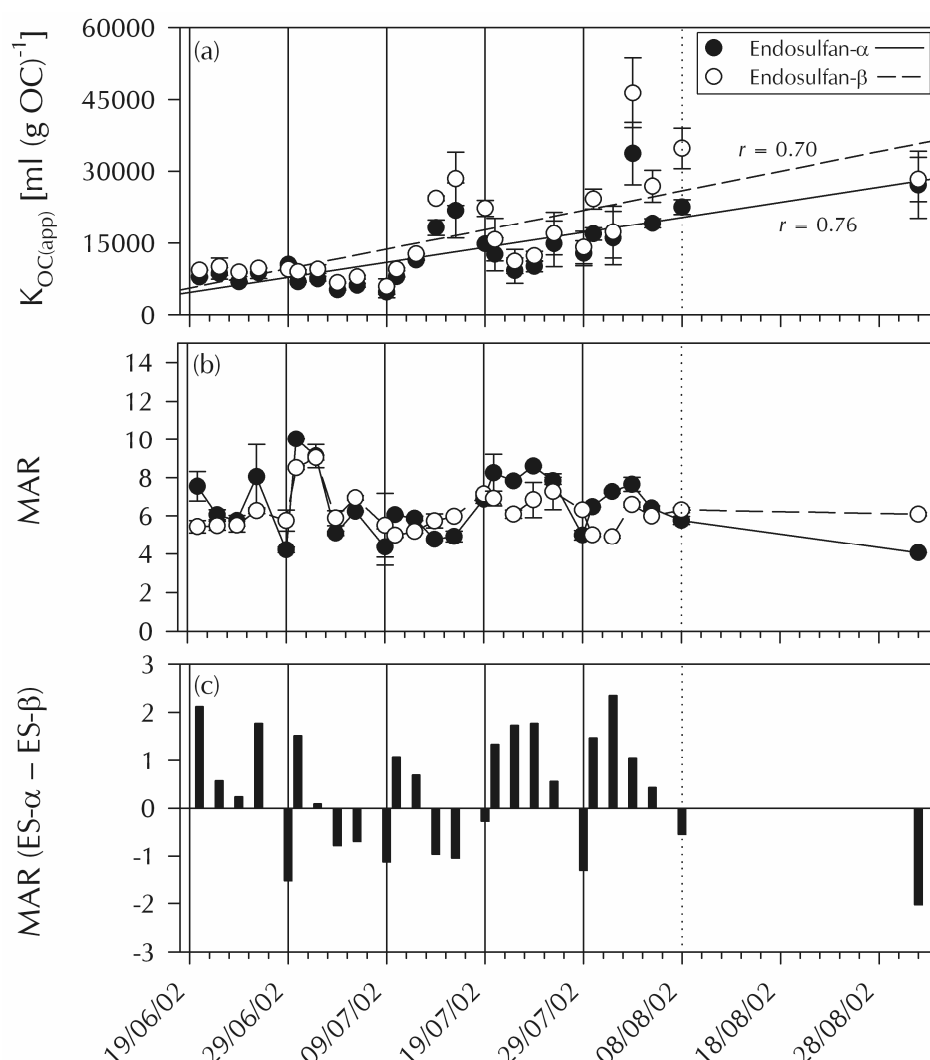
Figure 5.2: *Field aging of endosulfan isomers α and β after application to a tropical Acrisol. (a) shows the temporal course of apparent sorption coefficients ($K_{OC(app)}$; with linear regressions); (b) the methanol : AEW (acetone : ethylacetate : water; 3:1:1 by volume) ratios (MAR; means and standard errors, n=2). In (c) the differences between the MARs of endosulfan-α and β (data from (b)) are plotted. Vertical lines mark the application dates.*

reversibility of sorption) increases the closer the temperature of the experiment gets to T_g of the sorbent (which was, in their study, 43°C for water-wet humic acid). Consequently sorption reversibility should also be increased if, at a given temperature (determined by the relatively constant temperature conditions during our experiment), T_g is reduced by an increase in water content. The reduction in T_g after swelling of the organic matter is explained by the fact that sorbed water may disrupt intermolecular bonds within the organic matter, which reduces the energy needed to convert glassy to rubbery structures (Leboeuf & Weber, 2000a). We assume that in SC3, the opposite has happened. During the whole SC3, only 25% of the precipitation of SC2 fell (**Figure 5.1**). Although, due to the fine texture of the soil, the tensiometers did not react significantly on this dry phase before the end of SC3 it can be expected that the organic matter started to dry up and to contract, which should lead to an increased non-linearity of sorption and decreased desorption rate (Altfelder *et al.*, 1999). 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, $K_{OC(app)}$ decreased again sharply, especially after the soil had re-wetted on 22 Juli (**Figure 5.2a**). Thus, the DRM seems to be an adequate model to describe observed course of $K_{OC(app)}$ for both isomers. That is why we conclude that, after an initial lag during SC1, the organochlorine insecticide endosulfan underlies "classical" aging in the studied Acrisol.

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 and degradation (Koskinen *et al.*, 2001). Because microbes are able to adapt to HOC degradation (Ragnarsdottir, 2000) 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 (Johnsen *et al.*, 2005). However, as endosulfan accumulates in the soil of the research plot, and as the DT_{50}s of endosulfan do not shorten significantly from one SC to the next (**Table 5.1**) the increase of $K_{OC(app)}$ must, at least partly, go back on a an actually growing binding strength over time, that 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 5.2a**).

Although endosulfan is often treated as one single substance, the two isomers exhibit different affinities to the soil and its organic matter. The sorption coefficient of endosulfan-β was systematically higher than of endosulfan-α (**Figure 5.2a**). 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 stronger sorbed during aging which should be reflected by a shift from the MeOH into the AEW fraction. 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 5.2b**; $r=-0.17$ 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 re-fractionation within the sorbed fraction. Plotting the differences between the MARs of endosulfan-α and β, however, (**Figure 5.2c**) 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. We explain this observation by the fact that during microbial degradation, small portions of endosulfan-α can be transferred to endosulfan-β by *Pseudomonas* sp. (Perscheid *et al.*, 1973), so that there might be a constant input of MeOH-extractable endosulfan-β, whereas this pool is decreased for endosulfan-α.

5.4.4 Chlorpyrifos and malathion

Among the substances we investigated, chlorpyrifos and malathion have intermediate hydrophobicities (**Table 5.3**). Nevertheless, on the first sampling day, the $K_{OC(app)}$ of both substances was higher than for endosulfan (**Figure 5.3a**), 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 hours (time span between application and first sample) and, thereafter, does not underlie any form of field aging. The MAR revealed that the latter is not true (**Figure 5.3b**), as we observed a constantly ongoing re-fractionation of chlorpyrifos from the MeOH- to the AEW-extractable fraction, which resulted in a continuous decrease in MAR with time. Hence, just like endosulfan, also chlorpyrifos underlies field aging processes. However, it is obvious from our data that different structures or domains within the SOM are involved, because aging is 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, it has to be tested whether this difference holds up in the long term: Our experiment lasted several weeks only, whereas aging processes can evolve and go on
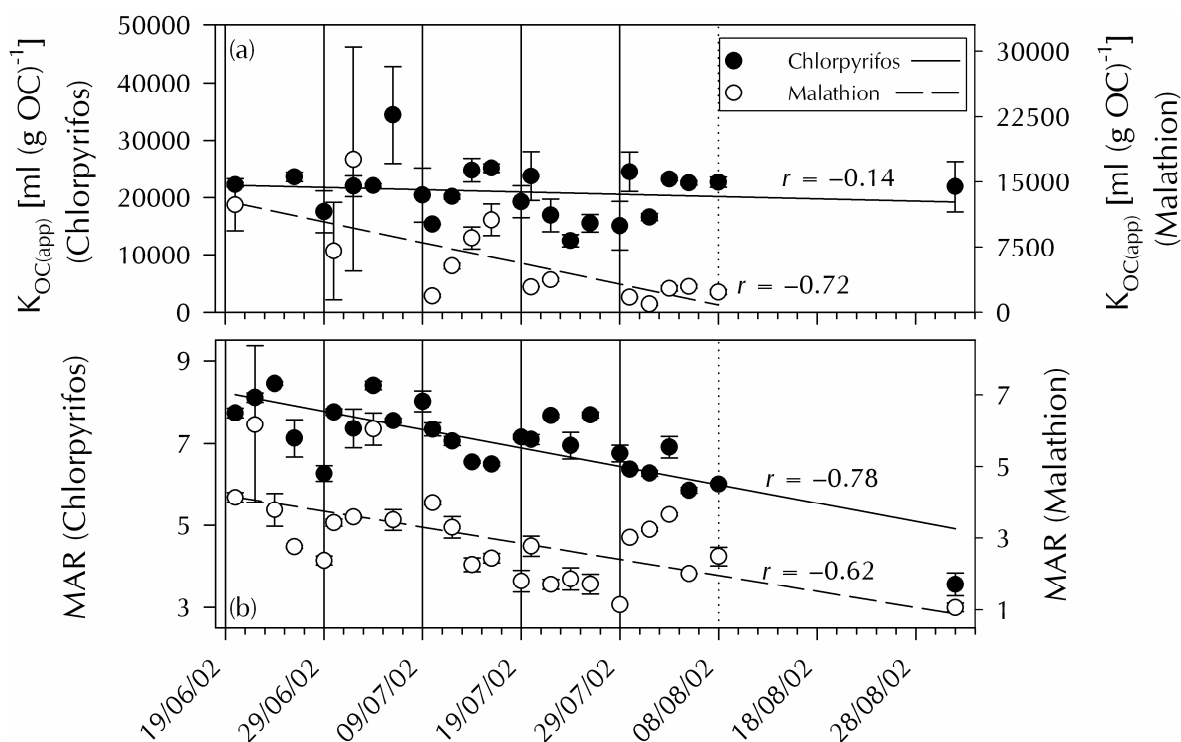
Figure 5.3: *Field aging of chlorpyrifos and malathion after application to a tropical Acrisol. (a) shows the temporal course of apparent sorption coefficients ($K_{OC(app)}$; with linear regressions); (b) the methanol : AEW (acetone : ethylacetate : water; 3:1:1 by volume) ratios (MAR; means and standard errors,* n=2*). Vertical lines mark the application dates.*

over years (Hatzinger & Alexander, 1995). Thus, it is possible that the differences in aging we observed here in the initial phase might vanish later on.

Malathion shows an overall decrease in $K_{OC(app)}$ during our experiment, which is unique for the insecticides we studied (**Figure 5.3a**). 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. However, 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 during our study. This clearly contradicts the concept of aging. The results appear even more paradox when the MAR is taken into account, because just as described for chlorpyrifos, this coefficient decreases over time, indicating an aging process (**Figure 5.3b**). Thus, it occurs as if malathion that was associated to 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 (2000) who reported that previously unextractable malathion became biodegradable after ca. 200h

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 (Pesticides Safety Directorate, 1995), and malathion is rather easily degradable by soil microbes (DT_{50} = 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 higher degradation rate than the water- and the AEW-extractble fractions, possibly due to surface-catalyzed microbial decay (Freed *et al.*, 1979). Such degradation, however, would not result in a 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 underlies very intense dynamics, and that it is reasonable to assume that this dynamics is related to some kind 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.* (2004), who reported that herbicide bioavailability to *Pseudomonas* sp. significant correlates significantly with extractability by methanolic solvent.

5.4.5 Dimethoate and mevinphos

Dimethoate and mevinphos have the highest water solubilities of the studied substances (24 g l^{-1} and completely miscible; Tomlin, 2000). As discussed before, 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 forth application it dropped back to a value just slightly higher than at the beginning of SC3 and raised again (**Figure 5.4a**). 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 raise in $K_{OC(app)}$ was less steep than 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 (**Figure 5.2a** and **Figure 5.3a**), 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 5.2**). Thus, dimethoate clearly shows field aging. However, dimethoate dissipates rapidly (**Table 5.1**), so that part of the increase of $K_{OC(app)}$ is probably caused by dissipation of the labile pool and not by an increase in sorption strength. 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
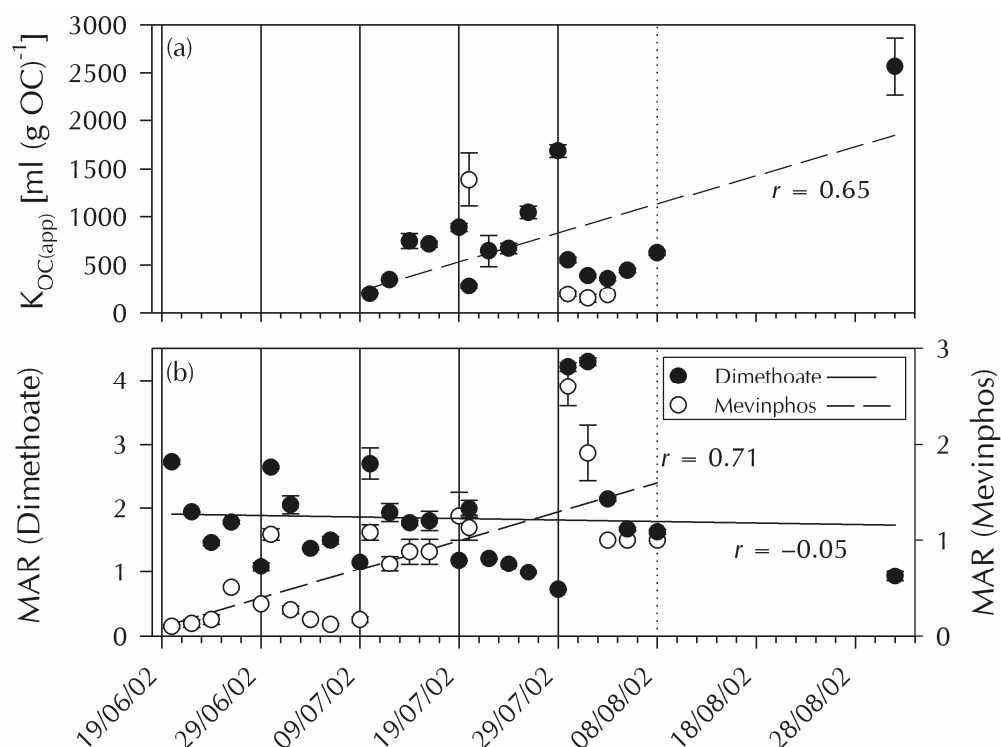
Figure 5.4: *Field aging of dimethoate and mevinphos after repeated application to a tropical Acrisol.* *(a) shows the temporal course of apparent sorption coefficients ($K_{OC(app)}$; with linear regressions); (b) the methanol : AEW (acetone : ethylacetate : water; 3:1:1 by volume) ratios (MAR; means and standard errors, n=2). Vertical lines mark the application dates. In SC1–2 no $K_{OC(app)}$ could be determined for dimethioate; see text for discussion.*

SC. This contrasts the pattern of aging of endosulfan, where the increase in $K_{OC(app)}$ is more a constant raise than a repeated pattern. We therefore conclude that the relative impact of previous applications on the $K_{OC(app)}$ measured in a later SC is higher for endosulfan than for dimethoate.

Like the $K_{OC(app)}$, also the MAR of dimethoate 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 5.4b**). Hence, also in the second coefficient, dimethoate showed aging within each SC. Due to 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 $K_{OC(app)}$ also the MAR 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 4a). Obviously, volatilization, leaching and degradation of the $CaCl_2$-extractable pool were so fast that it was instantaneously depleted (min. DT_{50} 1.4

d; **Table 5.1**). Consequently, even to a greater extent than 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 the more pronounced the higher the water-solubility (and thus the leaching potential and the biodegradability) is.

In contrast to all other substances studied, the MAR of mevinphos did not drop or remain constant, but it rose (Figure 4b; $r=0.71$) 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 (Ahmad *et al.*, 2004). That is why also mevinphos might undergo aging processes in the long term, even is the opposite is indicated here for the short term.

5.5   Conclusions

In our study, we observed aging phenomena for all studied substances except mevinphos although (i) "fresh", un-aged 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 due to 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 related to polarity of the compounds. Only the most hydrophobic compound (endosulfan) showed a steady raise of $K_{OC(app)}$, that means aging in the previously described form. This is in line with the results of **Chapter 4,** where endosulfan was the substance with the highest rate of accumulation in the studied orchard. Aging of pesticides with intermediate hydrophobicity (chlorpyrifos and malathion) could only be revealed by conducting sequential extractions of the soil and introducing the MAR as a new partitioning coefficient. 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, the MAR turned out to be more "robust" than the conventional partitioning coefficient, resulting in smaller standard errors and more complete data sets of the MAR than of the $K_{OC(app)}$. Processes known to 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 investigated explicitly in our study, our study might support the hypothesis that MeOH-extractable fraction is bioavailable for microorganisms. To improve the understanding of aging processes on 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, sophisticated laboratory experiments are necessary, however. Therein, not only the interaction between sorbent and sorbate with model substances should be studied on the microscale, but we also have to gather tangible knowledge on which pools are actually and truly accessed by the manifold of different extractants suggested in literature and how soil biota influence the process of aging.

6 Runoff and leaching of repeatedly applied pesticides in a sloped lychee orchard

6.1 Summary

High-quality production of tropical fruits requires repeated application of plant protection products, but consequences of this practice to the surrounding environment are only poorly understood. We assessed the surface runoff and leaching of insecticides in a 15°-slope lychee orchard in Thailand. Runoff was collected in metal troughs and leachate in 55-cm deep lysimeters. At 10-day intervals we carried out five consecutive applications of a six-insecticide "cocktail" directly to the soil surface. This routine built up a such a large pool of dischargable pesticides that, despite exceptionally low precipitation (156.7 mm, which was 22.6% of same period the year preceding our study), more than 200 mg ha^{-1} of malathion (total of leaching + runoff) was washed off. Peak concentrations were 3200 µg l^{-1} of malathion in runoff and 18 µg l^{-1} of dimethoate in leachate. Because these concentrations clearly exceeded toxicity levels tabulated for aquatic species (up to 1700fold, malathion), the environmental impact of lychee cropping needs further assessment, for example by event-triggered river-water monitoring.

6.2 Introduction

In the mountainous regions of Northern Thailand, fruit orchards are regarded as sustainable alternative to the cultivation of annual crops such as vegetables. The widespread lychee (*Litchi sinensis* Sonn.) plantations maintain a forest-like structure similar to indigenous vegetation, and the continuous cover by ground vegetation minimizes erosion. However, these considerations do not take into account that Thai lychee production requires high doses of insecticides and fungicides applied in 10 to 14-day intervals during fruit ripening. Such repeated use maintains a pool of readily available pesticides prone to surface runoff or leaching. Thus, even though dissipation times of pesticides in the tropics may be short (Laabs *et al.*, 2002a; **Chapter 4**), these substances can have negative effects on adjacent aquatic populations (Schulz, 2004). Because high temperatures promote biological uptake and metabolism of xenobiotics, tropical aquatic ecosystems are particularly sensitive to pesticide input and have been suggested as priority areas for toxicological research (Castillo *et al.*, 1997).

Spray drift, a point source of river water contamination, occurs exclusively during the application itself (Ganzelmeier *et al.*, 1995). Contrastingly, discharge of pesticides from the treated area can lead to diffuse inputs into surface waters for weeks after application, either directly by runoff (Wauchope, 1978) or indirectly when leachate drains into surface water (Flury, 1996). Because rain may pick up pesticides throughout the whole

catchment before concentrating them in the river, peak concentrations in river water during runoff events may substantially exceed those caused by spray drift (Schulz, 2001). Therefore, Dabrowski & Schulz (2003) recommend focusing mitigation efforts on runoff rather than on spray drift. Flury (1996) and Wauchope (1978) reported that leaching and surface runoff may each result in a loss of ca. 0.5 – 1% of the applied amount (up to 5% under extraordinary circumstances). Also on our research site in north Thailand, a single heavy rainstorm leached more than 1 % of the applied dimethoate into samplers installed in 55 cm soil depth (**Chapter 3**).

Although surface runoff and leaching are interdependent processes, they have rarely been investigated simultaneously (for fruit orchards, see Merwin *et al.*, 1996), and no generally accepted methods exist for this purpose. In plots without any constructed boundaries that limit the contributing area, surface runoff is often studied with so-called Gerlach troughs (Gerlach, 1967; Loughran, 1989). These are simple metal troughs that are installed perpendicular to the axis of slope and collect water and sediment in an attached container. To balance vertical fluxes (leaching), lysimeters generally are more suitable than suction cups (for example, Magid & Christensen, 1993). At present, however, many different types of lysimeters exist. For a temperate sandy soil, Siemens & Kaupenjohann (2004) compared the sampling efficiency of *active* glass lysimeter plates with *passive* wick lysimeters. The glass lysimeter plates had an adjustable, tension-controlled vacuum ("suction plates"). The wick lysimeters were simple pan lysimeters equipped with a fiberglass wick to improve the contact between soil and lysimeter and to apply a small tension to the lysimeter by a hanging water column (Boll *et al.*, 1992). The authors found that both techniques are appropriate to monitor water and solute fluxes at high soil water content, but wick lysimeters performed worse when the tension of the soil increased and the capillary forces of the soil exceeded those of the wick. Despite this shortcoming, wick lysimeters still have a better sampling efficiency than zero-tension lysimeters, and they are more robust and much easier to operate than suction plates (Holder *et al.*, 1991). The latter arguments might be especially relevant under tropical field conditions, where wick lysimeters have been successfully introduced to monitor pesticide fluxes (Laabs *et al.*, 2002a).

In a preceding study (**Chapter 3**), we elucidated the variation of water flow in a Northern Thai lychee orchard and demonstrated that pesticide concentrations in leachate peak after the first rainfall following the treatment. If the spraying is repeated frequently, and if monsoonal rainstorms occur more or less randomly throughout the spraying season, the risk that a rainstorm falls shortly after the treatment increases the oftener pesticides are sprayed. Therefore the local agricultural practice of at least fortnightly applications during fruit ripening bears the risk of substantial pesticide losses. This is true both for leaching and surface runoff; the latter, however, has not yet been investigated in our research area. Hence, the major soil processes of pesticide

leaching in the studied orchard are known, but comprehensive data on the overall fate of pesticides in Thai lychee orchards is still lacking. Thus, to further contribute to an evaluation of the sustainability of fruit cropping in Northern Thailand, the objective of our work was to measure simultaneously leaching and surface runoff of repeatedly applied pesticides.

6.3   Materials and methods

6.3.1   Research site

We conducted our experiment on a lychee orchard in Northern Thailand (18°53' N, 98°52' E). Due to former use for rice cultivation some decades ago, the slope still was slightly terraced so that relatively steep "steps" (microslopes) alternated with more or less even surfaces (microplains); the overall inclination was ca. 15° (**Figure 6.1**). The elevation was 820 m above sea level, and a creek passed the plot farther down the slope on 780 m. Mean annual precipitation was 1600 mm with distinct dry (November to April) and wet seasons (May to October). The 10 to 15-year-old trees were about 2.5 m tall and planted in a grid of 10 by 10 meters; the interspace was covered with grass and herbs that were mown fortnightly with a motorised scythe. The soils of our study area are fine, kaolinitc thermic Hapludults (Soil Survey Staff, 1998; Ciglasch *et al.*, 2005).
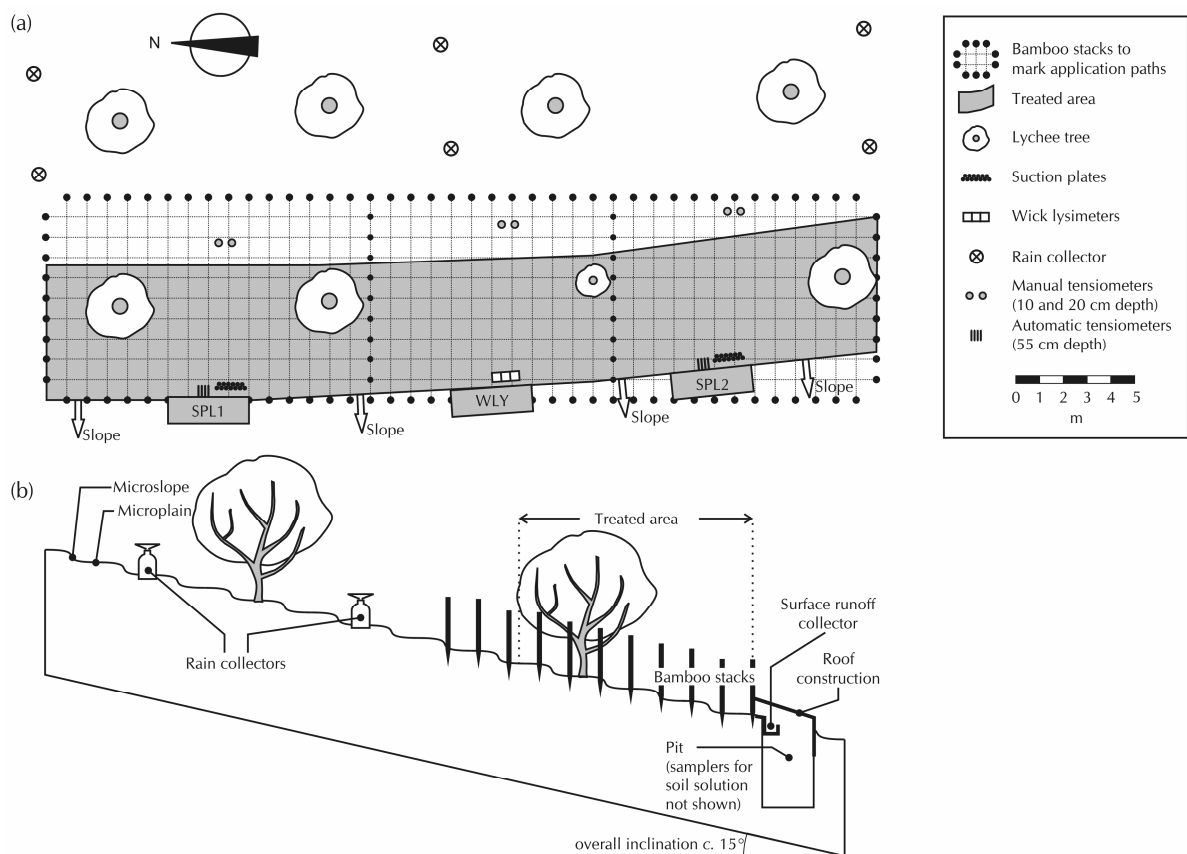
Figure 6.1: *Layout (a) top view, (b) cross section, of sloping plot established in a Northern Thailand lychee orchard to determine runoff and leaching of pesticides applied to the soil.*

6.3.2 Field experiment

For an experiment we conducted the year before (**Chapter 3**), we had equipped two soil pits with suction plates. Unfortunately during the dry season between the experiments ca. one third of the suction plates developed cracks, probably because they were connected too firmly to inflexible stainless steel tubes, making it impossible to compensate any subsidence (or other movement) of soil. Thus, we had to re-arrange the remaining plates, leaving us 10 suction plates in plot SPL1 and 13 in plot SPL2, all placed at the B1–B2 horizon transition in 55 cm soil depth (**Figure 6.1**). The suction plates were made of borosilicate glass ($\varnothing$ 90 mm; ecoTech, Bonn). A computer-based suction control system (SCS-8, UMS, München) measured the soil matric potential every 20 seconds (4 tensiometers per pit) and applied a vacuum equivalent to median soil tension to the suction plates so that percolating water could enter the suction plates similar to infiltration into the surrounding soil. The soil solution was then sucked through an online solid phase extraction system that was set up as described earlier (Nikolakis *et al.*, 1999; **Chapter 3**), except that 8 mL columns with 500 mg of graphitized non-porous carbon (Carbopack, Supelclean ENVI-Carb SPE Bulk Packing 120/400 mesh; Supelco, Bellefonte, PA) instead of 3 mL columns with 300 mg of Carbopack were used.

Between SPL1 and SPL2 a third soil pit was opened. In a vertical trench 55 cm below the soil surface, we installed a row of 3 wick lysimeters (stainless steel, 25 by 25 cm², lateral installation depth from the pit: 50 cm, **Figure 6.1a**). The design of these lysimeter was described in detail by Laabs *et al.* (2002a). Briefly, we inserted fiber-glass wicks (#1381, Pepperell Braiding Company, Pepperell MA) through the outlet of the lysimeters. There, they hung down 30 cm, causing a suction of max. 3 kPa when wet. We wrapped aluminum foil around the hanging part of the wick to reduce evaporation of water. To improve the drainage of water out of the lysimeter, we filled them with a layer of quartz gravel and a layer of quartz sand; both materials had been combusted prior to use to remove organic residues. The part of the wicks which was inside the lysimeter was then spread out onto the sand layer to cover as much of its surface as possible. The resulting filling level of the 8-cm high lysimeters was 5 cm. Consequently, we pushed the lysimeters 3 cm into the soil. These 3-cm high rims served to improve sampling efficiency by reducing the amount of water flowing around the lysimeter under unsaturated conditions. All three pits (SPL1–2 and WLY) were equipped with surface runoff collectors (SRC, stainless steel, length 2.5 m) to collect water flowing down the edge from microplain to microslope (**Figure 6.1b**). Both surface runoff and soil solution from the wick lysimeters were collected in amber glass bottles (2.5 l for surface runoff collectors, 1 l for wick lysimeters).

Adjacent to the area where pesticides were applied, we installed 3 tensiometers each in 10 and 20 cm soil depth (in a slope position comparable with the position of the automatic tensiometers installed in the soil pits; **Figure 6.1b**). Six rain collectors served to monitor the small scale spatial variability of precipitation. For the calculation of water fluxes, hourly data on precipitation amounts were provided by Klaus Spohrer, University of Hohenheim, who operated a weather station on the orchard. Tensiometers and rain collectors were not installed directly within the treated area to prevent them from contamination with pesticides upon application and to avoid disturbance of the plot when reading them. Both precipitation and soil tensions were recorded between 9:00 am and 10:00 am on every sampling day (every 1 –3 days, see below). Therefore, the readings we obtained from the manual tensiometers probably do not reflect the actual matric potentials with perfect accuracy, because we probably missed minimum values resulting from strong evaporation in the afternoons as well as maximum values caused by heavy rainfalls in the evenings.

From 19 June to 29 July 2002, we carried out five consecutive applications of pesticides (10-day intervals; sampling cycles SC 1–5). Each time, six insecticides (one combined "spraying cocktail" of commercially available formulations) were sprayed directly onto the soil surface of the experimental plot with a manual backpack sprayer. Of course, farmers do not apply the pesticides onto the soil, but into the crown of the trees. Thus, our treatment will reflect a worst-case scenario for the area between the trees, but it might be representative for the soil close to the trunks where spray-drift precipitates on the soil surface.

Before the first application, we marked the walking paths for the spraying person with a rectangular grid of bamboo stacks in order to ensure an even distribution of the spray (**Figure 6.1**). The active ingredients were: chlorpyrifos, dimethoate, endosulfan (α and β isomers), malathion, and mevinphos. The application rates were ca. 2 (mevinphos) to 6 kg ha^{-1} (endosulfan, chlorpyrifos; **Table 6.1**). Both the substances and the repeated applications are common in the studied production system. However, the dose we applied was 2 – 5 times greater. Furthermore, the substances are usually applied as single components and not simultaneously. This practice was changed to study pesticides with a variety of physicochemical properties (**Table 6.1**; (Tomlin, 2000)) under identical weather conditions. None of the agents had been used on our plot for at least 12 months. Six glass-fiber filters ($\varnothing = 6$ cm) were randomly placed on the plot before each application to control uniformity of deposition (S.E. within one application: < 13%; S.E. between applications: < 4%; data not shown).

Table 6.1: Chemical names, water solubilities (Tomlin, 2000), application rates (mean and standard error of 5 applications) of pesticides repeatedly applied to the soil of a lychee orchard in Northern Thailand and cumulative fluxes of pesticides in surface runoff (SRC, surface runoff collector; n=3) and leachate (WLY, wick lysimeter; n=3). The relative recovery %$_{appl}$ was calculated on the base of column 2 (that means 100 % = 1 of the 5 applications), contributing areas of the SRCs were defined as 15m²

Common name	Chemical name
Endosulfan-α	((3α,5aβ,6α,9α,9aβ)- 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide)
Endosulfan-β	((3α,5aα,6β,9β,9aα)- 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide)
Chlorpyrifos	(*O,O*-diethyl (*O*-3,5,6-trichloro-2-pyridinyl) phosphorothioate)
Malathion	(*S*-1,2-bis(ethoxycarbonyl)ethyl *O,O*-dimethyl phosphorodithioate)
Dimethoate	(*O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate)
Mevinphos	(1-Carbomethoxy-1-propen-2-yl dimethyl phosphate)

Common name	W.S.	Mean appl. rate	— Cum. flux SRC —		— Cum. flux WLY —	
	(mg l⁻¹)	(kg ha⁻¹)	(mg ha⁻¹)	(%$_{appl}$)	(mg ha⁻¹)	(%$_{appl}$)
Endosulfan-α	0.33	4.71 (0.18)	1.4 (0.9)	2.9 10^{-5}	130 (7.8)	2.8 10^{-3}
Endosulfan-β		2.33 (0.09)	4.6 (3.1)	2.0 10^{-4}	67 (4.1)	2.9 10^{-3}
Chlorpyrifos	2	6.42 (0.25)	1.6 (1.0)	2.4 10^{-5}	52 (3.8)	8.1 10^{-4}
Malathion	145	4.23 (0.15)	150 (120)	3.5 10^{-3}	57 (5.4)	1.3 10^{-3}
Dimethoate	24000	4.45 (0.17)	75 (55)	1.7 10^{-3}	150 (74.0)	3.3 10^{-3}
Mevinphos	c.m.	1.87 (0.08)	19 (15)	1.0 10^{-3}	n.d.	

c.m. = completely miscible
n.d. = not detectable

On day 1, 3, 5, 7 and 10 after application the solid phase extraction cartridges in the soil solution sampling device were exchanged and surface runoff and leachate from the wick lysimeters (if present) were collected. The sampling on day 10 was followed by the subsequent application. All samples were immediately put on ice and transported to the laboratory within 2 hours on normal sampling days or within 5 hours on application days. There, the SPE cartridges were frozen (–18 °C) until re-extraction; the other samples were immediately processed as described below.

6.3.3 Laboratory analyses

Samples from the wick lysimeters and surface runoff collectors were vacuum-filtrated through glass-fiber filters (GF6, Schleicher and Schuell Microscience, Dassel) to

remove soil particles (leachate) or floating organic matter (surface runoff) from the solutions. The filters were thoroughly washed with a surplus of de-ionized water. The filtrate was then quantitatively sucked through solid phase extraction cartridges as used in the soil solution sampling device (Ciglasch *et al.*, 2005). Afterwards, the cartridges were dried for ca. one minute in a stream of air and stored at –18 °C until re-extraction.

All cartridges were freeze-dried overnight before elution with 4 ml of methanol and 10 ml of a 9:1 (by volume) mixture of dichloromethane (DCM) and methanol (Di Corcia & Marchetti, 1991). The effluent was collected in pear-shaped flasks, and 50 µl of internal standard containing 5µg each of α-HCH (hexachlorocyclohexane) and terbuthylazine (N2-*tert*-butyl-6-chloro N4-ethyl-1,3,5-triazine-2,4-diamine) were spiked into the flasks. We added 150µl of toluene to prevent the samples from drying during the subsequent rotoevaporation of methanol and DCM. Despite freeze-drying before the elution step, some samples appeared to contain small residues of waters. To dry these samples, we plugged glass funnels with small amounts of glass wool and filled them with anhydrous Na_2SO_4 (oven-dried at 300°C overnight). After thorough rinsing of the funnels, the samples were washed through with a surplus of DCM. We collected the effluent in pear-shaped flasks and rotoevaporated the solvent. The residues were washed from the flaks into gas chromatography (GC) vials with additional 300 µl of toluene. We capped the vials and stored them at 4 °C until measurement. 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 full description of the GC method and its performance, see Laabs et al. (1999).

6.3.4 Numerical modeling

To evaluate the sampling efficacy of the soil solution sampling devices, we modeled water fluxes with the HYDRUS2d (V2.05) software package, a two-dimensional numerical model for water and solvent transport that is based on Richard's equation (Simunek *et al.*, 1999). Thickness of soil horizons was defined as observed in the field. The upper boundary condition was "atmospheric" (precipitation entered the soil as measured by the weather station; hourly data); the lower boundary condition was "free drainage" (in 1.5 m soil depth). Evapotranspiration, which was not measured directly, was assigned to 4 mm d^{-1}. The SPLs were represented by a rectangular box in the soil profile with "no-flux" conditions at the sides and at the bottom and "variable pressure" conditions at the top. As done in the field by the automatic suction control system that was connected to the suction plates, also in the model the variable pressure was permanently adjusted to the matric potential of the surrounding soil. In a first series of simulation runs, soil hydraulic parameters were estimated iteratively by fitting simulated soil tensions to measured data (inverse solution; soil hydraulic model: van Genuchten (van Genuchten, 1980); pore-connectivity factor l estimated to be 0.5

(Mualem, 1976)). After this parameterization, water fluxes were simulated in the "direct" mode of the model (forward simulation).

6.4   Results

6.4.1   Precipitation and matric potential of the soil

During the experiment, dry and rainy periods of several days each alternated, resulting in fluctuations of the matric potential of the topsoil (10 cm) from almost 0 to ca. –27 kPa (**Figure 6.2**). The matric potentials fluctuated less with increasing depth, so that in 55 cm, the automatically recorded tensions ranged only from ca. –2 to –12 and –17 kPa (profiles SPL1 and SPL2, respectively; **Figure 6.1b**). In SPL1, the increase in matric potential after rainstorms was steeper than in SPL2 (most clearly seen on 04 August 02, **Figure 6.2**), indicating a faster movement of water in SPL1 than in SPL2. Total rainfall during the entire experiment amounted to 156.7 mm, which was only 22.6% of the amount collected in almost the same period the year before (24 June – 17 August 2001; 693.1 mm). Also, rain intensities and frequencies were much lower than in the previous year (for example, 11 rain samples > 24 mm in 2001 but none in 2002; (Ciglasch *et al.*, 2005)). The median of the standard deviations between the 6 rain samplers (**Figure 6.1a**) was 1.7%, indicating low spatial variation of precipitation.
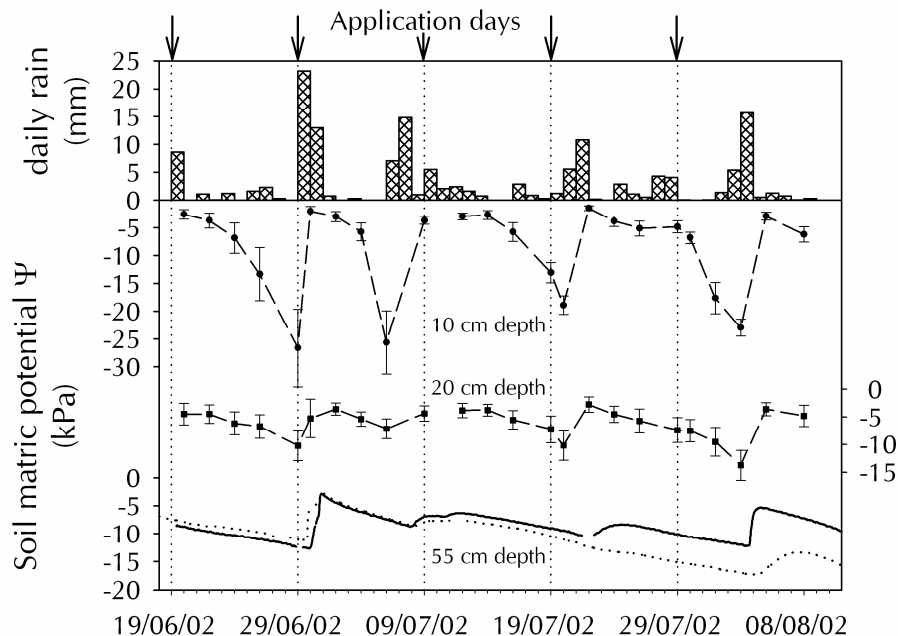
Figure 6.2: *Influence of rainfall on the soil matric potential at different soil depths below a lychee orchard in northern Thailand. In 10 and 20 cm three manually read tensiometers were installed (error bars indicate the standard errors); in 55 cm depth, two profiles were equipped with four automatic tensiometers each. Median values are shown as solid line for profile SPL1 and dashed line for SPL2.*

6.4.2 Surface runoff

Surface runoff occurred on five of the 25 sampling days, each of those times when the amount of precipitation exceeded the infiltration capacity of the soil, as indicated by topsoil matric potentials close to zero (**Figure 6.2**). Given the fact that samples were
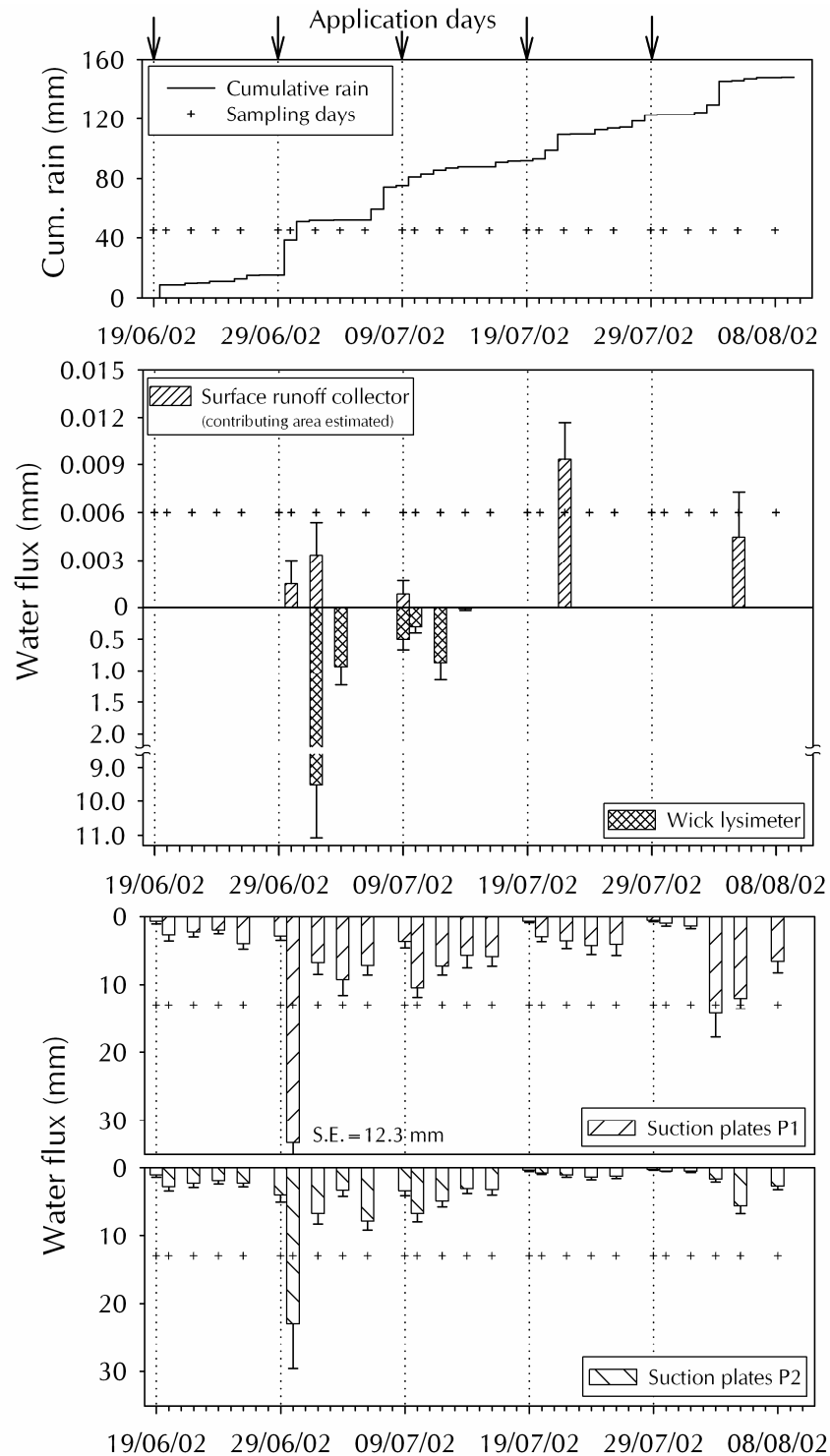
Figure 6.3: *Cumulative rain and water amounts collected on and below the soil of a lychee orchard in northern Thailand by three surface runoff collectors, three wick lysimeters, and 23 suction plates in two pits. Error bars indicate standard errors.*

collected only once every 1 to 3 days (as detailed in **Figure 6.3**), time lags might exist between the actual surface runoff event and the collection date. For example, the runoff sampled on 02 July 02 probably came from the rainstorm on 30 June 02, not to the minor precipitation event on 01 July 02. Similarly, the runoff collected on 22 July 02 likely came from two rainstorms, 20 and 21 July 02.

No physical boundaries defined the contributing area of the surface runoff collectors. Hence, we had to estimate it in order to relate the sampled volume to the amounts of precipitation and leachate (Loughran, 1989; Larsen *et al.*, 1999). We defined the whole area treated with pesticides (6 m uphill from the sampler) as the area that contributed the pesticide input. If, due to the terracing the slope, only the adjacent "microplain" (ca. 80 cm wide; see **Figure 6.1b**) delivered water to the surface runoff collectors, true runoff amounts would be underestimated by a factor of up to 7.5. Nevertheless, in terms of the water balance, even then the contribution of surface runoff to the total water balance was negligibe (0.002 vs. 0.017% of precipitation; calculated from **Figure 6.3**).

6.4.3 Leaching

The *passive* wick lysimeters delivered water only on six sampling days between 02 July 02 and 14 July 02 (**Figure 6.3**). Between 30 June and 01 July 02, two subsequent rainstorms (total: 36.2 mm) nearly saturated the profile with water (**Figure 6.2**). This wetted the wick and initiated a flux of soil solution ("self-priming"; (Laabs *et al.*, 2002a)) that persisted until field capacity was reached again. Because the matric potential of the bulk soil in 55 cm depth (installation depth of the wick lysimeters) did not rise above –3kPa (equivalent to the suction of the 30 cm long wick) throughout the remaining time of the experiment, the wick lysimeters collected no further percolate.

Contrastingly, at least some of the *active* suction plates provided soil solution samples on all sampling days. The level of vacuum applied to the suction system was essentially identical to the suction of the soil itself (data not shown, see **Chapter 3** for extended discussion) so that water was collected more effectively than by the wick lysimeters. Furthermore, due to their high spatial resolution, the SPLs also accounted for fingering, that means preferential flow through areas that have a higher hydraulic conductivity than the surrounding soil. This pathway is especially relevant when the soil is drying and may cause leaching even if the matric potential of the bulk soil has already fallen below field capacity (**Chapter 3**), that means when the wick lysimeters already stopped to deliver water. The total fraction of precipitation that leached into the samplers in 55 cm depth was 7.8 ± 1.5 % for the wick lysimeters and 77.7 ± 15.1 % for the suction plates (mean and standard error).

6.4.4   Numerical modeling

The model was optimized to match measured matric potentials (**Table 6.2**), so that the course of soil tension was depicted rather well by our simulations (see **Figure 6.4** for SPL2). Nevertheless, the model failed to simulate the steep increase in soil tension after the heavy rainstorms that occurred from 29 June to 01 July and 03 to 05 August 02. Accordingly, also the simulated cumulative water flux through the suction plates did not increase in relatively steep steps as observed in the field, but more or less continuously. Nevertheless, the total cumulative flux calculated from our simulation closely agreed with measured data (see **Figure 6.4** for SPL2), indicating that although our model could not simulate the velocity of infiltration into the soil profile, it *was* able to simulate the total movement of water through it. The increase in matric potential after rainstorms was even steeper in profile SPL1 than in SPL2 (**Figure 6.2**). That is why the model

Table 6.2: Effective hydraulic parameters of the soil identified by inverse simulation (profile SPL2; optimized to match measured soil matric potentials). θ_r = residual water content, θ_s=water content at saturation (both values provided by Klaus Spohrer, University of Hohenheim); α, n = parameters in the soil water retention function (van Genuchten, 1980); K_s = saturated hydraulic conductivity

Horizon and depth		θ_r	θ_s	α (cm^{-1})	n	K_s (cm d^{-1})
Ah	(0 – 20 cm)	0.18	0.41	0.02	1.66	18.6
Bt1	(20 – 55 cm)	0.19	0.41	0.03	1.54	78.5
Bt2	(> 55 cm)	0.24	0.42	0.03	1.57	8.0
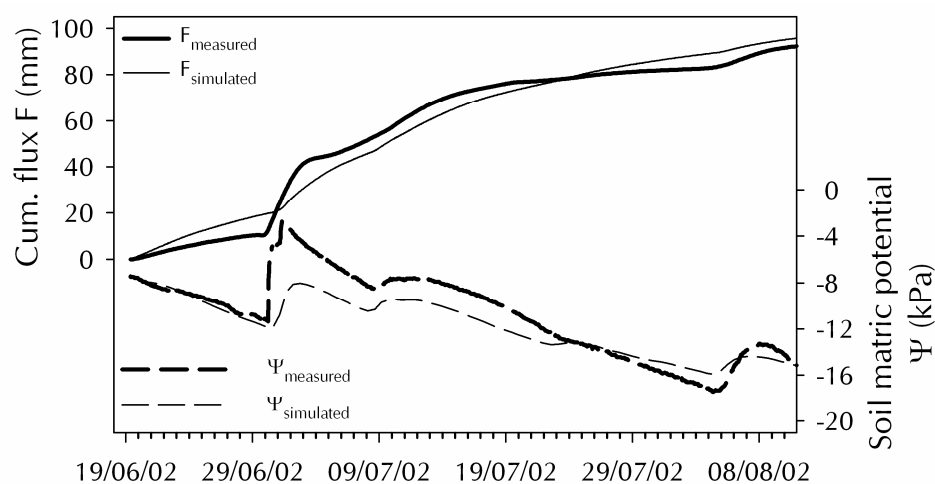
Figure 6.4: *Comparison between simulated and measured soil matric potentials and water fluxes through suction plates in 55 cm soil depth on a lychee orchard in northern Thailand. Results are shown for the profile SPL 2. (see **Figure 6.1**).*

matched measured potentials worse for SPL1 than for SPL2 despite intensive efforts of further optimization of parameters (data not shown).

6.4.5 Pesticide loads

Pesticides (most frequently endosulfan, data not shown) were detectable in several samples collected by the suction plates, but it was not possible to reliably *quantify* these due to unforeseeably low rainfall (see above) and thus small sample volumes (**Figure 6.5**), so no further results are presented here. Contrastingly, all samples from the surface runoff collectors and wick lysimeters contained all pesticides in sufficient amounts for quantification (**Figure 6.5**, **Figure 6.6**). The only exception was mevinphos, which we never detected in leachate. In surface runoff the concentrations of the polar pesticides (mevinphos, dimethoate, and malathion) generally were 10 to 100 times greater than for the unpolar pesticides (endosulfan and chlorpyrifos), whereas pesticide concentrations in soil solution were in a similar range for all substances studied (**Figure 6.6**). For the individual pesticides, the concentrations in surface runoff were 1 (endosulfan, chlorpyrifos) to 3 (malathion, dimethoate) orders of magnitude greater in surface runoff than in soil percolate.
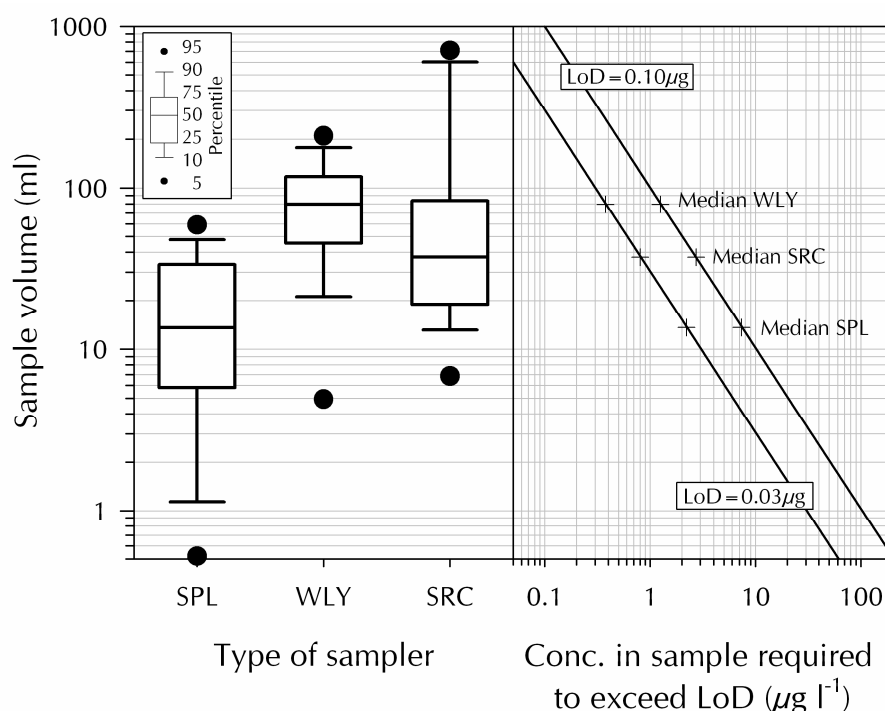
Figure 6.5: *Distribution of water amounts collected by suction plates (SPL; sampling volume = 0 ml excluded from the diagram; n = 567), wick lysimeters (WLY; n = 10), and surface runoff collectors (SRC; n = 16) and nomogram to show the concentrations of pesticides in samples needed to exceed the limit of detection (LoD) as a function of sampling volume. For example, to exceed the LoD of dimethoate and mevinphos (0.10 µg) in a "median" SPL-sample (13.6 ml) a concentration of 7.4 µg l^{-1} was needed; to exceed the LoD of endosulfan, chlorpyrifos or malathion (0.03 µg) in a "median" WLY-sample (79.5 ml), a concentration of 0.4 µg l^{-1} was sufficient.*
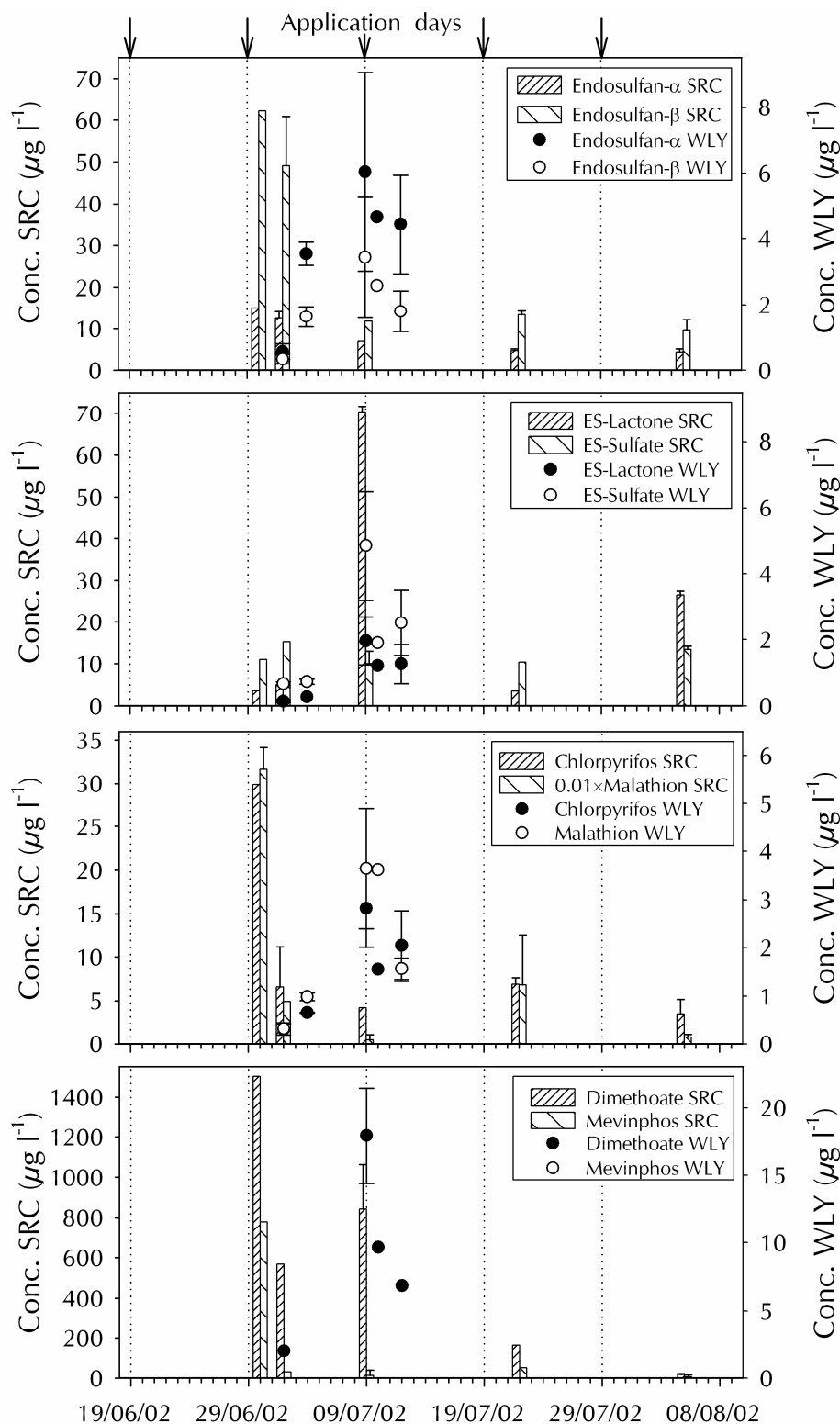
Figure 6.6: *Concentrations of pesticides in water samples from surface runoff collectors (SRC) and wick lysimeters (WLY). Error bars indicate standard errors; missing error bars show that only one of three sampling devices poured water. Note that measured concentrations of malathion in surface runoff were 100 times greater than plotted in the graph.*

The only time when several consecutive samples of both surface runoff and percolate could be collected was sampling cycle 2. During this period the pesticide concentrations in surface runoff clearly tended to decrease, while concentrations in percolate increased. This effect was most pronounced for malathion, which had a 70-fold decrease in concentration in surface runoff and a 20-fold increase in percolate during the cycle.

Total cumulative fluxes of polar pesticides in surface runoff amounted from 0.0010 % of one application (mevinphos) to 0.0035 % (malathion). For the unpolar pesticides, the fluxes were significantly lower (0.000024 % (chlorpyrifos) – 0.00020 % (endosulfan-β); **Table 6.1**). The cumulative amounts in leachate were similar for all pesticides (except mevinphos, which never was detected in soil solution, see above) and ranged from 0.00081 % (chlorpyrifos) to 0.0033 % (dimethoate) of one application. Thus, due to the higher relative sample volumes collected by the wick lysimeters (as compared with the surface runoff collectors, **Figure 6.3**) total discharge in soil solution was equal to discharge via surface runoff (polar pesticides except mevinphos) or even higher (unpolar pesticides).

The isomer ratio (α:β) of endosulfan in soil solution from the wick lysimeters was $1.97 \pm 0.15 : 1$ (mean and standard error of all samples), which corresponds well to the spraying cocktail ($2.02 \pm 0.01 : 1$). Contrastingly, in surface runoff, the isomer ratio ranged from $0.24 : 1$ (30 June 02) to $0.60 : 1$ (22 July 02; mean $\pm$ standard error: $0.38 \pm 0.07 : 1$). We detected both degradation products of endosulfan we investigated, lactone and sulfate, in all samples. In surface runoff, the concentration of endosulfan sulfate was almost constant ($10 - 15 \, \mu g \, l^{-1}$), whereas the concentrations of endosulfan lactone fluctuated from <3 to >70 $\mu g \, l^{-1}$. This resulted in a sulfate : lactone ratio of $0.14 - 3.1$. In percolate, however, this ratio changed little over time (2.7 ± 0.5). Both in surface runoff and percolate, the concentrations of metabolites of endosulfan tended to increase within the sampling cycles. The range of concentrations of endosulfan metabolites was similar to that of the parent compound (**Figure 6.6**).

6.5 *Discussion*

6.5.1 Water fluxes and numerical modeling

The numerical modeling of leaching showed that the water fluxes collected by our suction plates were realistic. The rapid leaching and large amount of percolate cannot be explained by matric flow alone, however, so we conclude that preferential flow must occur on our study site. Such a flow pattern is a common phenomenon in clayey tropical soils; clay particles often form micro-aggregates whose hydraulic conductivities are far below average rates of precipitation. This means that intra-aggregate bypass flow may occur even if the soil is not yet saturated (Radulovich *et al.*, 1992), and the apparent

hydraulic conductivities are much greater than expected from the texture of the soil. Consequently, the hydrologic parameters we fitted by inverse modeling have to be considered as "effective" parameters of the aggregated soil rather than "nominal" parameters of the soil matrix. We cannot quantify with the model we used the relative contributions of bypass and matric flow to total leaching.

The high infiltration capacity of the micro-aggregated soil is only one of the reasons why surface runoff was irrelevant for the water balance on our research site. Another is macropores, which may further enhance the infiltration of water (Chappell & Sherlock, 2005). The water arrived faster in profile SPL1 than in SPL2 (steeper increase in matric potential in SPL1), which led us to conclude that SPL1 contained more macropores than in SPL2, which also would explain (i) why it was impossible to simulate water fluxes properly with a model based on Richard's equation in profile SPL1 and (ii) why the suction plates in SPL1 collected larger amounts of percolate than did those in SPL2.The simulations probably would perform better if a dual porosity model (Durner, 1994) was used to parameterize the hydraulic properties of the soil. This was not an option for our simulations, however, because the dual porosity model is available only in the "direct" and not in the "inverse" mode of HYDRUS2d.

In an Oxisol in Brazil, soil water was reported to percolate into 30 cm depth within minutes after the onset of a rainstorm (Renck & Lehmann, 2004); in Udults under rainforest in Singapore, NaCl was detected in 50 cm depth 133 min after application of this tracer (Chappell & Sherlock, 2005). The vegetation on our plots would wither if the preferential flow drained down to groundwater, so we have to assume that the rapid percolation of water is probably interrupted somewhere below our soil solution sampling devices. This interruption might be due to an increase in the bulk density of the soil horizon that started underneath our sampling devices, which is also reflected by the 10fold drop of simulated hydraulic conductivities from Bt1 to Bt2 (**Table 6.2**). Also in the study of Renck and Lehmann (2004) rapid percolation significantly decreased between 30 and 90 cm, where bulk density of the soil rose and macropores were interrupted. Similarly, Flury et al. (1994) observed in a field study on a set of temperate soils that preferential flow exceeded 100 cm soil depth only in a few cases. From our simulations, we cannot predict how water behaves in the subsoil, and field observations are contradictive: In our previous study, interflow seemed to be almost negligible (Ciglasch *et al.*, 2005), so we assume that a major fraction of the water simply remains in deeper soil horizons until it is removed by evapotranspiration of plants and soil. Yet, after heavy rain events, a line of springs evolves further downslope (just above the creek that dewaters the valley), which indicates that at least some lateral water flux is likely to occur.

6.5.2 Discharge of pesticides

Pesticide loads in surface runoff were similar to those in leachate, so both pathways are relevant for pesticide discharge from the treated area. However, the total export was several orders of magnitude smaller than the 0.5 – 5% of the applied amount reported in literature reviews (Wauchope, 1978; Flury, 1996) and former experiments in tropical climate (Laabs *et al.*, 2002a; Ciglasch *et al.*, 2005). Obviously, the unusually low amounts of precipitation prevented higher rates of pesticide discharge. The first rainstorm that caused surface runoff (23 mm) occurred right after the second application (29 to 30 June 02, **Figure 6.6**), and the first leachate was sampled two days later after another 13 mm of rain had fallen (02 July 02). Thus, it took 10 and 12 days from the first application until runoff and leaching of pesticides started. At the same time, field half-lives in topsoil (0 – 10 cm) of the studied substances ranged from 1.2 – 7.2 days only (malathion and chlorpyrifos, respectively; **Chapter 4**). Therefore, we probably would not have detected significant amounts of pesticides in discharged water if they had not been applied again on 29 June 02, only few hours before the first major rainstorm occurred. This clearly shows how repeated applications can increase the risk of pesticide translocation into adjacent non-target ecosystems.

The wick lysimeters collected ca. 10 times less water than the suction plates, thus raising the question whether the flux of pesticides derived from data of the wick lysimeters underestimates the actual leaching of pesticides. Yet, pesticides are mainly transported by preferential flow (Flury, 1996), and in the study of Renck and Lehmann (2004, which was conducted on a comparable soil) rapid percolation of water was the deeper the wetter the soil was. In their study, the matric potential had to rise above –2 to –3 kPa to induce rapid flow. This matches the matric potential needed by our wick lysimeters to deliver samples (**Figure 6.2, Figure 6.3**), so we conclude that we caught most of the pesticide fluxes. To make certain of this, it would be desirable to collect water quantitatively in sufficient amounts for pesticide analysis to confirm this assumption. One way to do this would be to pool solution collected by several suction plates. We could not do that because we used an online SPE-system which could not be so modified. The second way would be to use suction plates with larger surface areas. That also could not be done because it currently is technically impossible to melt into glass frames larger porous plates of sintered glass than we used. After our fieldwork was finished, however, alternative samplers that do not comprise fragile porous plates were developed (Kosugi & Katsuyama, 2004; Masarik *et al.*, 2004): Both groups independently modified steel lysimeters similar to the ones we used as wick lysimeters by replacing the fiber-glass wick with conventional, tension-controlled suction cups. This approach might combine the advantages of wick lysimeters and suction plates and should therefore warrant further testing.

As a consequence of the bypass flow of water through the soil, all pesticides (except mevinphos, which we never found in soil solution) were detected simultaneously in all WLY samples (only on 04 July 02, dimethoate was lacking): Under preferential flow conditions, interactions of pesticides with the bulk soil are kinetically hindered, so that no chromatographic separation of the pesticides occurs during the passage through the soil. This might be the reason why all pesticides we studied could be recovered from soil solution in similar amounts. However, our observations from surface runoff show that sorption strength determines the relative amounts of pesticides are released from the soil surface. In accordance with the latter observation, pesticides were reported to move through soil at the same velocity, but the total amounts of translocated pesticides decreased with increasing hydrophobicity (Elliott *et al.*, 2000; Malone *et al.*, 2004). Also we observed such a fractionation in a previous study on the same research site (**Chapter 3**). Yet, our previous results were based on leaching data that mainly originated from one single rainstorm event that occurred in the night after application. Contrastingly, in the study presented here, leachate was sampled on six days at different stages of the application cycles, starting on day 13 after the first application (**Figure 6.3**). Because hydrophobicity of the pesticides we investigated was positively correlated with persistence in the topsoil (Busche *et al.*, in preparation) we believe that two processes overlapped: The polar pesticides probably were more prone than the unpolar ones to leaching, but it seems as if this was compensated by their shorter half-lives in soil. We conclude that, due to the repeated applications, similar total amounts of all pesticides leached, and no correlation between hydrophobicity and leaching potential was observed. Obviously, this overlap applied less to surface runoff, which maybe due to different degradation kinetics on the plant surface (where pesticides are washed off upon surface runoff) and the top layer of the soil (where pesticides are located before they are leached through the soil). For example, Kennedy et al. (2001) reported that the initial half-live of endosulfan was 7.1 days in soil, but only 1.6 d on plant surfaces (field study in New South Wales).

Endosulfan lactone, which is a product of photo-degradation of endosulfan (Archer *et al.*, 1972), peaks in the first sample of surface runoff obtained after dry periods (09 July 02, 05 August 02; **Figure 6.6**). Contrastingly, the main microbial metabolite, endosulfan sulfate (Goebel *et al.*, 1982), prevails in soil solution. Thus, it is highly relevant for the pathway of decomposition of endosulfan whether it is attached to plants and thus exposed to sunlight or whether it has been washed into the topsoil, where it can be accessed by soil biota. The relative enrichment of endosulfan-β in surface runoff (as compared with spraying solution and leachate) occurred because the water solubility of endosulfan-β is ca. 14 times higher than that of endosulfan-α. Furthermore, the vapor pressure of endosulfan-α is 10% higher than of endosulfan-β (4.4 and 4 mPa; (Shen & Wania, 2005)), so that the α isomer will volatilize from plant surfaces to a greater

extend than β and thus be depleted in surface runoff (Beard & Ware, 1969). The vapor pressure of mevinphos (17 mPa; Tomlin, 2000) is significantly higher than for endosulfan (and all the other compounds studied, data not shown). Thus, the volatilization of mevinphos should be highest, which might be the reason why mevinphos could never be detected in soil solution and why its concentrations in surface runoff decrease faster than for all other substances except the highly leachable malathion (**Figure 6.6**). Volatilization from the surface of the soil is lower than from plant surfaces, because the stagnant boundary layer above the soil is thicker and air flow is less turbulent than above leaves (Rüdel, 1997). Consequently, once the substances have been washed into the topsoil during the first rainfall after application, their fate will probably be governed by other processes than volatilization, such as leachability and microbial degradability (Kennedy *et al.*, 2001).

Although endosulfan-β is better soluble in water than endosulfan-α, the β-isomer has a higher sorption coefficient (**Chapter 5**). This might explain, at least partially, why more endosulfan-α than -β can be detected in leachate whereas the opposite is true in surface runoff. Still, this finding contradicts the result of Antonius and Byers (1997) who reported that on a silty loam (Kentucky) also in soil solution the β isomer prevailed. The authors assume a faster dissipation of the α isomer (as compared with β), which was also observed in a laboratory study (Laabs *et al.*, 2002b). However, that difference in dissipation times was less pronounced in our study (**Chapter 4**), probably because our repeated applications caused a permanent input of "fresh" endosulfan, which kept the concentrations of endosulfan in the topsoil on a relatively high level throughout our experiment. Antonius and Byers (1997) applied 0.6 kg of endosulfan per hectare and detected 6.4 µg l^{-1} (endosulfan-α + β + sulfate) in surface runoff shortly after application and 0.63 µg l^{-1} in leachate (average of three months, installation depth of lysimeter not specified), whereas we, at a 10fold application rate, found 88.4 µg l^{-1} (30 June 02, first surface runoff sample collected in soil profile WLY, **Figure 6.1a**) and 2.3 µg l^{-1} (leachate; flux-weighed average; calculated from **Figure 6.6**). Thus, despite difference in the isomer ratios, total concentrations of endosulfan in surface runoff as well as in soil solution seem to be in a comparable range in both studies.

6.5.3 Ecological relevance

The ground vegetation on our research site acted like a vegetative filter strip (Krutz *et al.*, 2005), keeping the total amount of surface runoff small and nearly free of soil particles. This filtering effect also mitigated the total discharge of pesticides, which are often transported in particle-bound form (Antonious & Byers, 1997; Schulz *et al.*, 1998). However, because farmers apply pesticides right to the edge of the creek, all surface runoff that forms in the downslope section of the orchard is likely to enter the

river directly. This risk is further increased as the slope gets steeper the closer it gets to the creek. Lychee orchards are the prevalent culture in the catchment where our research site is located (ca. 6 of 11 km², Carsten Riedel, University of Hohenheim, unpublished data). Therefore, the agricultural land in our catchment is treated uniformly, which means that identical pesticides are applied within the same period of time. Consequently, the pesticide-containing runoff cannot be diluted with uncontaminated water from the creek as effectively as it would be in a larger catchment with a diverse pattern of land use. This is the reason why Schulz (2004) reports that, until now, peak concentrations of insecticides $> 10 \mu g \ l^{-1}$ have only been detected in catchments smaller than 10–100 km².

Even though the amounts of pesticides recovered in the runoff and leachate are low, this does not mean they do not present a hazard. In fact, in surface runoff the concentrations of all compounds at least in individual samples and for one of the species were above acute toxicity levels reported for standard test organisms in static laboratory tests ((U.S. Environmental Protection Agency, 2002; Wan *et al.*, 2005); **Table 6.3**). Two of these in particular exert an outstandingly high ecological risk for invertebrates (represented by *Daphnia*). Malathion presents a 1680-fold of effect concentration and mevinphos a 520-fold of effect concentration. Fortunately, these two pesticides dissipate rapidly from river water (Ballarin *et al.*, in preparation), so they are not likely to cause long-term effects. The situation is contrary for endosulfan and chlorpyrifos: although their peak concentrations are much smaller than for the polar pesticides, they were found to be more persistent in surface waters (see Bondarenko *et al.*, 2004 for a comparison of chlorpyrifos with malathion). Furthermore, they sorb to the sediment, and subsequent ongoing desorption retards their dissipation (Peterson & Batley, 1993). As a result, endosulfan was detected in the Lourens River (South Africa) not only after runoff events, but also before the first precipitation of the rainy season fell (Dabrowski *et al.*, 2002). Thus, the sublethal effects of chlorpyrifos and endosulfan (see Schulz & Dabrowski, 2001 for endosulfan) might be worse than those of malathion and mevinphos in our research area, although the latter two substances might have lower minimal TERs upon runoff events (TER = toxicity : exposure ratio; low TER indicates high risk). In the case of endosulfan, the metabolites have also to be considered. Endosulfan sulfate is even more persistent in rivers than its parent compound (Leonard *et al.*, 2001), and has, at the same time, a comparable toxicity ((Wan *et al.*, 2005); **Table 6.3**).

Even if pesticides percolate into soil instead of being transported directly into the nearby river by surface runoff, they still may enter the surface water via lateral preferential flow (Chappell & Sherlock, 2005). This risk will probably be highest for chlorpyrifos and endosulfan, because area-related export of these substances in leachate is 100 times higher than in surface runoff, whereas leaching und runoff are more or less

Table 6.3: *Acute toxicities of the investigated pesticides to typical aquatic test organisms (laboratory data; exposure time in parentheses) and maximal concentrations ($Conc_{max}$) detected in surface runoff from a Northern Thai lychee orchard. Unless denoted differently, data are median values calculated from all data available in the ECOTOX Database (U.S. Environmental Protection Agency, 2002); data retrieval: 06/13/05. LC50 = concentration that causes 50% mortality, EC50 = concentration that causes some adverse effect on 50% of the individuals (activity, frequency of heart beats, etc.)*

Substance	Acute toxicity (μg l^{-1})		$Conc_{max}$ in surface runoff (μg l^{-1})
	Oncorhynchus mykiss (rainbow trout; LC50)	*Daphnia magna* (water flea; EC50)	
Endosulfan (α:β = 2:1)	0.8 (96 h)	328 (48 h)	
Endosulfan-α	0.5 (96 h)[a]	1180 (48 h, LC50)[a]	15.1 (06/30/02)
Endosulfan-β	3.3 (96 h)[a]	1520 (48 h, LC50)[a]	62.2 (06/30/02)
Endosulfan sulfate	1.5 (96 h)[a]	2120 (48 h, LC50)[a]	15.2 (07/02/02)
Endosulfan lactone	no data	> 10000 (48 h)	70.3 (07/09/02)
Chlorpyrifos	14.3 (96 h)	0.9 (48 h)	29.9 (06/30/02)
Malathion	119 (96 h)	1.9 (48 h)	3164 (06/30/02)
Dimethoate	7500 (96 h)	840 (48 h)	1502 (06/30/02)
Mevinphos	11.9 (96 h)	1.5 (96 h)	779 (06/30/02)

[a] Data from Wan et al. (2005)

equal for the more polar pesticides we studied (**Table 6.1**). However, because our experiment was designed to study pesticide translocation on the profile scale, we cannot tell how long the actual travel distances of surface runoff is nor do we know whether leachate drains into the river before pesticides have dissipated from the soil solution. Hence we suggest a high resolution, event-triggered measurement of pesticide concentrations in river water nearby tropical fruit orchards to further investigate the sustainability of this form of land-use.

7 Extended summary and conclusions

Lychee plantations have been introduced in mountainous Northern Thailand as an alternative to swidden farming ("slash-and-burn"). It is believed that fruit cropping is a more sustainable form of land-use than the cultivation of annual crops, because orchards imitate the structure of indigenous forests and because the ground vegetation of lychee farms effectively prevents erosion. However, these considerations do not take into account that, in contrast to natural forests, great amounts of pesticides have to be applied to lychee orchards. During fruit ripening, insecticides are sprayed up to once in 10 days. Although the local population knows about the environmental problems that are caused by the excessive use of pesticides in Northern Thailand, this issue has not yet been studied systematically. Our knowledge on pesticide fate has mainly been acquired in temperate regions; hence, it is not necessarily transferable to Northern Thailand, where soil and climatic conditions differ substantially.

The objective of this study was to assess the level of pesticide contamination in river-water and to investigate insecticide fate in the soil environment of a lychee plantation near Mae Sa Mai village, Northern Thailand. Therefore, concentrations of 24 commonly used pesticides in the baseflow of three creeks were monitored. Furthermore, I developed a sampling device for soil solution, which consisted of a set of tension-controlled borosilicate suction plates ($\varnothing = 9$ cm; 17 plates per profile) and an "on-line" (in the field) solid-phase extraction. This device and conventional surface runoff samplers were used to study vertical and lateral water and pesticide fluxes after manual application to the soil surface. The experiments were conducted during two rainy seasons (2001 and 2002) and lasted circa two months each. In the first year, a mixture of eight insecticides was applied once onto the soil; in the second year, five repeated applications of a mixture of six insecticides were performed (10-day intervals). Samples of the top soil collected in the second year were sequentially extracted in order to investigate the temporal courses of pesticide concentration in soil and changes in sorption strength over time ("aging"). My findings should be integrated in an overall assessment of the sustainability of lychee cropping in Northern Thailand.

7.1 Summary of results

The objectives of my thesis were split into five individual sub-studies, of which the results are summarized in the following:

7.1.1 Are there relevant concentrations of pesticides in the surface waters of the study area?

In a survey of three catchments in the study area, land-use had only a minor influence on the spectrum of detectable pesticides. Dominating substances were the insecticide endosulfan and several fungicides. European threshold values were exceeded even in baseflow samples; concentrations in peak discharge will probably be higher. Therefore it cannob be ruled out that pesticide residues in river water will have adverse effects on aquatic biota. That is why I further investigated the pedologic fate of pesticides in a lychee orchard in an in-depth process study.

7.1.2 How does water move through the soil of the studied orchard, and does this flow characteristic bear a specific risk of pesticide leaching?

My field experiment in 2001 showed that the combination of tension-controlled suction plates with on-line solid-phase extraction is suitable to detect water and pesticide fluxes simultaneously. Two independent statistical methods revealed that the flow field of water switches from homogeneous to heterogeneous flux if the amount of percolate falls below a trigger value of 2 mm d^{-1}. This means that infiltrating water is concentrated on so-called "fingers" if the amount of percolate is insufficient to maintain a flux of water across the whole soil. However, this fingering seems to be irrelevant for pesticide leaching, because pesticides were detectable in soil solution almost exclusively after a heavy rainstorm that occurred shortly after application and that saturated the upper 55 cm of the soil with water. According to the statistical analysis of the flow field, this specific rainstorm caused rather homogeneous infiltration. Within this single rainfall event all insecticides under study (irrespective of their solubility) were translocated from the soil surface to 55 cm soil depth, which can only be explained by preferential flow. Thus, preferential flow occurs both at low and high infiltration rates. The existence of preferential flow pathways that are "active" under saturated conditions might bear a substantial risk of pesticide leaching, especially if the time span between application and the first heavy rain is short.

7.1.3 At which rates do pesticides dissipate under common lychee farming?

The field half-lives of all substances were among the shortest reported in literature (1.4 – 7.2 d; mevinphos and chlorpyrifos. Probably, the humid tropical climate did not only promote rapid leaching and surface runoff, but it also guaranteed that soils remained moist, thereby promoting microbial decay. Furthermore, large fractions of the applied pesticides were probably prone to volatilization because they were stored on the ground vegetation before entering the soil. Yet, the fraction of the applied pesticides that rapidly dissipated decreased with increasing apolarity of the substances, and an

accumulation in soil was observed for all pesticides except mevinphos. The accumulation was taken as a first indicator of the occurrence of aging processes despite of the high initial dissipation rates.

7.1.4 How do binding strengths between pesticides and soil change with time and repeated applications?

To better understand the aging of pesticides on the investigated fruit orchard, I studied the temporal courses of sorption strengths of the applied substances using sequential extraction methods. Within the timeframe of my experiment, only endosulfan and dimethoate showed typical aging effects, reflected in an increased soil : solution partitioning coefficient K_{OC} with time. For chlorpyrifos this coefficient remained constant, for malathion it decreased over time, and for mevinphos it could not be calculated due to low concentrations in the aqueous soil extract. A clearer picture of pesticide aging was obtained by introducing an additional partitioning coefficient, MAR, that describes a redistribution of the aged compounds within two different fractions of *sorbed* pesticides not released with water (extractable either by methanol or by a mixture of acetone, ethylacetate and water). The MAR revealed that, despite repeated input of "fresh" pesticides, all studied substances except the rapidly dissipating mevinphos moved from methanol- to less easily extractable (and, hence, probably also less bioavailable) forms as time after application proceeded.

7.1.5 To what extend and on which pathways are pesticides washed off the orchard?

Under the given weather conditions of the second study year, the sum of leaching and surface runoff was ca. 0.001% of the applied amount for all studied substances, despite a wide variety of their physicochemical properties. Due to the ground vegetation of the research plot, only a small fraction ($< 0.02\,\%$) of precipitation was transported as surface runoff, and erosion was effectively prevented. Nevertheless, peak concentrations of all pesticides in runoff exceeded tabulated toxicity concentrations for either vertebrate or invertebrate test species, or both. Peak concentrations of pesticides in leachate were significantly lower than in surface runoff. Due to greater total amount of leachate (8% of precipitation), however, the cumulative discharge in leachate was similar to surface runoff for the hydrophilic pesticides or even higher for the hydrophobic pesticides. Obviously, the greater mobility of the hydrophilic substances was (over-)compensated by the greater persistence of the hydrophobic pesticides in the soil environment. Because all pesticides were present in the first sample of soil solution collected after application, preferential flow seems to be a major pathway of pesticide leaching.

7.2   General discussion and conclusions

7.2.1 Pesticides in the soil environment as a source for catchment-scale pollution

One day after pesticide application, only 2 – 38 % of the applied pesticides were still extractable from soil. It is not likely that the remaining fraction was degraded or irreversibly bound within that short period, but it probably volatilized (FOCUS, 2000; Racke, 2003a). In terms of factors controlling total pesticide residence, the atmosphere may therefore be more important than the soil in tropical Northern Thailand. However, pesticides that have volatilized will immediately *disperse* over large areas, and thus be diluted (Laabs *et al.*, 2002c). Contrastingly, pesticides that remain on the soil surface or in the topsoil can be picked up by rainwater from throughout the application area and then be *concentrated* in ground and surface water (Schulz, 2001). This is especially the case in areas like the Mae Sa Valley and comparable catchments throughout Northern Thailand, where land-use is characterized by specialization on single crops. This lack of diversification leads to a uniform pesticide treatment throughout individual cropping areas, resulting in outstandingly high local pesticide emissions. That is why, the fate of pesticides on plot and catchment scale is more relevant for direct environmental impact related to their application than pesticide volatilization and should therefore be studied first.

7.2.2   Potential accumulation of pesticides in the studied Acrisol

Soil serves as a buffer for pesticides, thereby protecting ground and surface water from direct pesticide inputs. Large fractions of pesticides retained in soil can be degraded by the soil microbial community (Ragnarsdottir, 2000), and in the Acrisol I studied, degradation was faster than generally reported for temperate regions. Nevertheless, it important to note that degradation is not necessarily equal to detoxification, because metabolites may affect non-target organisms as severe as the parent compound. This fact is especially relevant if the metabolites are more persistent than the parent compounds, as observed for endosulfan in my study. Therefore, my results show that knowledge about major metabolites is crucial for a comprehensive assessment of pesticide fate. Additionally, pesticides that are held back in soil do not necessarily degrade completely, but they can feed long-term leaching (Flury, 1996) and runoff (Wauchope, 1978), or accumulate (de Andrea *et al.*, 2003).

The repeated applications in 10-day intervals promoted pesticide accumulation for all substances except mevinphos despite of the high dissipation rates that prevail under tropical climate. **Microbial adaptation to pesticide degradation was not induced by multiple applications**. Especially the hydrophobic pesticides (endosulfan and chlorpyrifos) showed an over-proportional enrichment in soil if repeatedly applied. At

least partially, **that enrichment goes back on aging processes, which are accompanied by an increase of field half-lives**. This relationship indicates that degradability and binding strength are interdependent properties: The longer the pesticide resides in soil, the more it will be stabilized. However, even at the end of my experiment, the soil concentrations of the metabolites of endosulfan still increased, proving that degradation of endosulfan had not yet stopped although the partitioning coefficient K_{OC} had increased by a factor of > 3. I conclude that the **aging that occurred within the duration of the experiment was insufficient to shift the pesticides into a binding state that is persistent to degradation**. Yet, bound residues need to be investigated in an upcoming experiment with radio-labeled pesticides in order to reliably answer the question whether pesticides accumulate in the long term on the studied orchard or whether the accumulation is only a temporary effect that occurs exclusively during the spraying season.

7.2.3 Water flux and pesticide mobility in the studied Acrisol

Traveling times from the soil surface to the lysimeters were more or less identical for all studied pesticides despite of their different physicochemical properties: In both profiles and in both study years pesticides were detected already in the first sample of soil solution collected after application. Thus, the leaching of pesticides must be caused by preferential flow. In both study years this "first flush" occurred after heavy rainstorms that nearly saturated the soil profile, but no pesticides were detected in soil solution when only little amounts of leachate were collected. I therefore conclude **that saturated preferential flow is responsible for pesticide leaching in the studied Acrisol**. It is remarkable, however, that two independent statistical methods showed that the flow field is more heterogeneous if the amount of percolate is little, which may lead to the conclusion that preferential flow is more pronounced at low percolation rates. Yet, if I combine the finding that preferential flow occurs when the soil is nearly saturated with the finding that the flow field appears homogeneous under these conditions, I conclude that in the studied Acrisol **the preferential flow pathways must be so numerous that sampling devices with a diameter of 9 cm just pretend a homogeneous infiltration pattern**. Water seems to be concentrated on fast flow pathways in the inter-aggregate pore space, while the soil matrix is excluded from water and solute transport. Thus, there is only little interaction between pesticides and the soil matrix so that pesticides are hardly retarded. If the amount of water percolating through the profile is insufficient to fill the whole inter-aggregate pore space, flux further concentrates on individual fingers, which is then reflected by an increase of flow field heterogeneity.

A peculiarity of my experiment was the ground cover with plants. The vegetation retained parts of the pesticides even before they reached the soil. Therefore, the

substances were directly exposed to sunlight, which probably promoted both volatilization and photo-decomposition. Yet, pesticides were also washed off the plants by rain and dewfall so that the topsoil received a more or less continuous input of "fresh" pesticides despite of the discrete application events. For this reason, the **ground vegetation directly retarded the increase in K_{OC} over time**.

The studied Acrisol had an exceptionally high infiltration capacity, which probably goes back on flow pathways of water through inter-aggregate pores (Radulovich *et al.*, 1992). In combination with the ground vegetation (Patty *et al.*, 1997), this property effectively prevented surface runoff. Under local practice, however, pesticides are sprayed right to the edge of creeks, so that **even "minor" surface runoff events may lead to substantial river-water contamination** and result in severe effects on aquatic biota.

IN SUMMARY, the main factor that controlled processes of pesticide dissipation was climate, especially the precipitation pattern: Precipitation was strong enough to cause preferential flow that was widely independent of the physicochemical properties of the pesticides (**Chapter 3**), fully masked possible effects of microbial adaptation to pesticide degradation (**Chapter 4**), significantly influenced aging processes (**Chapter 5**), and induced surface runoff despite of high infiltration rates and ground vegetation (**Chapter 6**). Besides, it is known that volatilization is generally enhanced at moist soil conditions, that means after precipitation events (Lembrich *et al.*, 1999). Although not studied directly, volatilization seemed to be the major pathway of pesticide dissipation, because up to 98% of the applied pesticides dissipated within 24 h after application even if no rainfall occurred (**Chapter 4**). Volatilization was followed by degradation and aging as well as leaching and runoff, the latter two processes accounting for less than 1 % of pesticide dissipation only (**Chapters 3, 6**).

It is difficult to evaluate the environmental impact of volatilized pesticides as long as the deposition area is not exactly known. Degradation and aging generally reduce the risk of adverse side effects of pesticide application (**Chapters 4, 5**), and my simulations showed that the leaching on preferential flow pathways probably will not go down to the groundwater (**Chapters 3, 6**). Thus, despite of its low relevance for the mass balance of pesticides applied to the studied lychee orchard, the highest direct environmental impact of pesticide use will probably emanate from runoff that enters surfaces waters (**Chapters 2, 6**). From a soil scientific point of view, I therefore recommend further efforts to minimize both runoff and, if possible, volatilization in order to improve the sustainability of lychee cropping in Northern Thailand.

8 Outlook

My soil solution sampling device with online solid-phase extraction was useful to monitor water and pesticide fluxes with high temporal and spatial resolution. However, the suction plates were fragile, and the volumes of soil solution collected tended to be too small for proper determination of pesticide loads. Furthermore, the optimization of pump parameters turned out to be challenging, but crucial to the successful operation of the system: wrong tension in the "upper chamber" of my sampling devices dramatically altered the sampling efficiency, insufficient suction in the "lower chamber" led to an overflow of the solid-phase extraction cartridges. To overcome these problems I suggest to further develop the system and to combine my ideas of online solid-phase extraction with the soil solution samplers independently suggested during project work by Kosugi & Katsuyama (2004) and Masarik *et al.* (2004). Their systems show two major differences to the one I worked with: (i) instead of suction plates they used steel lysimeters, in which conventional suction cups were inserted. (ii) The authors did not apply a permanent suction equivalent to soil matric potential to the samplers, but whenever water was percolating through the profile, they operated the pump at maximum strength until a tensiometer installed above the sampler measured the same matric potential as a reference tensiometer installed in the same depth adjacent to the sampler. That means that soil solution was rapidly pumped out of the lysimeters whenever the soil in the lysimeters was wetter than the surrounding soil. In tracer experiments, the authors showed that the well-defined surface areas of the lysimeters allow balancing the fluxes, and that the closed bottoms of the lysimeters enable the system to collect preferential flow.

Because inert borosilicate suction cups are available (Wessel-Bothe *et al.*, 2000), modification (i) allows replacing the breakable suction plates I used by robust, individually shaped samplers of virtually any size. Also modification (ii) helps to improve my sampler: Because only two states of the pump exist ("on" or "off"; instead of accurate adjustment to the nearest kPa) the "lower chamber" of my sampling device becomes obsolete: With the mode of operation suggested by Kosugi & Katsuyama (2004) and Masarik *et al.* (2004), the suction can be applied directly through the solid-phase extraction cartridges to the suction cup, thereby also excluding the risk of overflowing cartridges. Additionally, this setup would effectively prevent the cartridges from drying, because the pump is operated exclusively when there is water in the lysimeter. I recommend to apply these alterations to my sampling device and to test it under various climatic and pedogenic conditions.

It becomes clear, however, that technical improvements of the sampling device alone will not lead to a better understanding of the environmental fate of pesticides in tropical orchards. Moreover, also the scale of investigation has to be re-defined in upcoming studies. My experiments were necessary to quantify key mechanisms of pesticide transport, dissipation and aging and to address the major environmental risks related to these processes Yet, sampling devices of 9 cm in diameter were too large to detect individual pathways of preferential flow, but too small to predict exact inputs of pesticides into the creek that flowed along the experimental plot. I therefore recommend two different directions for further research:

i) Downscaling: especially in the field of pesticide aging, exact understanding of processes on molecular scale is still lacking. For example, we do not know the "domains" of organic matter that are assessed by the different organic solvents we used, which would be crucial to estimate the risk of future release. For upcoming research in this field, methods in the field of microcalorimetry or differential scanning calorimetry should be further developed to become standard tools also in soil scientific research.

ii) Upscaling: Due to the great heterogeneity, for example of soil and weather conditions, it will not be possible to predict pesticide fate on plot or catchment scale with deterministic models based on measured model parameters. Therefore, efforts should focus on the derivation of effective parameters and / or probabilistic modeling approaches.

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Curriculum vitae

1976	Born on 13 May in Diepholz (Germany)
1995	Graduation (Abitur) at Graf-Friedrich-Schule, Diepholz (Germany)
1995-2000	Study of Geoecology at the University of Bayreuth (Germany), specialization in soil science and soil physics
2000	Diploma in Geoecology, Department of Soil Science and Soil Geography (Prof. Zech); thesis: "Gelöste organische Substanz (DOM) in Oxisolen unter Kiefernforst und natürlicher Savanne"
2000-2004	PhD student at the Institute of Soil Science (Prof. Kaupenjohann), University of Hohenheim, Stuttgart (Germany) as member of the special research program SFB 564 "Sustainable land-use in the mountainous regions of South-East Asia"

Places of employment:

2000-2002: University of Bayreuth (Germany)

2002-2004: TU Berlin (Berlin University of Technology; Germany)

2005	PhD student at the Department of Soil Science (Prof. Kaupenjohann), TU Berlin (Germany)
Since 2006	Laboratory manager, University of Hannover, Institute of Soil Science

Research stays abroad (excerpt)

1999	Field work, Uberlandîa, Brazil (6 weeks)
2001, 2002	Field work, Chiang Mai, Thailand (6 months each)
2004	Marie Curie Fellowship "Pesticide Fate Modelling", Università Cattolica del Sacro Cuore, Piacenza, Italy (3 months)

Appendix

Appendix 1: Rain data

App. 1.1: Amounts of precipitation (ml) collected in study year 2001 by 10 rain collectors (R1–R10) evenly spread across the research plot. The diameter of the entry of the rain collectors was 14.6 cm; the dates indicate the day on which the collectors were emptied out

Date	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
24/06/01	1260	1410	1390	1380	1350	n.a.	1360	1400	n.a.	1300
26/06/01	13	14	15	9	8	9	9	9	9	10
28/06/01	5	7	7	4	6	6	7	10	7	5
30/06/01	320	300	310	315	310	310	315	320	315	315
02/07/01	440	460	450	440	435	440	440	460	450	450
04/07/01	T	T	T	T	T	T	T	T	T	T
06/07/01	240	250	240	240	240	230	230	230	220	230
08/07/01	45	48	46	46	44	46	48	48	49	42
10/07/01	620	610	580	635	615	600	615	645	680	625
12/07/01	110	100	110	110	115	115	115	115	110	110
14/07/01	20	22	27	22	19	22	20	22	21	22
16/07/01	47	48	49	49	48	49	50	48	49	47
18/07/01	15	14	16	15	15	16	14	14	15	15
20/07/01	60	68	60	60	58	60	58	62	62	60
22/07/01	1030	1120	1020	1050	1060	1100	1100	1100	1100	1100
24/07/01	1000	1040	1040	1020	1030	1030	1030	1040	1020	1000
26/07/01	0	0	0	0	0	0	0	0	0	0
28/07/01	290	310	325	300	310	295	310	330	330	300
30/07/01	T	T	T	T	T	T	T	T	T	T
01/08/01	90	100	95	100	95	95	95	105	100	100
03/08/01	1700	1780	1730	1920	1800	1800	1800	1800	1960	1670

n.a.: no data available
T: Traces (< 2ml)

Appendix 2: Soil matric potentials (55 cm) and suction applied to soil solution sampling device

App. 2.1: *Full set of logged soil matric potentials in Profile 1 (4 tensiometers, installation depth 55 cm) and vacuum applied to the automatic soil solution sampling device, study year 2001*

– on CD-ROM only, available on request if not attached to this document –

App. 2.2: *Full set of logged soil matric potentials in Profile 2 (4 tensiometers, installation depth 55 cm) and vacuum applied to the automatic soil solution sampling device, study year 2001*

– on CD-ROM only, available on request if not attached to this document –

App. 2.3: *Full set of logged soil matric potentials in Profile 1 (4 tensiometers, installation depth 55 cm) and vacuum applied to the automatic soil solution sampling device, study year 2002*

– on CD-ROM only, available on request if not attached to this document –

App. 2.4: *Full set of logged soil matric potentials in Profile 2 (4 tensiometers, installation depth 55 cm) and vacuum applied to the automatic soil solution sampling device, study year 2002*

– on CD-ROM only, available on request if not attached to this document –

Appendix 3: Manually read soil matric potentials and water contents of the topsoil (study year 2002)

App. 3.1: Manually read soil matric potentials (microslope; 3 tensiometers T1–T3 per depth), study year 2002; data corrected for length of the tensiometer and size of the air bubble

Date	10 cm, microslope			20 cm, microslope			45 cm, microslope		
	T1	T2	T3	T1	T2	T3	T1	T2	T3
20/06/02	20	25	51	18	25	58	27	46	74
22/06/02	29	21	79	28	39	74	36	43	74
24/06/02	46	74	86	42	57	87	37	55	88
26/06/02	120	174	228	59	80	133	46	56	90
29/06/02	310	379	360	123	151	203	60	83	124
30/06/02	16	23	35	36	86	34	44	52	71
02/07/02	26	33	57	27	30	49	28	35	42
04/07/02	45	62	94	43	50	71	34	41	57
06/07/02	272	250	226	147	98	116	44	61	78
09/07/02	27	36	59	21	33	51	50	45	58
10/07/02	n.a.	n.a.	25	n.a.	n.a.	17	n.a.	34	77
12/07/02	22	32	52	22	35	51	37	38	53
14/07/02	14	32	60	22	33	55	27	35	52
16/07/02	69	75	128	40	56	87	39	52	72
19/07/02	271	197	250	97	124	141	44	69	90
20/07/02	354	291	347	156	197	177	56	82	97
22/07/02	11	18	28	10	21	41	63	86	103
24/07/02	23	37	78	27	39	76	57	67	91
26/07/02	39	57	112	30	58	102	56	73	83
29/07/02	50	47	79	66	95	111	62	89	111
30/07/02	77	73	104	82	108	127	69	96	121
01/08/02	281	279	284	151	221	129	70	109	124
03/08/02	386	349	319	264	317	236	78	123	133
05/08/02	15	31	63	42	40	81	66	75	118
08/08/02	68	80	138	91	87	114	51	66	96
11/08/02	455	486	398	445	394	274	64	98	137
13/08/02	373	359	187	430	393	243	73	124	141
15/08/02	57	53	64	316	220	146	84	135	151
18/08/02	21	54	46	184	177	128	78	120	139
20/08/02	11	46	47	148	147	88	71	102	124
22/08/02	38	113	84	155	169	117	84	109	129
24/08/02	58	69	68	46	73	71	85	92	108
26/08/02	34	60	71	48	79	89	74	93	99
28/08/02	14	19	19	15	22	29	7	17	24
30/08/02	18	22	37	21	29	40	13	29	37
01/09/02	20	24	35	24	37	45	28	43	53

n.a.: no data available

App. 3.2: Manually read soil matric potentials (microplain; 3 tensiometers T1–T3 per depth), study year 2002; data corrected for length of the tensiometer and size of the air bubble

Date	10 cm, microplain			20 cm, microplain			45 cm, microplain		
	T1	T2	T3	T1	T2	T3	T1	T2	T3
20/06/02	12	24	43	19	32	84	33	55	74
22/06/02	15	35	62	19	40	76	24	52	68
24/06/02	24	64	119	25	64	96	37	67	87
26/06/02	48	140	214	32	64	106	41	64	90
29/06/02	129	318	353	56	101	150	44	80	114
30/06/02	3	28	30	10	26	122	4	27	47
02/07/02	12	35	44	15	41	52	21	36	44
04/07/02	25	75	74	28	61	72	28	51	60
06/07/02	210	370	190	36	83	95	33	62	75
09/07/02	23	40	48	18	48	66	29	51	64
10/07/02		13	16		25	39		45	56
12/07/02	19	30	41	14	43	58	24	50	58
14/07/02	11	31	39	17	42	54	21	43	60
16/07/02	29	57	89	24	63	80	33	62	78
19/07/02	97	137	160	29	79	111	28	62	90
20/07/02	157	198	214	57	101	149	39	59	97
22/07/02	8	15	23	9	20	55	41	81	118
24/07/02	21	41	54	19	47	70	41	75	90
26/07/02	27	54	75	17	67	89	45	74	83
29/07/02	42	34	71	31	86	106	45	81	112
30/07/02	54	63	89	36	85	104	50	84	117
01/08/02	124	220	186	47	102	137	51	90	121
03/08/02	205	226	259	88	145	180	67	107	137
05/08/02	15	35	39	18	33	58	36	51	108
08/08/02	35	81	72	15	49	82	27	58	89
11/08/02	245	428	233	89	116	161	41	91	121
13/08/02	135	126	130	121	136	385	56	101	137
15/08/02	20	26	57	66	73	145	69	98	151
18/08/02	12	28	47	43	91	107	68	102	144
20/08/02	4	24	38	7	60	71	54	81	127
22/08/02	20	43	74	27	87	97	71	96	137
24/08/02	56	80	70	52	63	59	89	86	111
26/08/02	39	65	47	53	59	56	60	77	55
28/08/02	12	9	20	13	19	20	8	17	26
30/08/02	19	25	38	20	15	43	12	29	40
01/09/02	19	24	32	17	25	67	22	48	62

n.a.: no data available

App. 3.3: *TDR measurements of soil water contents (%) of the topsoil (0–10 cm; microslope; 3 measuring points M1–M3 with three repetitions a–c each), study year 2002*

Date	M1-a	M1-b	M1-c	M2-a	M2-b	M2-c	M3-a	M3-b	M3-c
20/06/02	21.9	n.a.	n.a.	19.8	n.a.	n.a.	23.1	n.a.	n.a.
22/06/02	29.5	n.a.	n.a.	28.9	n.a.	n.a.	20.1	n.a.	n.a.
24/06/02	26.5	24.1	25.9	26.1	25.2	26.8	17.6	23.7	29.4
26/06/02	23.4	23.6	21.9	20.0	19.5	22.6	18.0	16.0	26.9
29/06/02	20.7	18.7	19.9	19.4	18.5	18.0	12.5	15.7	16.9
30/06/02	14.0	16.8	16.8	19.2	14.5	15.6	15.8	16.7	12.5
02/07/02	30.2	27.8	28.7	31.1	30.0	32.8	22.4	24.6	27.9
04/07/02	22.5	25.7	23.7	24.3	26.5	26.4	27.2	21.0	22.6
06/07/02	22.5	22.4	18.1	22.4	20.4	23.2	16.9	15.6	17.4
09/07/02	15.4	14.9	16.3	17.9	18.2	17.2	13.6	14.8	16.1
10/07/02	29.0	29.4	27.8	25.9	27.1	22.7	23.9	22.9	25.1
12/07/02	31.5	31.3	30.3	31.5	33.5	30.1	31.0	32.8	27.6
14/07/02	32.0	35.2	29.5	26.9	28.0	29.2	28.5	23.9	27.0
16/07/02	30.2	26.1	23.8	22.0	24.2	25.8	23.7	22.7	23.5
19/07/02	18.5	18.8	16.6	16.1	17.9	16.2	17.4	16.7	16.3
20/07/02	14.7	20.6	15.3	20.9	18.3	20.5	18.8	16.2	18.3
22/07/02	23.9	25.3	19.9	23.2	24.3	25.2	25.0	20.2	25.8
24/07/02	34.2	25.3	31.2	31.0	33.9	29.5	31.5	32.1	31.2
26/07/02	26.3	22.9	26.6	21.6	16.5	22.7	21.3	19.7	24.5
29/07/02	25.0	22.8	20.4	21.6	25.1	24.9	23.7	28.8	26.2
30/07/02	28.9	27.1	27.1	23.5	26.8	26.6	32.4	26.4	25.2
01/08/02	23.9	24.7	23.4	24.7	22.7	24.0	26.5	28.4	25.5
03/08/02	20.9	17.9	15.7	19.7	15.0	20.5	21.2	18.4	19.4
05/08/02	26.0	25.7	28.0	19.1	26.0	21.3	29.0	25.2	25.7
08/08/02	22.6	22.4	19.3	26.1	23.7	25.9	25.9	21.2	29.2
11/08/02	20.2	19.7	17.1	18.9	23.1	20.7	25.7	21.5	22.4
13/08/02	25.0	20.5	22.3	20.0	19.4	25.5	21.6	17.6	20.4
15/08/02	21.8	24.1	24.0	19.4	18.9	18.7	21.8	20.1	17.2
18/08/02	24.4	25.1	23.8	26.3	23.1	21.1	23.2	19.3	23.9
20/08/02	26.0	24.0	28.4	29.0	28.8	28.8	22.7	24.6	26.9
22/08/02	21.2	21.4	23.4	26.5	22.8	25.2	21.3	21.6	20.4
24/08/02	21.9	27.2	23.9	29.6	27.2	23.5	23.5	26.4	25.5
26/08/02	28.9	31.9	31.0	34.6	30.0	34.6	29.9	32.0	30.6
28/08/02	32.8	29.4	26.9	25.6	30.7	28.0	23.7	28.3	22.1
30/08/02	40.8	38.0	41.5	31.3	37.4	39.8	36.1	36.5	34.9
01/09/02	34.8	35.2	32.1	33.3	32.4	34.1	33.8	33.3	37.1
20/06/02	29.4	32.2	30.0	33.1	33.4	29.0	27.8	30.3	25.7

n.a.: no data available

App. 3.4: *TDR measurements of soil water contents (%) of the topsoil (0–10 cm; microplain; 3 measuring points M1–M3 with three repetitions a–c each), study year 2002*

Date	M1-a	M1-b	M1-c	M2-a	M2-b	M2-c	M3-a	M3-b	M3-c
20/06/02	21.5	n.a.	n.a.	23.1	n.a.	n.a.	22.4	n.a.	n.a.
22/06/02	26.8	n.a.	n.a.	30.4	n.a.	n.a.	31.6	n.a.	n.a.
24/06/02	26.5	27.6	28.9	25.4	28.8	23.2	22.1	25.7	21.7
26/06/02	23.9	25.6	23.9	24.7	24.3	24.8	24.2	23.9	22.3
29/06/02	18.9	22.4	21.9	21.1	20.3	21.6	18.7	19.7	16.3
30/06/02	15.7	17.5	18.8	17.8	17.5	14.4	15.1	16.4	14.0
02/07/02	32.6	31.6	26.3	27.8	26.5	27.9	28.6	29.0	32.0
04/07/02	26.8	30.0	27.4	21.0	30.2	26.5	28.4	31.0	30.9
06/07/02	18.4	23.1	22.5	17.7	21.4	25.2	23.4	32.0	33.7
09/07/02	15.4	21.6	18.5	16.9	20.2	16.2	18.5	18.8	20.6
10/07/02	26.9	29.3	24.2	32.0	25.6	24.3	29.9	28.9	30.2
12/07/02	32.7	30.6	30.2	38.3	35.2	32.5	32.6	33.3	26.6
14/07/02	26.8	31.8	27.2	26.9	27.7	26.0	30.7	31.6	28.3
16/07/02	26.8	25.6	28.6	21.4	23.8	29.9	25.4	24.3	27.0
19/07/02	20.3	19.1	17.8	21.4	14.3	19.0	15.0	19.4	22.1
20/07/02	21.8	20.1	20.5	22.0	18.0	18.5	22.2	21.9	20.5
22/07/02	24.8	27.1	28.5	28.5	21.9	24.3	24.8	25.4	24.0
24/07/02	39.6	38.8	35.7	32.4	33.9	34.2	37.5	37.7	34.8
26/07/02	31.6	25.6	25.2	22.7	26.5	24.3	27.8	27.3	25.1
29/07/02	28.8	29.6	26.7	26.6	27.5	28.7	25.7	29.1	28.2
30/07/02	31.5	29.1	33.1	31.5	32.3	25.4	31.4	32.1	30.3
01/08/02	26.8	21.9	27.0	25.0	25.8	26.4	26.6	31.2	29.2
03/08/02	27.0	20.7	22.9	20.6	25.1	19.5	20.4	22.3	20.9
05/08/02	28.1	30.6	26.3	23.6	32.8	31.1	27.5	29.2	21.6
08/08/02	25.4	26.9	26.8	29.7	26.1	30.3	29.4	29.6	28.3
11/08/02	24.3	21.0	25.1	18.0	23.1	23.7	29.7	23.9	23.8
13/08/02	26.1	23.1	24.2	23.6	31.4	27.2	28.7	25.9	23.5
15/08/02	24.5	26.3	23.9	27.7	27.6	21.0	21.9	21.3	24.3
18/08/02	30.8	27.9	25.4	25.1	32.0	27.9	29.0	28.1	28.0
20/08/02	27.7	28.3	27.1	27.3	28.1	31.5	29.9	32.9	30.3
22/08/02	25.0	29.4	28.5	24.8	23.2	23.5	26.2	29.7	28.0
24/08/02	33.4	29.5	28.9	36.1	35.6	31.0	33.6	30.0	34.3
26/08/02	34.4	35.2	37.9	30.4	35.6	30.4	39.6	35.8	38.2
28/08/02	27.4	26.3	29.5	27.4	31.7	25.7	30.3	31.6	31.3
30/08/02	36.0	39.4	40.8	37.2	34.1	38.3	38.1	36.9	33.1
01/09/02	34.2	32.4	36.1	31.0	34.3	36.0	30.1	35.5	32.6
20/06/02	29.6	32.3	31.3	31.8	29.5	30.5	32.8	33.8	34.1

n.a.: no data available

Appendix 4: Water volumes collected by suction plates, surface runoff gutters, and wick lysimeters

App. 4.1 (p. 136): *Volumes of water (ml) collected by the suction plates in Plot 1 (installation depth 55 cm), study year 2001. Dates indicate when the cartridge was from the soil solution sampling device*

App. 4.2 (p. 137): *Volumes of water (ml) collected by the suction plates in Plot 2 (installation depth 55 cm), study year 2001. Dates indicate when the cartridge was removed from the soil solution sampling device*

App. 4.3 (p. 138): *Volumes of water (ml) collected by the suction plates in Plot 1 (installation depth 55 cm), study year 2002. Dates indicate when the cartridge was removed from the soil solution sampling device*

App. 4.4 (p. 139): *Volumes of water (ml) collected by the suction plates in Plot 2 (installation depth 55 cm), study year 2002. Dates indicate when the cartridge was removed from the soil solution sampling device*

Further Explanations for App. 4.1–4:

In all tables of App. 4, **raw data** is presented. If overflow occurred, however, the volumes were corrected in the following way for further calculations:

a) Overflow in upper chamber: It was assumed that overflow of each cartridge was proportional to the volume collected by the respective suction plate. Fictitious example to illustrate the procedure: Volumes in bottles: 50 and 100 ml, overflow (upper chamber): 30 ml ⇨ corrected volumes would be 60 and 120 ml

b) Overflow in lower chamber: Equal fractions of the total volume of overflow were added to all bottles that actually did overflow. Overflowed bottles can be identified by a sampling volume of 270 ml

Labeling of the suction plates (also see **Figure 3.1**, **Figure 6.1**):

First number: Identifier of the profile (1 or 2 for SPL1 and SPL2)
Capital letter: Identifier of the "row": A = front row (closer to soil pit), B = back row
Final number: Identifier of the position of the plate (from left to right)

App. 4.1: Water fluxes Profile 1, study year 2001 (full caption and further explanation: p. 135)

The last two columns (upper, lower) are headed **overflow**.

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9	upper	lower
18/06/2001				30.0	20.0			50.0	5.0	220.0	80.0	70.0		70.0	80.0	180.0			
20/06/2001		5.0							5.0		5.0	40.0		10.0	5.0	20.0	5.0		
23/06/2001										10.0		10.0							
24/06/2001	2.0	13.5		105.5	28.5	110.5	201.0	71.5	17.5	189.5	137.0	159.5	78.5	103.5	46.5	175.5	72.0		
26/06/2001				10.5		34.5	2.5		5.0	63.5	1.5	47.0		14.0	14.0	49.5			
28/06/2001																			
30/06/2001						12.5				29.5	32.5			9.5	2.0	18.5			
02/07/2001			15.5	13.0		53.5	70.5	2.5		253.5	67.5	127.0	62.0	55.0	22.5	136.0	70.0		250
04/07/2001						37.0	23.0			141.5	40.0	45.0	4.5	15.5	14.0	87.0			
06/07/2001			10.0	2.0		42.5	17.5	5.0	2.0	44.0	24.5	26.5	10.5	18.0	22.0	43.0	6.0		50
08/07/2001						13.8				57.9		22.9	3.0	3.0	3.0	25.0			
10/07/2001			19.0	13.0	13.0	56.5	50.5	16.0		45.0	33.0	128.5	62.5	59.5	29.0	67.0	44.5		
12/07/2001			36.5	4.0	6.0	19.0	69.5	7.0		143.5	55.5	69.0	40.5	42.5	22.0	39.0	18.5		230
14/07/2001			10.5			36.0	17.5			67.0	16.0	39.0	3.0	16.0	13.5	62.0			30
16/07/2001						16.5				56.0				3.5	3.5	41.0			
18/07/2001				1.0						21.0	12.5					16.0			
20/07/2001										18.0	9.5			8.0	1.5	8.0			
22/07/2001	1.0		24.5	20.0	9.0	69.5	165.0	13.0	86.5	166.5	107.0	90.5	121.0	92.0	8.0	151.0	95.0		
24/07/2001	88.0	64.5	44.5	191.0	104.0	224.5	269.0	146.0	86.5	270.0	270.0	270.0	270.0	270.0	270.0	270.0	270.0	500	1100
26/07/2001			1.5	2.0	4.0	27.5	37.0			111.0	27.5	50.5	17.5	5.0	4.5	7.0	7.0		
28/07/2001	1.5	2.0	5.0	24.5	15.5	51.0	48.5	21.0	2.0	93.0	38.0	37.5	25.0	45.5	16.5	96.0	19.0		50
30/07/2001			26.5	8.5	3.5	36.0	21.0	6.0		62.5	26.0	35.0	11.0	19.0	12.5	29.5	4.5		
01/08/2001			8.0	12.5	14.5	26.5	21.5	19.5	8.5	29.0	17.5	14.0	19.5	26.5	7.5	27.0	7.5		
03/08/2001	67.5	56.0	7.5	112.0	97.5	133.5	202.5	135.5	103.5	207.0	264.5	213.0	268.0	193.0	81.5	180.0	162.5		700
05/08/2001	9.5	7.5	1.0	25.0	4.5	40.5	37.0	36.5	12.0	92.0	88.5	100.0	44.5	43.0	16.5	46.0	16.5		
07/08/2001	51.5	66.5	156.0	173.0	299.0	114.0	225.0	114.0	128.0	200.0	270.0	221.0	227.0	214.0	130.5	250.5	229.0		
09/08/2001			3.5	5.0	15.5	41.0	50.5	13.5	3.0	29.5	60.0	55.5	24.0	33.5	6.5	55.5	17.5		
11/08/2001			3.5	5.0	15.5	41.0	50.5	13.5	3.0	29.5	60.0	55.5	24.0	33.5	6.5	55.5	17.5		
13/08/2001	70.0	75.5	3.0	177.0	197.5	133.5	221.0	136.5	159.0	157.5	269.0	200.5	241.5	203.0	118.0	263.0	163.5		700
15/08/2001			1.5	3.5	11.5	40.0	38.0	20.0		70.5	36.5	48.5	28.5	24.5	5.5	51.0	12.0		
17/08/2001				17.5	25.0	41.5	30.0	29.5	10.0	70.0	40.0	26.0	24.0	43.0	5.0	44.0	9.0		

App. 4.2: Water fluxes Profile 2, study year 2001 (for caption and further explanation: p. 135)

Date	2 A 1	2 B 1	2 A 2	2 B 2	2 A 3	2 B 3	2 A 4	2 B 4	2 A 5	2 B 5	2 A 6	2 B 6	2 A 7	2 B 7	2 A 8	2 B 8	2 A 9	overflow	
																		upper	lower
18/06/2001		10		10		30		40	5	30	30	20	10	100		30	5		
20/06/2001		20		10		10		10		10	15	10	10	15		5			
23/06/2001										10				20					
24/06/2001	41	98.4	149.5	117		272	151	270	154.5	160.5	267.5	240	270.5	206.5	59	218	28.5		
26/06/2001		1		3		68.5		72.5		24.5	16.5	29	19.5	17		20			
28/06/2001						30.5		33		6	20.5	22.5	5.5	59		59			
30/06/2001		3				25.5		9.5		22.5	3	11.5		46		1			
02/07/2001		36.5	56.5	59		65	52.5	117.5	45.5	115.5	265	130.5	93.5	107		100	3	800	
04/07/2001		17		7		65		45		34	59	46	30.5	87.5		31.5		50	
06/07/2001		15		10.5		40		36		27	32.5	34	20	44.5		20		30	
08/07/2001		12				27.5		13		19	20	14.5	10	27		10			
10/07/2001		26		40.5		24	19	84	26	48	30.5	62	46	78.5		53.5	3		
12/07/2001		22	16	32.5		79.5	18	75	13.5	31	127.5	80.5	120	95.5		44		250	
14/07/2001		19		10		21.5		41.5		20	39	47.5	20.5	29.5		22		120	
16/07/2001		2.5				15		5		10		11.6		14.3					
18/07/2001						4.5				4				10					
20/07/2001										1.5									
22/07/2001				2		36.5	1	69	6.5	12	88	36.5	17.5	29		39.5			
24/07/2001	62	147	242.5	181.5		270	262	245.5	270	270	270	270	270	270	92	270	35.5	1300	2300
26/07/2001									2.5						1.5				
28/07/2001		3.5		1.5		29.5		20		12	3	6.5		13.5					
30/07/2001						2													
01/08/2001																			
03/08/2001																			
05/08/2001		24	9			43.5	27.5	28	6	22.5	5.5	4	26	4.5		36.5		1500	
07/08/2001		54	66			144.5	54	231.5	78	144	248	121	244.5	70		69		2000	
09/08/2001	66.5	225.5	270			270	270	270	270	270	270	217	270	270	139	270	31.5	2000	3000
11/08/2001		21				38	1	89.5	9	60	51	72.5	78.5	92.5		71		200	
13/08/2001	59.5	270	270			270	270	270	270	270	270	270	270	270	169	520	73	2500	3000
15/08/2001		27.5	3			56	15	63	15.5	35	68.5	65	86.5	95		100			
17/08/2001		12.5	4.5			32.5	7.5	28.5	7	28	64.5	40.5	58	73.5		62.5			

Note (column 2 A 3): suction plate broke

App. 4.3: Water fluxes Profile 1, study year 2002 (full caption and further explanation: p. 135)

Date	1A 2	1A 3	1A 4	1B 4	1A 5	1B 5	1B 6	1B 7	1A 8	1B 8	overflow
19/06/2002	0.4	0.2	0.6	0.5	0.5	1.4	0.5	0.3	0.3	7.6	
20/06/2002	0.7	2.7	0.8	0.6	0.6	8.9	4.0	0.4	0.6	26.8	
22/06/2002	3.1	13.7		21.3		46.1		22.2	19.0	43.5	
24/06/2002	8.0	17.6		22.4		42.1		10.3	17.7	30.2	
26/06/2002	7.1	16.4		18.5		18.6		18.7	16.2	33.7	
29/06/2002	23.1	25.9	0.1	38.6	8.1	47.8	7.0	30.6	31.6	42.9	
30/06/2002	20.6	21.3	1.1	32.4	11.9	39.1	2.9	9.5	23.3	23.9	
02/07/2002	40.5	28.5	33.6	41.2	46.0	34.0	40.2	266.7	41.6	47.1	1500
04/07/2002	34.8	34.3	28.8	36.9	24.1	48.6	24.7	128.7	8.4	62.9	
06/07/2002	28.3	29.0	11.7	11.6	8.3	53.0	10.3	58.9	13.3	65.9	300
09/07/2002	41.7	39.3	16.1	88.4	29.4	70.3	7.2	40.6	34.4	88.7	
10/07/2002	23.3	9.0	0.5	33.7	4.4	38.9	4.5	46.1	32.3	42.4	
12/07/2002	53.5	44.8	22.0	55.0	21.3	46.7	16.3	55.6	76.0	54.3	220
14/07/2002	16.8	38.1	6.5	26.6	18.4	13.4	50.3	51.8	39.0	50.9	150
16/07/2002	8.0	8.0	5.1		16.4	48.7	0.6	59.3	43.8	37.9	135
19/07/2002	32.1	11.1	6.9	0.5	20.5	53.2	12.4	44.4	12.4	43.2	140
20/07/2002		6.4		11.0		8.9		8.1		9.7	
22/07/2002	13.9	11.1	1.1	36.7	6.1	35.6	26.8	4.8	25.5	9.3	20
24/07/2002	9.8	15.4	0.4	14.1	0.5	9.2	8.0	34.7	31.8	57.4	50
26/07/2002	17.3	21.7	0.2	27.2	0.5	67.4	6.2	12.3	25.7	32.2	65
29/07/2002	8.4	5.3		7.2		8.2	8.7	49.7	40.9	10.3	125
30/07/2002	0.7	3.5	0.5	14.0	0.4	6.0		3.5		7.4	
01/08/2002	2.5	7.7		8.7		2.5		6.0	7.3	28.8	
03/08/2002	2.6	10.3		12.4		23.7		11.8	9.3	21.3	
05/08/2002	39.7	12.2	11.9	80.7	27.5	4.0	32.3	105.2	41.4	57.0	500
08/08/2002	34.8	38.9	2	61.9	12.7	41.5	26.0	45.5	46.8	41.0	400
11/08/2002	6.8	33.1	5.6	45.1	2.2	88.9	8.7	53.4	55.2	70.3	50

App. 4.4: Water fluxes Profile 2, study year 2002 (full caption and further explanation: p. 135)

Date	2 A 1	2 B 1	2 A 2	2 B 2	2 A 3	2 B 3	2 A 4	2 B 4	2 B 5	2 A 6	2 A 7	2 B 7	2 A 8	lower upper overflow
19/06/2002	0.6	5.6	18.3	4.1	0.5	31.5	28.3	28.9	8.3	24.6	16.2	31.6	9.9	
20/06/2002	0.4	3.4	7.8	2.5	0.7	11.2	12.3	5.0	2.6	7.8	7.6	26.7	0.5	
22/06/2002	4.7	7.7	18.7	4.8		3.6	26.7	35.9	8.2	26.2	14.3	4.6	18.2	
24/06/2002		5.7	13.2	4.4		21.4	21.7	26.6	6.2	27.4	13.2	43.9	7.6	
26/06/2002		5.4	1.7	3.0		17.9	19.4	24.7	5.6	20.0	7.8	42.8	4.3	
29/06/2002	6.1	0.9	12.1	8.5	0.3	17.2	19.3	35.3	8.9	31.4	14.4	23.8	1.6	
30/06/2002	0.5	3.2	27.6	1.0	0.5	36.4	42.3	48.6	4.7	43.2	9.6	65.9	44.4	
02/07/2002	39.9	28.9	37.7	1.1	7.0	53.3	64.9	33.9	34.4	32.5	32.4	197.5	31.4	1300
04/07/2002	45.7	11.8	52.9	5.8		59.4	35.5	86.8	15.8	27.7	24.3	116.1	74.6	
06/07/2002	12.9	7.4	24.6	3.6		45.9	25.2	33.8	5.5	19.5	1.8	7.3	13.6	
09/07/2002	39.3	11.1	32.6	6.2	6.9	45.5	55.5	67.5	9.8	59.0	24.4	53.6	53.3	180
10/07/2002	18.1	7.6	27.7	3.4	0.3	36.4	31.5	37.3	7.5	33.5	1.4	53.6	16.6	
12/07/2002	56.5	11.3	39.8	5.8	2.1	34.4	45.9	36.3	13.6	62.6	16.9	63.5	4.7	125
14/07/2002	43.3	1.8	38.2	5.4	1.9	42.8	46.4	44.0	14.3	47.2	15.2	62.5	33.2	
16/07/2002	1.8	4.6	24.7	4.4	2.0	36.4	3.7	4.9	9.6	4.7	9.9	36.5	2.1	
19/07/2002	25.5	6.9	9.5	2.2	0.4	28.3	28.9	32.0	8.7	8.5	7.8	5.7	15.5	40
20/07/2002	0.7	1.7	1.9	1.8			7.5	5.6	3.3		0.5	13.4		
22/07/2002	0.9	2.4	5.0	0.9	0.3	7.6	10.0	12.3	3.8	0.5	2.6	17.9	0.5	
24/07/2002	1.0	3.9	3.2	2.3	0.6	7.2	1.5	14.3	5.0	1.2	2.6	24.8	2.2	
26/07/2002	0.5	4.7	8.3	2.7	0.8	9.2	15.5	16.9	6.0	12.7	1.2	29.6	6.4	
29/07/2002	2.9	5.7	9.3	3.4		9.4	18.0	7.9	6.4	11.2		27.6	6.5	
30/07/2002	0.3	1.8	2.2	1.4			3.6	5.5	1.3			7.9		
01/08/2002		3.8	6.4	2.9		0.1	8.6	6.6	3.0			8.7		
03/08/2002		3.9		1.9		4.6	9.8	8.2	2.6			1.7		
05/08/2002	5.7	8.6	0.4	5.9	0.8	27.9	8.5	3.9	9.4	24.1	5.1	1.2	3.2	
08/08/2002	7.9	12.1	31.5	1.7	1.6	18.0	48.5	34.4	14.8	47.6	11.8	52.7	32.4	140
11/08/2002	27.2	11.6	24.3	6.3	3.8	26.4	25.1	27.8	9.5	18.1	0.3	35.3	4.6	

App. 4.5: Water volumes (ml) collected by surface runoff collectors, study year 2001. No water was collected on sampling days that are missing in the table. For positions of the collectors on the research plot, see **Figure 6.1**

Date	SPL1	SPL2
24/06/2001	511	577
24/07/2001		186
05/08/2001		230

App. 4.6: Water volumes (ml) collected by surface runoff collectors, study year 2002. No water was collected on sampling days that are missing in the table. For positions of the collectors on the research plot, see **Figure 6.1**

Date	SPL 1	WLY	SPL 2
30/06/2002		67	
02/07/2002		105	45
09/07/2002		38	0
22/07/2002	92	209	118
05/08/2002		145	55
11/08/2002		13	

App. 4.7: Water volumes (ml) collected by wick lysimeters, study year 2002. No water was collected on sampling days that are missing in the table

Date	WLY 1	WLY 2	WLY 3
02/07/2002	623	748	411
04/07/2002	76	78	22
09/07/2002	16	51	28
10/07/2002	13	31	14
12/07/2002	34	90	41

Appendix 5: Concentrations of pesticides in samples from suction plates, surface runoff gutters, and wick lysimeters

App. 5.1: *Pesticide residues (µg) detected in soil solution collected by suction plates in Profile 1 (study year 2001). The dates indicate the day the cartridge was taken off the system; no residues were found on sampling days that are not listed here*

a) Cypermethrin

(never detected in profile 1)

b) Endosulfan-α

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9
24/06/01	0.06	0.04			0.03			0.06		0.01			0.02	0.02	0.01		0.04
26/06/01						0.001						0.001		0.01			
28/06/01			0.04														

c) Chlorpyrifos

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9
24/06/01	0.11	0.07	0.16	0.02	0.05	0.001		0.001	0.1		0.03	0.001	0.03		0.03		0.08
26/06/01						0.03		0.02		0.05		0.05		0.07			
28/06/01	0.06		0.05			0.04											

d) Malathion

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9
24/06/01	0.05	0.07	0.08	0.06	0.03	0.03	0.04	0.03	0.06	0.05	0.05	0.03	0.07	0.05	0.04	0.03	0.07
26/06/01						0.02		0.02				0.04		0.07	0.001	0.04	
28/06/01	0.03		0.03					0.03	0.03		0.03						
30/06/01														0.03			
02/07/01												0.03					

e) Triazophos

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9
24/06/01		0.03								0.001		0.04	0.03	0.001			0.07

f) Dicrotophos

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9
24/06/01	0.19	1.24		0.51	0.13	1.26	0.78	1.51	0.19	2.14	0.53	0.56	1.06	1.18	0.26	0.12	1.05
26/06/01						0.24								0.31			
30/06/01												0.27					

g) Mevinphos

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9
24/06/01	0.09	0.2	0.12	0.19	0.1	0.37	0.28	0.19	0.08	0.36	0.11	0.22	0.19	0.19	0.1	0.04	0.18
26/06/01						0.06		0.04		0.13		0.1		0.12			
28/06/01	0.03					0.04			0.04								

h) Dimethoate

Date	1 A 1	1 B 1	1 A 2	1 B 2	1 A 3	1 B 3	1 A 4	1 B 4	1 A 5	1 B 5	1 A 6	1 B 6	1 A 7	1 B 7	1 A 8	1 B 8	1 A 9
24/06/01	0.34	8.59	0.07	5.33	0.04	22.6	28.4	5.98	0.77	36.1	1.02	15.0	11.8	15.2	0.35	0.51	10.0
26/06/01						2.39		0.17		0.24		3.12		1.93	0.30	0.27	
28/06/01											0.04						
30/06/01						0.25						0.27	0.65				
02/07/01		0.06		0.18				0.09									
04/07/01	0.13												0.18				
06/07/01			0.04					0.11	0.19				0.12		0.02		0.02
08/07/01	0.12		0.13		0.15								0.13				
12/07/01			0.06														
24/07/01		0.47															
13/08/01		0.03										0.02					

i) Monocrotophos

Date	1 A 1	1 B 1	1 A 2	1 B 2	1 A 3	1 B 3	1 A 4	1 B 4	1 A 5	1 B 5	1 A 6	1 B 6	1 A 7	1 B 7	1 A 8	1 B 8	1 A 9
24/06/01	0.28	1.54	0.2	0.94	0.18	2.73	2.15	1.66	0.35	4.29	0.65	2.64	1.91	2.84	0.61	0.26	1.88
26/06/01						0.42								0.36			

App. 5.2: Pesticide residues (µg) detected in soil solution collected by suction plates in Profile 2 (study year 2001). The dates indicate the day the cartridge was taken off the system; no residues were found on sampling days that are not listed here

a) Cypermethrin

Date	2A1	2B1	2A2	2B2	2A3	2B3	2A4	2B4	2A5	2B5	2A6	2B6	2A7	2B7	2A8	2B8	2A9
24/06/01	0.01	0.05	0.18	0.22		0.54	0.02	0.60	0.17		0.22	0.45	0.17	0.45	0.06	0.51	0.10
26/06/01						0.04											
28/06/01									0.09								
02/07/01			0.002								0.002						

b) Endosulfan-α

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9
02/07/01	0.001																
06/07/01																	0.08

c) Chlorpyrifos

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9
24/06/01						0.01		0.01							0.02		0.02
06/07/01			0.01														

d) Malathion

Date	2A1	2B1	2A2	2B2	2A3	2B3	2A4	2B4	2A5	2B5	2A6	2B6	2A7	2B7	2A8	2B8	2A9
24/06/01	0.03	0.05	0.09	0.35		0.18	0.07	0.04	0.03		0.04	0.17	0.08	0.62	0.17	0.09	0.21
26/06/01		0.02		0.02		0.01				0.03		0.03				0.03	
28/06/01									0.05		0.001						
02/07/01	0.02			0.016													0.049

e) Triazophos

Date	1A1	1B1	1A2	1B2	1A3	1B3	1A4	1B4	1A5	1B5	1A6	1B6	1A7	1B7	1A8	1B8	1A9
24/06/01				0.10		0.16	0.03	0.01			0.03	0.24	0.13	0.40	0.05	0.08	0.09

f) Dicrotophos

Date	2A1	2B1	2A2	2B2	2A3	2B3	2A4	2B4	2A5	2B5	2A6	2B6	2A7	2B7	2A8	2B8	2A9
24/06/01	1.51	2.60	5.15	13.9		4.96	5.02	4.23	3.49		3.88	11.5	9.44	24.2	17.4	5.97	7.69
26/06/01		0.25				0.09						0.22		0.19		0.21	
28/06/01									11.5								
02/07/01	0.07		0.13								0.20		0.15				0.15

g) Mevinphos

Date	2A1	2B1	2A2	2B2	2A3	2B3	2A4	2B4	2A5	2B5	2A6	2B6	2A7	2B7	2A8	2B8	2A9
24/06/01	0.17	0.38	1.07	1.01		0.33	0.28	0.31	0.25		0.27	0.32	0.65	0.78	1.06	0.30	0.54
26/06/01				0.07		0.13		0.08				0.04	0.13	0.02			
28/06/01									0.83						0.02		
02/07/01	0.07	0.08	0.11	0.08		0.08					0.11	0.08	0.13				

h) Dimethoate

Date	1 A 1	1 B 1	1 A 2	1 B 2	1 A 3	1 B 3	1 A 4	1 B 4	1 A 5	1 B 5	1 A 6	1 B 6	1 A 7	1 B 7	1 A 8	1 B 8	1 A 9
24/06/01	1.29	31.9	113	32.8		39.1	10.5	19.1	18.6		33.8	26.4	73.7	40.6	36.1	8.59	10.1
26/06/01		0.66		1.23		5.35		0.03		0.20	0.22	3.41	3.81	2.18		0.69	
28/06/01	0.30								3.33		0.10		2.01				
30/06/01						0.54						1.09					
02/07/01	0.03	0.82	0.30	2.79													0.36
04/07/01				0.17													
06/07/01		0.28	0.07	0.03					0.03								
08/07/01						0.01											
10/07/01			0.16					0.01	0.14								0.15
12/07/01			0.03														

i) Monocrotophos

Date	2 A 1	2 B 1	2 A 2	2 B 2	2 A 3	2 B 3	2 A 4	2 B 4	2 A 5	2 B 5	2 A 6	2 B 6	2 A 7	2 B 7	2 A 8	2 B 8	2 A 9
24/06/01	1.3	3.95	8.08	16.34		8.58	4.43	6.42	5.78		5.99	11.5	12.5	7.13	10.7	6.9	4.29
26/06/01		0.49		0.59		0.63						0.65		0.58		0.54	
28/06/01									13.3								
02/07/01	0.14		0.31						0.25		0.38		0.34				0.59

App. 5.3: *Pesticide concentrations (µg l⁻¹) in surface runoff, study year 2002. No water was collected on sampling days that are missing in the table. ES = endosulfan, S = sulfate, L = lactone, ChP = chlorpyrifos, Mal = malathion, Dim = dimethoate, Mev = mevinphos*

Date	Profile	ES-α	ES-β	ES-S	ES-L	ChP	Mal	Dim	Mev
30/06/2002	SPL1								
	WLY	15.1	62.2	11.0	3.58	29.9	3160	1500	779
	SPL2								
02/07/2002	SPL1								
	WLY	14.4	60.9	12.2	6.48	11.1	669	788	48.8
	SPL2	10.9	37.3	18.2	3.56	2.00	314	346	12.0
09/07/2002	SPL1								
	WLY	7.11	11.8	10.0	70.3	4.21	46.3	842	13.7
	SPL2								
22/07/2002	SPL1	5.22	12.6	10.7	2.39	7.83	403	169	41.7
	WLY	5.12	15.6	9.04	2.73	5.45	1340	166	61.3
	SPL2	3.90	12.1	11.6	5.42	7.46	313	155	51.1

App. 5.4: *Pesticide concentrations (µg l⁻¹) in soil solution collected by wick lysimeters (study year 2002). No water was collected on sampling days that are missing in the table. ES = endosulfan, S = sulfate, L = lactone, ChP = chlorpyrifos, Mal = malathion, Dim = dimethoate, Mev = mevinphos*

Date	Sampler	ES-a	ES-b	ES-S	ES-L	ChP	Mal	Dim	Mev
02/07/2002	WLY1	0.84	0.52	0.71	0	0	0	0	0
	WLY2	0.67	0.38	0.58	0.19	0.48	0.48	0	0
	WLY3	1.47	0.88	0.73	0.10	0.59	0.64	2.84	0
04/07/2002	WLY1	3.24	1.35	0.81	0.27	1.34	2.14	0	0
	WLY2	3.95	1.97	0.66	0	0.66	0.92	0	0
	WLY3								
09/07/2002	WLY1	11.3	6.88	8.13	3.13	4.38	4.38	0	0
	WLY2	0.82	0.61	2.86	0.61	1.63	1.22	14.7	0
	WLY3	6.07	2.86	3.57	2.14	2.50	5.36	21.4	0
10/07/2002	combined	4.66	2.59	1.90	1.21	1.55	3.62	9.66	0
12/07/2002	WLY1	4.01	1.54	4.32	1.85	3.39	1.85	0	0
	WLY2	2.15	0.90	0.90	0.68	0.79	1.13	6.89	0
	WLY3	7.39	3.06	2.29	0	2.04	1.78	0	0

Appendix 6: Pesticide concentrations in soil samples

(see next pages)

App. 6.1: *Sequential extraction of pesticides in topsoil: concentrations in CaCl$_2$ extract (µg · 10 g soil^{-1}). ES = endosulfan, S = sulfate, L = lactone, ChP = chlorpyrifos, Mal = malathion, Dim = dimethoate, Mev = mevinphos; T = traces (below limit of quantification)*

Date	ES-α	ES-β	ES-S	ES-L	ChP	Mal	Dim	Mev
20/06/2002	0.32	0.16	0.12	T	0.11	T	1.22	T
20/06/2002	0.49	0.21	0.13	0.04	0.14	T	1.20	T
22/06/2002	0.22	0.13	0.22	0.04	0.14	T	0.77	T
22/06/2002	0.13	0.11	0.19	0.03	T	T	0.06	T
24/06/2002	0.22	0.15	0.27	0.04	T	T	0.35	T
24/06/2002	0.26	0.20	0.34	0.04	T	T	0.37	T
26/06/2002	0.32	0.17	0.14	0.04	0.10	T	0.15	T
26/06/2002	0.62	0.31	0.23	0.05	0.19	T	0.24	T
29/06/2002	0.03	0.06	0.13	0.04	0.05	T	T	T
29/06/2002	0.04	0.05	0.11	0.04	0.03	T	T	T
30/06/2002	1.13	0.55	0.44	0.11	0.05	0.24	2.65	T
30/06/2002	1.14	0.54	0.45	0.12	0.03	0.03	1.17	T
02/07/2002	0.89	0.62	0.56	0.32	0.30	T	1.49	T
02/07/2002	0.99	0.66	0.64	0.28	0.34	0.06	1.54	T
04/07/2002	0.23	0.28	0.39	0.19	0.10	T	0.12	T
04/07/2002	0.18	0.22	0.30	0.18	0.08	T	0.16	T
06/07/2002	0.37	0.34	0.37	0.15	0.06	T	0.34	T
06/07/2002	0.35	0.33	0.38	0.14	0.11	T	0.16	T
09/07/2002	0.25	0.40	0.68	0.23	0.12	T	0.07	T
09/07/2002	0.21	0.33	0.52	0.15	0.15	T	T	T
10/07/2002	0.62	0.43	0.52	0.03	0.41	0.20	16.54	T
10/07/2002	0.59	0.40	0.44	T	0.38	0.16	15.37	T
12/07/2002	0.59	0.50	0.76	0.03	0.51	0.05	9.25	T
12/07/2002	0.49	0.42	0.61	0.03	0.39	0.04	9.17	T
14/07/2002	0.15	0.16	0.42	T	0.20	T	2.61	T
14/07/2002	0.13	0.17	0.53	T	0.20	T	2.15	T
16/07/2002	0.13	0.18	0.69	T	0.27	T	2.10	T
16/07/2002	0.16	0.19	0.57	T	0.19	T	2.17	T
19/07/2002	0.11	0.13	0.49	T	0.23	T	1.25	T
19/07/2002	0.17	0.22	0.55	T	0.24	T	1.51	T
20/07/2002	0.33	0.24	0.60	T	0.29	0.15	13.16	T
20/07/2002	0.20	0.20	0.48	T	0.09	0.04	6.27	T
22/07/2002	0.29	0.40	0.94	T	0.30	T	5.54	T
22/07/2002	0.23	0.30	0.90	T	0.30	T	2.69	T
24/07/2002	0.39	0.39	1.15	T	0.32	0.03	3.39	T
24/07/2002	0.30	0.35	1.13	T	0.27	T	3.48	T
26/07/2002	0.12	0.25	1.04	T	0.30	T	1.56	T
26/07/2002	0.23	0.29	0.88	T	0.34	T	1.74	T
29/07/2002	0.03	0.13	0.84	T	0.10	T	0.62	T
29/07/2002	0.04	0.19	0.80	T	0.17	T	0.62	T
30/07/2002	0.19	0.17	0.39	T	0.18	0.40	6.28	0.15
30/07/2002	0.22	0.18	0.37	T	0.23	0.37	6.91	0.17
01/08/2002	0.73	0.48	0.60	T	0.44	1.38	10.59	0.15
01/08/2002	0.45	0.31	0.65	T	0.51	1.24	12.26	0.34
03/08/2002	0.16	0.15	0.58	T	0.34	0.19	6.51	0.06
03/08/2002	0.21	0.19	0.62	T	0.34	0.18	8.55	0.06
05/08/2002	0.18	0.15	0.45	T	0.22	0.05	3.63	T
05/08/2002	0.18	0.19	0.51	T	0.22	0.07	4.06	0.06
08/08/2002	0.08	0.11	0.52	T	0.21	0.04	2.43	T
08/08/2002	0.08	0.12	0.45	T	0.16	0.04	1.83	T
01/09/2002	T	0.13	0.61	T	0.04	T	0.21	T
01/09/2002	0.05	0.27	0.93	T	0.04	T	0.25	T

App. 6.2: *Sequential extraction of pesticides in topsoil: concentrations in methanol extract* ($\mu g \cdot 10$ *g soil^{-1}). ES = endosulfan, S = sulfate, L = lactone, ChP = chlorpyrifos, Mal = malathion, Dim = dimethoate, Mev = mevinphos; T = traces (below limit of quantification)*

Date	ES-α	ES-β	ES-S	ES-L	ChP	Mal	Dim	Mev
20/06/2002	13.30	7.46	5.61	T	13.13	0.76	10.27	0.03
20/06/2002	21.54	10.42	5.77	T	17.39	0.94	10.30	0.03
22/06/2002	10.80	7.82	7.39	0.06	14.91	0.48	5.17	T
22/06/2002	4.93	4.35	4.69	T	7.89	0.25	3.05	T
24/06/2002	7.27	6.59	7.11	0.06	11.03	0.34	4.45	T
24/06/2002	9.11	8.86	8.99	0.09	14.46	0.40	5.05	T
26/06/2002	11.09	7.72	4.66	0.07	10.67	0.67	3.77	T
26/06/2002	29.63	13.85	5.98	0.07	22.08	0.68	4.52	T
29/06/2002	1.62	2.64	3.98	0.06	3.22	0.09	1.38	T
29/06/2002	1.58	2.29	3.42	0.06	2.97	0.10	1.31	T
30/06/2002	44.06	26.79	9.53	0.24	32.67	1.73	10.99	0.09
30/06/2002	46.52	28.57	9.08	0.28	34.46	1.86	13.13	0.10
02/07/2002	38.64	35.21	26.78	0.33	37.81	1.45	11.70	0.03
02/07/2002	37.89	31.28	21.67	0.32	36.93	1.35	14.54	0.04
04/07/2002	6.24	10.42	11.55	0.16	12.52	0.28	2.72	T
04/07/2002	5.04	7.68	8.54	0.14	9.72	0.26	2.72	T
06/07/2002	10.86	12.84	10.85	0.18	13.29	0.71	6.34	T
06/07/2002	11.68	13.72	12.29	0.18	14.78	0.57	4.45	T
09/07/2002	7.14	14.63	17.01	T	15.11	T	2.21	T
09/07/2002	3.24	6.24	12.99	T	11.84	T	2.04	T
10/07/2002	28.33	23.12	18.90	0.18	37.03	1.81	15.44	0.06
10/07/2002	26.44	20.45	14.94	0.17	34.27	1.74	15.53	0.07
12/07/2002	35.50	33.38	31.26	0.28	55.04	1.37	13.21	0.05
12/07/2002	30.11	27.67	24.09	0.24	43.70	0.93	13.15	0.04
14/07/2002	13.01	21.60	24.59	0.27	24.91	0.31	7.13	0.03
14/07/2002	13.47	21.58	24.52	0.26	29.47	0.44	7.13	0.03
16/07/2002	18.10	31.49	33.56	0.42	34.39	0.54	6.24	0.03
16/07/2002	12.68	22.41	22.61	0.30	25.66	0.37	5.57	0.03
19/07/2002	8.38	15.97	17.11	0.20	19.46	0.12	3.34	0.03
19/07/2002	12.80	23.37	23.01	0.34	27.27	0.21	4.48	0.03
20/07/2002	25.79	23.02	21.23	0.29	26.86	1.77	12.28	0.05
20/07/2002	8.70	10.55	11.58	0.19	11.93	0.45	6.73	0.03
22/07/2002	8.59	15.20	31.63	0.66	19.07	0.22	7.56	T
22/07/2002	12.33	17.86	34.80	0.63	26.73	0.26	6.05	T
24/07/2002	17.46	25.40	32.99	0.43	17.64	0.26	7.29	T
24/07/2002	16.58	18.75	29.28	0.39	17.87	0.17	6.27	T
26/07/2002	11.45	26.14	38.06	0.49	24.72	0.13	4.74	T
26/07/2002	11.16	17.08	27.72	0.46	23.05	0.22	4.61	T
29/07/2002	2.15	10.99	24.51	0.57	9.58	0.08	2.48	T
29/07/2002	1.90	9.99	21.34	0.53	9.60	0.08	2.24	T
30/07/2002	17.40	21.67	18.00	0.85	25.34	2.82	17.07	0.14
30/07/2002	17.28	19.24	15.71	0.86	24.28	2.89	17.17	0.12
01/08/2002	36.90	26.09	17.84	0.83	33.49	4.73	19.38	0.11
01/08/2002	47.25	32.26	21.03	0.96	41.73	5.45	20.63	0.13
03/08/2002	30.25	37.23	26.12	1.43	37.14	2.40	8.88	0.03
03/08/2002	26.59	34.08	26.73	1.63	36.07	1.81	10.63	0.03
05/08/2002	15.96	21.92	17.81	1.16	23.56	0.62	5.43	0.03
05/08/2002	17.76	21.72	18.31	1.21	24.44	0.73	6.76	0.03
08/08/2002	9.18	20.70	20.49	1.73	21.97	0.40	5.14	T
08/08/2002	7.92	17.63	16.72	1.29	18.09	0.33	4.08	T
01/09/2002	2.91	19.48	23.75	1.71	2.96	0.13	1.60	T
01/09/2002	4.31	29.26	34.44	1.55	4.29	0.16	1.39	T

App. 6.3: *Sequential extraction of pesticides in topsoil: concentrations in AEW (acetone :* *ethyacetate : water = 3:1:1) extract ($\mu g \cdot 10$ g soil^{-1}). ES = endosulfan, S = sulfate, L = lactone,* *ChP = chlorpyrifos, Mal = malathion, Dim = dimethoate, Mev = mevinphos; T = traces (below* *limit of quantification)*

Date	ES-α	ES-β	ES-S	ES-L	ChP	Mal	Dim	Mev
20/06/2002	1.96	1.46	1.45	T	1.72	0.19	3.71	0.42
20/06/2002	2.59	1.81	1.55	T	2.21	0.22	3.84	0.25
22/06/2002	1.71	1.49	1.85	0.03	1.81	0.12	2.65	0.23
22/06/2002	0.85	0.76	1.20	T	0.99	0.03	1.58	0.06
24/06/2002	1.33	1.28	1.53	0.03	1.31	0.08	2.97	0.08
24/06/2002	1.51	1.51	1.88	0.04	1.70	0.12	3.55	0.09
26/06/2002	1.75	1.26	1.16	0.05	1.60	0.24	2.15	0.04
26/06/2002	3.04	2.16	1.39	0.04	2.91	0.25	2.49	0.04
29/06/2002	0.40	0.51	1.19	0.05	0.53	0.04	1.20	0.03
29/06/2002	0.36	0.36	0.99	0.04	0.46	0.04	1.29	0.03
30/06/2002	4.40	3.19	2.06	0.04	4.16	0.49	4.11	0.08
30/06/2002	4.63	3.32	2.08	0.05	4.48	0.56	5.00	0.10
02/07/2002	4.53	3.95	4.58	0.09	5.48	0.40	6.13	0.13
02/07/2002	3.89	3.41	3.85	0.07	4.71	0.38	6.63	0.13
04/07/2002	1.20	1.66	2.22	0.06	1.47	0.05	1.96	0.06
04/07/2002	1.01	1.40	1.74	0.06	1.17	0.04	2.02	0.06
06/07/2002	1.75	1.82	2.18	0.07	1.77	0.22	4.06	0.08
06/07/2002	1.86	2.01	2.46	0.08	1.94	0.15	3.09	0.09
09/07/2002	1.34	2.04	3.34	0.14	1.94	0.09	1.93	0.07
09/07/2002	0.95	1.63	2.46	0.11	1.43	0.06	1.78	0.05
10/07/2002	4.66	4.74	5.10	0.07	4.93	0.46	6.30	0.06
10/07/2002	4.38	4.02	4.14	0.06	4.77	0.43	5.25	0.06
12/07/2002	5.93	6.35	7.31	0.08	7.67	0.38	6.37	0.06
12/07/2002	5.24	5.43	5.83	0.08	6.29	0.31	7.37	0.06
14/07/2002	2.69	3.54	4.33	0.09	3.82	0.15	3.94	0.04
14/07/2002	2.86	4.02	4.92	0.09	4.48	0.18	4.10	0.03
16/07/2002	3.48	5.27	5.92	0.16	5.25	0.21	3.21	0.04
16/07/2002	2.74	3.75	4.21	0.10	3.98	0.16	3.38	0.03
19/07/2002	1.26	2.27	4.40	0.14	2.74	0.08	2.87	0.03
19/07/2002	1.81	3.22	5.68	0.19	3.78	0.10	3.76	T
20/07/2002	2.80	3.16	5.22	0.21	3.72	0.58	5.80	0.04
20/07/2002	1.19	1.62	2.77	0.10	1.71	0.18	3.61	0.03
22/07/2002	1.10	2.41	5.23	0.36	2.47	0.14	6.18	0.03
22/07/2002	1.58	3.04	6.57	0.34	3.50	0.14	5.05	0.03
24/07/2002	2.02	3.28	5.97	0.30	2.66	0.12	6.37	T
24/07/2002	1.94	3.17	5.43	0.23	2.46	0.11	5.71	T
26/07/2002	1.43	3.19	6.24	0.32	3.24	0.09	4.69	T
26/07/2002	1.46	2.70	5.10	0.34	2.97	0.11	4.71	T
29/07/2002	0.41	1.76	4.57	0.36	1.46	0.07	3.39	T
29/07/2002	0.40	1.57	4.03	0.31	1.38	0.07	3.19	T
30/07/2002	2.69	4.27	4.66	0.28	3.96	0.94	4.12	0.05
30/07/2002	2.68	3.91	4.31	0.27	3.83	0.96	4.01	0.05
01/08/2002	5.02	5.24	4.71	0.34	5.28	1.44	4.45	0.05
01/08/2002	6.59	6.65	5.69	0.39	6.72	1.71	4.88	0.08
03/08/2002	3.77	5.53	5.51	0.28	5.18	0.65	4.20	0.03
03/08/2002	3.65	5.28	6.30	0.34	5.43	0.50	4.91	0.03
05/08/2002	2.53	3.67	4.58	0.26	4.07	0.31	3.30	0.03
05/08/2002	2.72	3.63	4.77	0.27	4.12	0.36	4.00	0.03
08/08/2002	1.54	3.21	4.63	0.40	3.66	0.18	3.07	T
08/08/2002	1.43	2.85	4.14	0.33	3.01	0.12	2.56	T
01/09/2002	0.72	3.25	5.64	0.51	0.77	0.11	1.60	T
01/09/2002	1.06	4.74	7.65	0.46	1.31	0.17	1.63	T

Appendix 7: Pesticide concentrations in river water samples

*App. 7.1 (p. 151): Pesticide concentrations in baseflow samples collected in the BPK catchment. Now samples were collected on the days marked in grey; T = traces (concentration below limit of quantification). Raw data is presented, the data discussed in **Chapter 2** was corrected for the blind values listed in the second column*

*App. 7.2 (p. 152): Pesticide concentrations in baseflow samples collected in the BNH catchment. Now samples were collected on the days marked in grey; T = traces (concentration below limit of quantification). Raw data is presented, the data discussed in **Chapter 2** was corrected for the blind values listed in the second column*

*App. 7.3 (p. 153): Pesticide concentrations in baseflow samples collected in the MSM catchment. Now samples were collected on the days marked in grey; T = traces (concentration below limit of quantification). Raw data is presented, the data discussed in **Chapter 2** was corrected for the blind values listed in the second column*

App. 7.1: *Pesticide concentrations in river water of the BPK catchment (full caption: p. 150)*

Pesticide	11/10/2002	10/10/2002	09/10/2002	08/10/2002	07/10/2002	06/10/2002	05/10/2002	04/10/2002	03/10/2002	02/10/2002	01/10/2002	30/09/2002	29/09/2002	28/09/2002	27/09/2002	26/09/2002	25/09/2002	24/09/2002	23/09/2002	22/09/2002	21/09/2002	20/09/2002	19/09/2002	18/09/2002	17/09/2002	16/09/2002	15/09/2002	14/09/2002	13/09/2002	12/09/2002	11/09/2002	10/09/2002	09/09/2002	blind values
Atrazin																																		
Cabofuran																																0.02		
Captan																																		
Chlorothalonil	0.02	0.16	0.41	0.02	0.02			0.05	0.09	0.12	0.05	0.03			0.05	0.04	0.03		0.04			0.16	0.03			0.02			0.02	0.05		0.03		0.03
Chlorpyrifos									0.05			0.07			0.16	0.08			0.05	0.07		0.07								0.06				*0.05*
Cyhalothrin	0.05	0.15	0.05																															
Cypermethrin																																		
DCBP																																		*0.13*
DDT					0.02				0.04													0.03												*0.03*
Deltamethrin																																		
Dicofol																																		
Dicrotophos																																		
Difenoconazole																																T	T	
Dimethoate																																		
Endosulfan-α	0.16	0.13	0.12	0.14					0.14		0.24	0.12				0.13			0.31	0.27		0.27				0.13				0.13		0.23		*0.11*
Endosulfan-β	0.15	0.12	0.13	0.12	0.20				0.18	0.10	0.18	0.10			0.10				0.20	0.16			0.19			0.15			0.12	0.14		0.19		*0.09*
EPN															0.05											T								
Malathion																																0.03		
Metalaxyl												0.02			0.10	T	T	T	0.02	0.04		0.06			0.02		0.03	0.02	0.04		0.08	0.09	
Metribuzin																																		
Mevinphos																																		
Monocrotofos																																		
Parathion-Methyl	0.02							0.03	0.07	T	0.04	T							T	0.05										T		0.01		
Permethrin	0.02	0.04	0.06	0.03	0.07			0.10	0.09	0.14	0.21	0.23			0.15	0.20	0.26	0.25	0.13	0.08		T			0.08		0.09	0.07	0.11					
Profenofos												0.17																	0.19					*0.15*

App. 7.2: Pesticide concentrations in river water of the BNH catchment (full caption: p. 150)

Pesticide	blind values	09/09	10/09	11/09	12/09	13/09	14/09	15/09	16/09	17/09	18/09	19/09	20/09	21/09	22/09	23/09	24/09	25/09	26/09	27/09	28/09	29/09	30/09	01/10	02/10	03/10	04/10	05/10	06/10	07/10	08/10	09/10	10/10	11/10
Atrazin																																		
Cabofuran																																		
Captan																																		
Chlorothalonil						0.02			0.03			0.03	0.29																					
Chlorpyrifos	0.05											0.06	0.06											0.08	0.06	0.07				0.00	0.04		0.07	
Cyhalothrin																																		
Cypermethrin																																		
DCBP	0.13 0.30								0.24			0.05	0.07												0.07	0.07	0.16				0.14		0.17	0.16
DDT	0.03		0.03				0.04									0.08							0.04											
Deltamethrin																																		
Dicofol																																		
Dicrotophos																																		
Difenoconazole		T		T	T	T	T		T			T	T			T	T	T	T	T			T	T	T	T	T			T	T	T	T	T
Dimethoate				0.12	0.17							0.24	0.43			0.27							0.14	0.22	0.16	0.18	0.23			0.15	0.23	0.24		
Endosulfan-α	0.11																																	
Endosulfan-β	0.09		0.17	0.16					0.10			0.16	0.19			0.18							0.09	0.14	0.17	0.17	0.22			0.15	0.15	0.12	0.16	0.15
EPN																																		
Malathion																																		
Metalaxyl		T	T			0.04	0.46		0.12			0.02	0.02			0.02	T	T	T	T			T	T	T	0.06	0.15			0.07	T	T	T	T
Metribuzin												0.05	0.11			T	T	T																
Mevinphos																	T	T																
Monocrotofos																																		
Parathion-Methyl									T											T						T				T			T	
Permethrin				0.17	0.31	0.13	0.06										0.41	0.17					0.27	0.34	0.36	0.17	0.23			0.08	0.08	0.07		
Profenofos	0.15			0.24								0.15								0.20							0.18							

App. 7.3: *Pesticide concentrations in river water of the MSM catchment (full caption: p. 150)*

	blind values	09/09/2002	10/09/2002	11/09/2002	12/09/2002	13/09/2002	14/09/2002	15/09/2002	16/09/2002	17/09/2002	18/09/2002	19/09/2002	20/09/2002	21/09/2002	22/09/2002	23/09/2002	24/09/2002	25/09/2002	26/09/2002	27/09/2002	28/09/2002	29/09/2002	30/09/2002	01/10/2002	02/10/2002	03/10/2002	04/10/2002	05/10/2002	06/10/2002	07/10/2002	08/10/2002	09/10/2002	10/10/2002	11/10/2002
Atrazin																																		
Cabofuran																																		
Captan																																		
Chlorothalonil																																		
Chlorpyrifos	*0.05*								0.06																									
Cyhalothrin																																		
Cypermethrin																																		
DCBP	*0.13*																																	
DDT	*0.03*																																	
Deltamethrin																																		
Dicofol																																		
Dicrotophos				T					T			T																						
Difenoconazole		T	0.02													0.07																		
Dimethoate																	T																	
Endosulfan-α	*0.11*	0.25	0.21	0.17								0.28	0.27			0.33							0.21		0.11	0.12							0.27	0.18
Endosulfan-β	*0.09*	0.18	0.18	0.15	0.14	0.11			0.13			0.21	0.19			0.21		0.12		0.15			0.19	0.10	0.17	0.13				0.15	0.17	0.14	0.19	0.15
EPN																																		
Malathion			0.03								0.02															0.02				0.03	T	0.03		
Metalaxyl		0.01	0.01						0.02		0.02		0.59			0.04	T							0.03						T		0.03	0.03	
Metribuzin			0.02				T		0.05																									
Mevinphos							0.03																											
Monocrotofos																																		
Parathion-Methyl			0.01				T		T																									
Permethrin				0.12	0.11	0.11	0.24		0.10			0.04	0.06			0.12	0.34	0.20	0.17	0.26			0.22	0.19	0.28	0.08	0.11			0.04	0.06			
Profenofos	*0.15*		0.17								0.29									0.16														

Appendix 8: Setup of the modeling in Hydrus2d

App. 8.1: *Geometry and boundary conditions of a model to simulate water flux and sampling efficiency of suction plates in the soil of a Thai lychee orchard. Green: atmospheric boundary, white: no flux, red: free drainage, blue: variable pressure.*
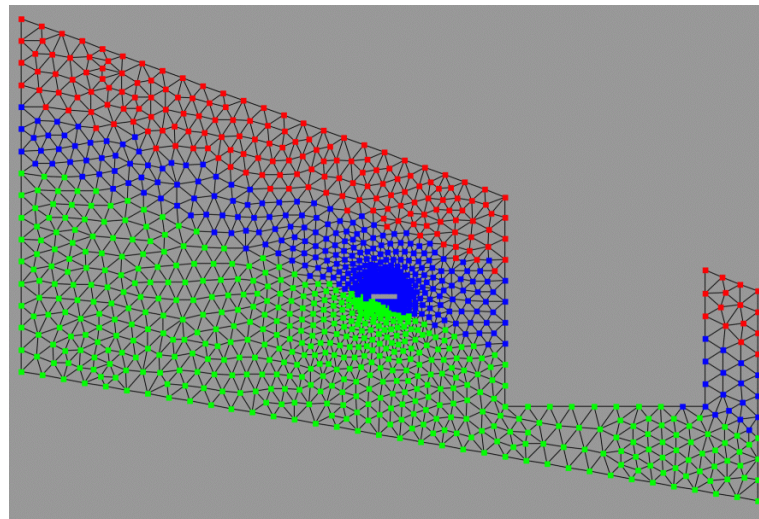
App. 8.2: *Distribution of soil materials in a model to simulate water flux and sampling efficiency of suction plates in the soil of a Thai lychee orchard. Red: material no. 1 (Ah horizon), blue: material no. 2 (Bt1 horizon); green: material no. 3 (Bt2 horizon).*