Institute of Soil Science and Land Evaluation (310)

Faculty of Agricultural Sciences

University of Hohenheim

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Transport of pesticides in a river of a tropical mountainous watershed in northern Thailand

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"Nothing is impossible, the word itself say 'I' m possible' "

Audrey Hepburn

Table of Contents

Preface

The work presented in this thesis was funded by Deutsche Forschungsgemeinschaft (DFG) within the framework of the Collaborative Research Centre SFB 564 "Sustainable Land Use and Rural Development in Mountainous Regions of Southeast Asia" (The Uplands Program).

The objective of the Uplands Program is to contribute through agricultural research to the conservation of natural resources and the improvement of living conditions of the rural population in the mountainous regions of Southeast Asia. Study areas are in northern Thailand and Vietnam.

The studies of this dissertation were performed within the third phase of the subproject B2, which investigates transport of agrochemicals in the mountainous areas of northern Thailand on the watershed scale. In the first phase, the focus was set on investigating water flow patterns at plot scale, its variability during the rainy season, and its relevance for agrochemical transport. The second phase aimed at measuring and modeling water flow and transport of agrochemicals at the field scale. Special emphasis was put on lateral water flow and transport of pesticides from a Litchi orchard in Mae Sa Noi sub-catchment. In the third phase, the research extended to the entire catchment. Contamination of pesticides in surface water, discharge and weather data were measured. The transport of pesticides at the watershed scale was modeled. At last, in the forth phase, the impact of different land use options on the loss of agrochemicals from the watershed scale will be assessed.

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Walaya Sangchan
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Abbreviation

AF	Assessment factor
amu	Atomic mass units
a.s.l	Above sea level
^oC	Degree Celsius
cm	Centimeter
DDT	Dichlorodiphenyl trichloroethane
EC_{50}	Half of effective concentration
EI	Electron impact ionization
FD	Frequency of detection
g	Gram
GCB	Graphitized carbon black
GC-µECD	Gas chromatograph-micro electron capture detector
GC-NPD	Gas chromatograph-nitrogen phosphorus detector
GC-MS	Gas chromatograph-mass spectrometer
GIS	Geographic information system
h	Hour
HCH	Hexachlorocyclohexane
I.D.	Internal diameter
K_{oc}	Organic carbon content
K_{ow}	Octanol-water partition coefficient
$K_{susp\text{-}water}$	Partition coefficient between the water and the suspended matter phase
km^2	Square kilometer
OL	Outlet
$L\ kg^{-1}$	Liter per kilogram
LC_{50}	Half of lethal concentration
LLE	Liquid-liquid extraction
LOD	Limit of detection
MAE	Microwave-assisted extraction
Max.	Maximum
min	Minute
µL	Micro liter
$µg\ L^{-1}$	Microgram per liter

mg L^{-1}	Milligram per liter
m^2 g^{-1}	Square meter per gram
MgSO4	Anhydrous magnesium sulfate
mL	Milliliter
mL min	Milliter per minute
mm d^{-1}	Millimeter per day
m^3 s^{-1}	Cubicmeter per second
MSN	Mae Sa Noi
m/z	Mass-to-charge ratio
n.a.	Not available
n.d.	Not detected
NaCl	Sodium Chloride
ng g^{-1}	Nanogram per gram
NOEC	No observed effect concentration
PEC	Predicted environmental concentration
PLE	Pressurized liquid extraction
PNEC$_{sed}$	Predicted no effect concentration in sediment
PNEC$_{wate}$r	Predicted no effect concentration in water
PSA	Primary secondary amine
PS-DVB	Polystyrene-divinylbenzene
PTV	Programmable temperature vaporizers
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
R^2	Linear correlation coefficient
RC	Runoff coefficient
RHO$_{susp}$	Bulk density of wet suspended matter
rpm	Round per minute
RCR	Risk characterization ratio
RSD	Relative Standard Deviation
S	Solubility in water
SFE	Supercritical fluid extraction
S/N	Signal to noise ratio
SPE	Solid phase extraction
SWAT	Soil and water assessment tool
TBME	Tert-butyl methyl ether

UE	Ultrasonic extraction
V	Voltage
VP	Vapour pressure
v/v	Volume by volume
w/w	Weight by weight

1. General introduction

In the tropical uplands of Southeast Asia, rapid changes in land use practices are taking place. This is especially true for the agriculture in the northern part of Thailand. Continuous intensifications in population pressure result not only from natural growth but also from migration. Declining crop productivities in lowland are forcing the continued expansion of cultivation to increasingly vulnerable highland areas. High rates of economic growth and escalating market demands for agricultural products are encouraging upland farmers to replace food crops by cash crops (Burgers et al., 2005). The expansion of agriculture to vulnerable areas (i.e. shallow soil depth, steep slope and high soil erosion) raise concerns about sustainability of natural resources such as soil, ground- and surface water which are contaminated due to excessive use of agrochemicals in these regions (Praneetvatakul et al., 2001; Chalermphol and Shivakoti, 2009).

Pesticides are widely used to protect crops from insects, weeds and diseases. However, insufficient farmer training and uncertain effectiveness of pesticides have let to inappropriate use with excessive application doses and frequencies. The negative consequences of incorrect use of pesticides are becoming relevant. Firstly, it causes direct poisoning of local farmers and their families (Stuetz et al., 2001, Dasgupta et al., 2007; Panuwet et al., 2009). Secondly, the application of pesticides adversely affects consumers indirectly through the chemical residues in food (Athisook et al., 2007; Prapamontol et al., 2007). Moreover, the overuses especially in vulnerable regions represent the risk of environmental contamination, particularly of aquatic life in rivers draining agricultural areas. Numerous studies have evaluated the transport of pesticides from agricultural lands to rivers (e.g., Kruawal et al., 2005 and Claver et al., 2006) and its adverse effects to aquatic systems (Liess and von de Ohe, 2005 and Hela et al., 2005), but very few studies were performed in the montainous tropics of Southeast Asia.

1.1. Studies on pesticides in Thailand

Over the past decades, Thailand has faced environmental problems caused by an increasing use of pesticides. Large amounts of pesticides were imported to the country mainly for agricultural production. Unfortunately, pesticides have been used without considering adverse effects to human and environment. Many studies reported the presences of pesticides and their contaminations in Thailand. Boonyatumanond et al. (2001) monitored the residues of organochlorine pesticides in four main rives including Chao Praya, Mae Klong, Bang Pakong

and Tha Chin, and coastal areas of Thailand. DDT and its metabolites were found in the range of 18-20 ng L^{-1} at Krabi province (West coast). Aldrin (5 ng L^{-1}) was detected at the lower part of Cho Praya River. The concentration of HCH and its isomers ranged from 10 to 17 ng L^{-1} in three provinces in south of Thailand. Thapinta and Hudak (2003) used geographic information system (GIS) to create a vulnerability map of groundwaters, which were contaminated by pesticides in central Thailand. Shallow groundwater wells located in agricultural areas had the highest vulnerability. The risk of groundwater contamination in mountainous regions was medium because of low pesticide use. However, the rapid increase of pesticide use will increase the contamination of groundwater dramatically.

In northern Thailand, Ciglasch et al. (2006a, 2006b) addressed pesticide pattern in a field soil at the Mae Sa watershed. They measured background concentrations of pesticides in surface water of the Mae Sa River and dissipation of pesticides in an Acrisols. Their screening results show that many pesticide concentrations exceeded toxicity criteria for aquatic vertebrate and invertebrates. Volatilization and microbial degradation were found to be important pathways of pesticide dissipation in tropical soils. All studied pesticides, especially α-endosulfan accumulated strongly in soil. The accumulation of pesticides increased with increasing hydrophobicity and aging. Kahl et al. (2007, 2008, 2010) studied water flow and pesticide transport at the same study site on plot and on field scale. The transport of applied pesticides (methomyl and chlorothalonil) into the adjacent stream was measured and modeled. A few pesticide peaks were detected in the stream before and with the discharge peaks indicating existence of fast-flow components. Thereafter, preferential interflow becomes the dominant transport pathways. Many pesticides peaked in stream several hours after rainfall event. Up to 11.4 % of methomyl and 3.5 % of chlorothalonil were lost to the stream within 2 months. A two-domain reservoir model indicated that preferential interflow via macropores caused most of the pesticide concentration peaks in the stream. Many factors such as rain amount and antecedent soil moisture affect transport by interflow. For example, under wet soil condition, rainfall events induce water release to the fractures and lead to desorption of pesticides from the fracture walls and outflow to the stream. Duffner et al. (2010) combined hydrograph separation and transport of the pesticides atrazine and chlorpyrifos at the hillslope orchard in the Mae Sa Noi sub-catchment. About 0.4 % and 0.01 % of applied mass for atrazine and chlorpyrifos, respectively, were lost to the stream over a period of 30 days. During single runoff events, atrazine was clearly transported. First, surface runoff was the dominant transport pathway. Later, interflow was the dominant pathway of the herbicide.

1.2. Fate and transport of pesticides in the environment

Pesticides applied to the environment may undergo many processes within soil and on their way to water, air or food. In this dissertation, three major types of processes are addressed: (I) sorption, pesticides are bound with soil; (II) degradation, pesticides break down; (III) transfer processes, pesticides are moved away from an application area.

Sorption

Sorption is one of the major processes affecting the fate of pesticides. Sorption results in binding between pesticides and soil particles. It plays an important role in regulating rates and magnitudes of the other processes that control the fate and transport of pesticides. For example, sorption decreases the degradation of pesticides by reducing their partitioning into the soil liquid phase (Moyer et al., 1972; Gou et al., 2000). It is postulated that sorbed chemicals are less accessible to microbes (Smith et al., 1992). Many soil factors influence the sorption of pesticides. High organic matter or clay content increases the extent of sorption. This occurs because organic soil has a greater particle surface area or number of sites to which pesticides can bind. Sorption is often quantified by a partitioning coefficient normalized for the organic carbon content (K_{oc}). This value is useful to predict the mobility of pesticides and their risk of leaching. Pesticides with higher K_{oc} values more strongly sorb to soil and are therefore less mobile in the environement.

Degradation

Several processes, i.e. biological, chemical and photochemical, are achive in degrading pesticides in soil or water environment.

Biological degradation is a breakdown of pesticides by fungi, bacteria and other microorganisms that use pesticides as a source of carbon and/or energy. Most biological degradation of pesticides occurs in soil. Soil conditions such as moisture content, temperature, aeration, pH, and the amount of organic matter affect the rate of biological degradation because of their direct influence on microorganism growth and activity.

Chemical degradation is a breakdown of pesticides through abiotic processes. Many chemical processes such as hydrolysis, oxidation, and reduction are responsible for degradation and transformation of pesticides in soil and water. Among these, hydrolysis is stressed as major process where the pesticides interact with water. The reaction can occur in aqueous phase or with the absorbed forms on the solid phase

surfaces. Hydrolysis is sensitive to temperature and pH-dependent. Many pesticides (i.e. chlorpyrifos, cypermethrin, and endosulfan) are particularly susceptible to hydrolysis under alkaline conditions (EXTOXNET, 1996). The rate of hydrolysis may be slower under acidic to neutral conditions (EXTOXNET, 1996).

Photodegradation is a breakdown of pesticides by light exposure, particularly sunlight. Pesticides on foliage, on soil, in water and even in the air can be destroyed by solar radiation. The rate at which pesticides are degraded by photolysis depends on a combination of light intensity, exposure time and organic matter content. Gohre and Miller (1983) reported that oxygen-reactive species (e.g., singlet oxygen, peroxide) were produced when soil was exposed to sunlight, and contributed to enhance photodegradation. Depending on their type, the content of minerals in soil was the dominant feature in catalyzing the oxidation reactions (Spencer et al., 1980).

Transfer process

There are many processes through which pesticides can dissipate from an application area to the environment. Pesticides can be lost to ambient air by volatilization, transported as solute or attached to sediment. Understanding dynamics of pesticides in the environment is crucial for effective prevention and management of water resources.

Volatilization is the process through which pesticides convered from the solid or liquid phase to gas, which can move into the ambient air away form an application area. Vapor pressure is an important factor in determining the volatilisation of pesticides. A pesticide with higher vapor pressure is more volatile. In contrast, a pesticide tightly adsorbed to soil particles is less likely to be volatilized; therefore, soil conditions such as texture, organic matter content, and moisture can influence pesticide volatility.

Surface run-off or overland flow is considered as a major non-point source of pesticides to surface water in agricultural areas (Ng and Clegg, 1997; Kookana et al., 1998; Schulz, 2001). Generally, surface water travels at a rate in the order of meters to tens of meters per minute (van der Perk, 2006). Infiltration-excess, saturation-excess, and variable area process are considered as the key runoff generating processes (Scherrer and Naef, 2003). When the rate of rainfall exceeds the rate of infiltration into the soil, infiltration–excess runoff occurs even if the soil is not saturated (Horton, 1933). This situation is relevant in areas of low vegetation cover and high rainfall intensity. In contrast, saturation-excess runoff occurs only when rainfall cannot

infiltrate as the total soil pore space is already filled with water (Dunne and Black, 1970). At a particular location many variables of the area such as topography, climate, soil and management can trigger runoff generation. Downslope lateral flow insaturated or unsaturated soil, usually within the soil (subsurface storm flow) may locally exceed the soil storage capacity and returns to the surface where it may reach much higher velocities (Musgrave and Holtan, 1964; Dunne and Black, 1970). Particularly at the bottom of hillslopes, downslope lateral flow was identified as the main additional input of water gradually increasing saturated area in soil.

Preferential flow may be defined as a phenomenon in which water and solutes take pathways through total pore network (heterogeneous porous media), non-capillary cracks, bypassing of water through biopores such as root channels, ant, termite and earthworm burrows. Therefore it creates rapid movement by allowing much faster contaminant transport through soil and diminishes degradation and sorption processes due to non-equilibrium conditions, which result from a rate of transport exceeding the rate of degradation or adsorption (Kördel et al., 2008). Many factors can affect the rate of preferential flow and leaching of solutes such as soil type, soil structure, initial water content, rainfall duration and intensity. Soil type and soil structure strongly influence the formation of macropores. In silty soil, macropores are predominantly formed as biopores such as earthworm burrows and decaying of taproots, whereas cracks and fissures are formed in clayey soil during drying. Depending on soil texture, leaching of pesticides in loamy and clayed soils is pronounced when the soils were exposed to a strong rainfall shortly after pesticide application (Flury, 1996).

Baseflow is generated from the water present in the saturated zone beneath the water table (groundwater). Compared to surface water, groundwater travels at a much lower rate, of centimeter per day or even less (van der Perk, 2006). Therefore this flow component usually reacts slowly to rainfall. Leaching of pesticides into deep groundwater and an input of pesticides into surface water by outflowing groundwater may possibly occur locally or in low concentration. For example, Leu et al. (2004) studied the loss of herbicides in a small catchment in Switzerland. They observed sustained herbicide concentrations during long-lasting decrease of discharge after rainfall. This indicates that herbicides may contaminate the groundwater, which was filled up by vertical fast flow components during rainfall events and subsequently leached into the river as baseflow.

1.3. Pesticides in Sediment

Apart from the pesticide dissolved in surface water, the consideration of sediment-associated pesticides is also important to understand pesticide transport and the potential effects on aquatic organisms. Many factors such as agricultural practices, vegetation weather conditions, soil type and topography can lead to losses of pesticides through processes as leaching with soil surface runoff and soil erosion (Flury, 1996; Hladik et al., 2009). Sediment can be an important sink for chemicals through sorption to particulate matter and a source through resuspension. During a runoff event, both pesticides in solution and pesticides sorbed to sediment particles, can be transported into a river. Partitioning between the solution and soil solid phases is influenced by factors like the organic carbon content of the solid particle (Karickhoff, 1984; Warren et al., 2003). Sediment, with total organic carbon content higher than 0.1 % has been proven to be a dominant sorbent for hydrophobic organic substances (Karickhoff, 1984; Ying and Williams, 2000; Chefetz et al., 2004). On the other hand, incomprehensible sorption of polar compounds is proportional to the cation exchange capacity. SETAC (1993) stated that the substances with a K_{oc}<500–1000 L kg^{-1} are not likely be sorbed to sediment. In general, fine sediments have higher organic carbon content and higher surface area to volume ratio than coarse sandy sediment. Therefore, fine sediment is likely to contain higher concentration of pesticides, on a weight by weight basis (Warren et al., 2003). Johnson et al. (1998) studied sorption of octylphenol in laboratory to bed and suspended sediments collected from the rivers Aire and Calder, England. It was found that on a weight by weight and on organic carbon content basis, the suspended sediment adsorbed much larger quantizes of organophosphate substances than the bed sediment. This can be explained by higher small particle size material and organic aggregates in the suspended sediment.

1.4. Risk assessment of pesticide contamination to aquatic environment

The exposure of organic contaminants to human and ecological systems is related to their fate in each environmental compartment, i.e. atmosphere, soils, surface water and groundwater, and their distribution between various environmental compartments. This also includes their availability for chemical uptake and accumulation by organisms. The presence of pesticides in surface water as well as in sediments, both parent pesticides and metabolites, may exert a toxic action to organisms living in a river, whenever the concentrations of a compound is sufficient to trigger such an effect. Many studies have quantified exposure

concentration of pesticides and their adverse effects on aquatic life. For instance, in the Kokai River, which receives drained water from rice paddy fields in Japan, a combination of field, artificial channel and laboratory studies revealed that high mortality of two mayfly larvae species (*Epeorus latifolium and Ecdynonurus yoshida*) as well as freshwater shrimp (*Paratya compressa improvisa*) was mainly caused by single, combined, and/or synergistic effects of pesticides contaminating the river (Hatakeyama et al., 1997). Matthiessen et al. (1995) demonstrated that contamination by the insecticide carbofuran in agricultural run-off produced acute sublethal and lethal effects on in situ population of surface water shrimp (*Gammarus pulex*). A monitoring project in western Switzerland, including 165 sites at 47 rivers, showed that the macroinvertebrate diversity increased with the altitude of the site, reflecting the upward decrease of human impact on the rivers and their catchments (Lang, 2000).

To evaluate the impacts of pesticides on ecosystems, environmental risk assessments are performed. The protection of a specific ecosystem, such as a lake or a river, requires the preservation of its ecological functionality. For modern pesticide management, risk assessment is used as a useful tool for screening and evaluating the potential impact of pesticides on non-target organisms. To date, in many countries registration of agrochemicals requires the evaluation of all potential risks. The measure typically used in European Union is, for example, the directive 91/414/EEC which focuses on a risk assessment for placing plant production products on the market (European commission, 1991). To assess the risks of chemical substances to human heath and environment the technical guidance document in support of the commission Directive 93/67/EEC on risk assessment for new notified substances and the commission regulation (EC) No. 1488/94 on risk assessment for existing substances is generally used (European Commission, 2003).

In general, the ecological risk of pesticides is expressed as a function of environmental exposure and pesticide toxicity (Baker and Richards, 1990). It is assessed on the basis of a risk characterization ratio (RCR) as the ratio of the predicted environmental concentration (PEC) to predicted no-effect concentration (PNEC). PEC values can be derived from available measured data and/or model calculations (European Commission, 2003). For existing substances, it is reasonable that the risk assessment should initially be undertaken using the worst case scenario. Because the intention of risk assessment is to be protective, therefore, in many reports measured mean and peak concentrations were used for the calculation of RQ (risk quotient) (Palma et al., 2004; Vryzas et al., 2009). In addition, PNEC value is regarded as the lowest concentration at which unacceptable effects will be most likely not to occur. The value is usually derived on the basic of critical concentrations i.e. actual toxicity as half of

effective concentration (EC$_{50}$) or half of lethal concentration (LC$_{50}$) and chronic toxicity as no observed effect concentration (NOEC).

1.5. Analysis of pesticides in water and sediment samples

The use of pesticides and their contaminations in food products and environment raises concerns about impacts of pesticides to human health and ecological system. To measure toxicological effects of pesticides on living organisms and to discover fate and transport of pesticides in environment, numerously analytical strategies are developed.

Water is generally considered as a simple matrix for pesticide residue analysis because it often contains low interferences and is usually sampled as a homogeneous liquid. Water samples are often filtered to remove suspended particles, which allow the separation of dissolved analysts from those associated with the particle phase. Very low detection limits can be achieved by concentrating extracts from large sample volumes. Solid phase extraction (SPE) has become the primary method for extracting and cleaning up water samples. The typical sorbents for analysis of pesticides in water samples are octyl (C$_8$) and octadecyl (C$_{18}$) bonded to porous silica. However, these sorbents achieve good recovery only for non-polar compounds (Colina et al., 1993; Chiron et al., 1994; Schülein et al., 1995). Other materials, based on highly cross-linked copolymer of poly-styrene-divinylbenzene (PS-DVB) or graphitized carbon black (GCB), have been recently used. The introduction of GCB has led to modifications of some multi-residue analysis of pesticides in water and other environmental samples (Crescenzi et al., 1996).

Sediment can be categorized as environmental solid sample. Sediments are essentially the same as soil samples. Contrast to the water matrix, soil, sediment and other environmental solid samples tend to have much stronger chemical interactions. Sediment samples are highly variable and show high interferences because they consist of different particle size, texture (sand, silt, and clay), mineral content, and organic composition, etc. Therefore, in general the analysis method for sediment is more complex. Numerous analysis methods have been proposed for extraction of pesticide residues in solid samples such as Soxhlet extraction (US EPA, 1996), ultrasonic extraction (UE) (Tor et al., 2006; Castro et al., 2001), Liquid-Liquid extraction (Hassan et al., 2010), pressurized liquid extraction (PLE) (Dąbrowski et al., 2002, Dagnac et al., 2005, Schäfer et al., 2008), or microwave-assisted extraction (MAE) (Pastor et al., 1997; Shen and Lee, 2003).

Traditional pesticide analysis methods such as sonication and Soxhlet extraction consume much more time and solvent than environmentally friendly methods such as MAE and PLE although the latter have similar or even higher extraction efficiencies (Sanchez-Brunete et al., 2002; Sapozhnikova et al., 2004). However, intensive extraction techniques with high temperatures and pressures also extract organic-rich compounds from the sediments, which can interfere with instrument analysis (Bergamaschi et al., 1999). In addition, recently a novel analytical method for multi-residue analysis in soil samples was adopted from the analysis of foodstuff. This method is named QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe). It was introduced by Anastassiades (2003) as a new extraction method for a wide range of pesticide properties from different food matrices with high water content. The basic procedure is based on a liquid partitioning with acetonitrile followed by a dispersive SPE clean-up with primary secondary amine (PSA). Several applications of the method for pesticide analysis in soil samples have been reported. Lesueur et al. (2008) compared four extraction methods including UE, LLE, PLE, and QuEChERS for the analysis of 24 pesticides in soil samples. The result showed that the QuEChERS method was the most efficient extraction method with recoveries from 27 % to 121 %. The modification of the QuEChRES method for the analysis of three chlorinated compounds (chloroform, 1, 2-dichlorobenzene, and hexachlorobenzene) in garden soil and Vertisol was reported (Pinto et al., 2010). Recoveries of the three compounds were between 62 % and 93 %.

1.6. References

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2. Objectives and outline

To gain a better understanding of the transport of pesticides to surface water and of their environmental impacts on aquatic ecosystems under tropical conditions, seven frequently used pesticides were monitored in surface water and sediments at two time scales: during single rainfall events lasting several days and throughout the year. Finally, the possible risk for aquatic ecosystem of the watershed was evaluated using the RQ approach.

In detail, the objectives of the present study were

1. to adapt the QuEChERS method for extracting pesticides from sediment samples,

2. to investigate the transport patterns of pesticides with different physico-chemical properties during single runoff events under field and farmer's practice conditions in a tropical catchment,

3. to quantify the seasonal dynamics of residue concentrations of frequently used pesticides in surface water and sediment in a tropical river in northern Thailand,

4. to quantify the loads of these pesticides in river water over the season, and

5. to assess the ecological risk of pesticides to aquatic organisms in the study watershed.

The remaining part of the thesis is structured as follows. Chapter 3 and 5 were submitted for publication. Chapter 4 has been published. Chapter 3 presents the results of adapting the QuEChERS method to extract pesticides with widely different polarities from bed and suspended sediments. Several extraction conditions such as type of solvent, effect of salt to pesticide partitioning and clean up steps with dispersive SPE were tested. The performance of the extraction methods was evaluated by considering analytical aspects such as acceptable high recovery, selectivity and the ability to cover the desired analytical polarity range.

In chapter 4, the results of the short-term sampling campaigns are presented. Input patterns of pesticides during three runoff events were investigated using a high-resolution sampling scheme and a statistical time series analysis. Additionally, the role of the sampling scheme for environmental assessment studies in tropical regions will be discussed.

Chapter 5 presents the results of a long-term monitoring program. Seven pesticides frequently applied in the study watershed were monitored in water and sediment from the Mae

Sa River between July 2007 and November 2008. The concentrations of pesticides were used as exposure concentrations to evaluate aquatic risks for surface water and sediment compartments.

Chapter 6 contains a final discussion of the results. Analysises of residue pesticides in water and sediment sample were discussed. Moreover, the losses of pesticide during single runoff event and long-term monitoring were compared.

In chapter 7, final conclusions and outline of important implications of the thesis were drawn.

3. Publication 1

Extraction of pesticides from bed and suspended sediment samples with a modified QuEChERS method

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3.0. Abstract

Sediment-associated pesticides have the potential to adversely affect ecosystems, resources and human health. The present study adapts the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method to extract eight pesticides differing in volatility and polarity from bed and suspended sediment samples. The original QuEChERS procedure involves simple liquid extraction of sediment samples with acetonitrile, the addition of NaCl and anhydrous MgSO$_4$ in citrate buffer, followed by dispersive solid phase extraction with primary secondary amines (PSA). The extract solutions were analyzed by capillary gas chromatography with micro-electron capture detector (μ-ECD) and/or nitrogen phosphorus detector (NPD). The selected pesticides were one triazine (atrazine), three organochlorines (α- and β-endosulfan, chlorothalonil), four organophosphates (dichlorvos, chlorpyrifos, dimethoate) and one pyrethroid (cypermethrin). Several steps of the QuEChERS method were optimized. For this, we tested the efficiency of an alternative extraction solvent (ethyl acetate) and of varying concentrations of salt and PSA in the salting-out and the clean up procedure, respectively. Acceptable recovery ranges (81-116 %) were achieved for nearly all pesticides except for dichlorvos in the bed sediment sample and for dimethoate in both sediment types. We conclude that the adapted QuEChERS method is a suitable alternative for extracting pesticides from sediment samples.

Keywords: Multiresidue analysis, pesticides, modified QuEChERS,   sediment samples

3.1. Introduction

Urbanization and the increased demand for agricultural products have caused agriculture to expand to the vulnerable areas of the mountainous regions of Southeast Asia (Valentin et al., 2008). Land use changes have several on-site impacts, e.g. runoff and soil erosion, which may then contribute to off-site impacts such as flooding and environmental pollution (Valentin et al., 2008). Many reports show that significant amounts of numerous pesticides are transported from the agricultural application areas to rivers and other surface waters, where they contaminate the aquatic ecosystem and the water resources downstream (Kahl et al., 2008; Sangchan et al., 2012, 2013). Pesticides are not only transported as solutes with surface runoff, interflow and possibly baseflow, but may also be transported with eroded soil particles.

Sediments have been analysed for pesticides 1) to identify pollution sources (Tan et al., 2009), 2) to evaluate trends and historical profiles (Jones et al., 1992) and 3) to assess exposure concentrations of biota in aquatic ecosystems (Schulz, 2001, Sangchan et al., 2013). Analytical procedures for pesticide residues in environmental samples have to cope with the complexity of sample matrices. Water is generally considered a simple matrix because it is commonly sampled as homogeneous liquid, which causes little interference in analytical instruments. In soils and sediments, pesticides undergo much stronger physical and chemical interactions with the matrix. Conventionally, pesticides are extracted in multiple steps using various organic solvents. The traditional extraction methods such as Soxhlet extraction are time- and solvent-consuming (Tan et al., 2004), and are being increasingly replaced by user-friendly procedures including ultrasonic extraction (UE; Castro et al., 2001, Villaverde et al., 2008), pressurised liquid extraction (PLE; Dąbrowska et al., 2002), microwave assisted extraction (MAE; Pastor et al., 1997) or supercritical fluid extraction (SFE; Kreuzig et al., 2000). These extraction steps are sometimes complemented by additional clean-up steps such as solid-phase extraction (SPE) (Kim et al., 2008). Although the PLE, MAE and SFE methods do not require much solvent or extraction time, they are expensive and complex in operation. Moreover, high temperatures and pressures may additionally extract organochemical components that can interfere during instrumental analysis (Smalling and Kuivila, 2008).

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method has been developed to extract pesticides from food and agricultural products (Anastassiades et al., 2003). The basic procedure is based on a liquid partitioning with acetonitrile followed by a dispersive SPE clean-up with primary secondary amine (PSA). The method has been

successfully applied to determine non-polar, semi-polar and polar pesticides in various food matrices (Lehotay et al., 2010; Cieślik et al., 2011; Furlani et al., 2011; Paíga et al., 2012). It has also been applied to determine further compounds in non-food matrices such as pharmaceutical substances in blood (Plössl et al., 2006; Usui et al., 2010).

Recently the QuEChERS method has attracted attention fot the extraction of volatile compounds, chlorinated pollutant compounds and pesticides in environmental samples such as water, soil, and sediment (Yang et al., 2010; Pinto et al., 2010; Lazartigues et al., 2011; Kvíčalová et al., 2012). In the present study, we modified the QuEChERS method to extract pesticides from bed and suspended sediment samples. The selected eight pesticides have been frequently used in agriculturally mountainous watershed in Chiang Mai province, Thailand. To optimize the QuEChERS method for this type of samples, we tested an alternative organic solvent (acetyl acetate) and modified the salting-out step as well as the clean-up step with dispersive SPE. The new method is easier, faster, safer and environmentally friendlier than conventional methods. Finally, we applied the new method to analyse environmental bed and suspended sediment samples from the Mae Sa watershed in northern Thailand.

3.2. Experimental

3.2.1. Chemicals

A mixture of eight pesticide standard substances in toluene was purchased from LGC Standards GmbH (Germany). Anhydrous magnesium sulfate (ReagentPlus®), sodium chloride, sodium citrate dibasic sesquihydrate and sodium citrate tribasic dihydrate were obtained from Sigma-Aldrich (Germany). Bondesil-PSA (Primary Secondary Amine, 40 µm) was purchased from Varian Inc. (Germany). Acetonitrile of pestilyse grade (ROTISOLV®) was obtained from Carl-Roth GmbH (Germany).

3.2.2. Pesticides

The pesticides examined were seven insecticides (dichlorvos, dimethoate chlorpyrifos, α- and β-endosulfan, cypermethrin), one herbicide (antrazine), and one fungicide (chlorothalonil). These pesticides were selected because (i) they have been widely applied by farmers for pest management within the watershed of the Mae Sa River, (ii) they are detectable by GC-µECD, GC-NPD and GC-MS, and (iii) they distinctly differ with regard to sorption and persistence. Physico-chemical properties of the investigated pesticides are compiled in Table 3.1.

Table 3.1: Classification, type of use and key physico-chemical properties of the selected pesticides (Footprint PPDB, 2011).

Pesticide	Substance class and pesticide type	S^a (mg L^{-1})	VP^b (mPa)	Log K_{ow}^c	Log K_{oc}^d
Dichlorvos	Organophosphate, insecticide	18,000	2100	1.9	1.7
Atrazine	Triazine, herbicide	1	0.04	2.7	2.0
Dimethoate	Organophosphate, insecticide	39,800	0.25	0.7	1.5
Chlorothalonil	Miscellaneous, fungicide	1.05	0.08	2.9	2.9
Chlorpyrifos	Organophosphate, insecticide	0.81	1.43	4.7	3.9
(α-,β)- Endosulfan	Organochloride, insecticide	0.32	0.83	4.6	4.1
Cypermethrin	Pyrethroid, insecticide	0.009	0.00023	5.3	4.9

[a] solubility in water, [b] vapour pressure, [c] octanol-water partition coefficient, [d] organic carbon coefficient.

3.2.3. Standard solutions

The stock standard solution (10 mg L^{-1}) was prepared in a cychlohexane-toluene mixture (9:1, v/v). Using this stock solution, working standard solutions were prepared to produce standard calibration curves in the concentration range of 1-250 μg L^{-1}. To avoid adverse effects of the carrier solvent in the standard solutions on the sediment samples, the working solutions (100 and 300 μg L^{-1}) were prepared by flushing the organic solvent with nitrogen before dissolving the dried pesticide residues with de-ionized water. The stock solution was stored at 4 °C in the dark. Working solutions were prepared shortly before use.

3.2.4. Sediment sampling and preparation

The present work was a part of the Collaborative Research Centre SFB 564 "Sustainable Land Use and Rural Development in Mountainous Regions of Southeast Asia (Uplands Program)". One of the main study areas of this program was the Mae Sa area, a mountainous, agriculturally used watershed in northern Thailand. The watershed is described in detail in Sangchan et al. (2013). In brief, the watershed covers 77 km^2 (Fig. 1). About 24 % of this area

is used for agricultural activities, e.g. vegetables (cabbage, bell pepper, bean, etc), fruit (litchi) and flower production (gerbera, chrysanthemum, etc.).

About 500 g of the upper bed sediment layer (1-3 cm) was collected biweekly at 6 locations in the Mae Sa River (S1-S3, S6-S8) and at 2 locations (S4 and S5) in the Mae Sa Noi tributary (Fig. 3.1). In total, 176 bed sediment samples were taken between 2007 and 2008. Moreover, the sixteen grab samples of the bed sediments from July and August 2008 were combined to a single standard sample for method development.

Samples of suspended sediment were taken as suggested by Liess et al. (1996). The sampler consisted of a 3-liter collection vessel mounted on a concrete block buried in the bed. The upper inlet tube and the lower outlet tube were located 10 cm above the bed. One sample was collected from one storm event at each sampling station. In total, we collected 22 suspended sediment samples from ten storm events in 2010 at the headwater (S7), in the Mae Sa Noi sub-catchment (S4) and at the outlet of the watershed (S1). Ten grams of each sample were kept for pesticide analysis and the rest of samples were combined to be a single sample for method development.

During transport from field to lab, all samples were kept on ice. The sediment samples were dried and passed through a 1-mm sieve. To remove residue contaminations and humidity, sediment samples were dried for 48 h at 90 $^{\circ}$C. Then, the samples were stored in a freezer (-18 °C) until the next preparation step. Physical properties of the sediment samples are given in Table 3.2.

Each 10 g of dried sediment samples was spiked with 1 mL of the above-mentioned working standard solutions, yielding pesticide concentrations of 1 ng g^{-1} and 30 ng g^{-1}. Before extraction, the samples were shaken for 10 min to ensure homogenization. To test the extraction efficiency of the method over time, spiked sediment samples were stored in refrigerator at 4°C for 14 days.
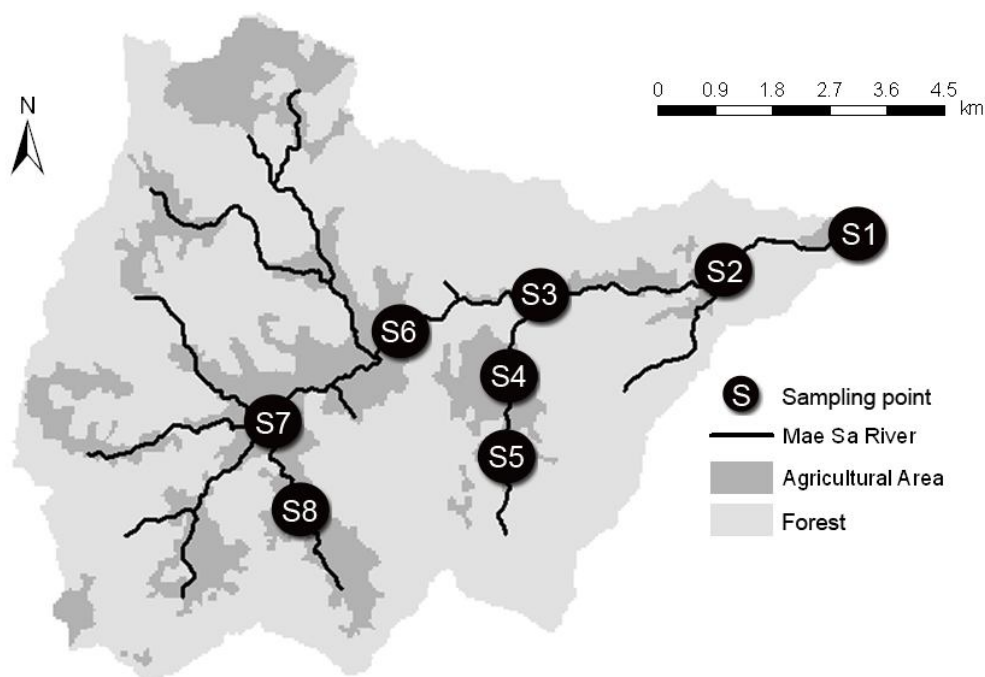
Figure 3.1: Land use map of the Mae Sa watershed with sediment sampling points.

Table 3.2: Characteristics of the sediment samples

Parameter	Organic matter content (% by mass)	pH in water	Texture [a] (Sand:Silt:Clay) (% by mass)
Bed sediment	0.31	7.16	87:7:4 (98)
Suspended sediment	2.75	7.40	53:25:21 (99)

[a] (Clay < 2 µm < Silt < 63 µm < Sand < 2 mm), the missing of percent texture for the both sediments could be explained by uncertainty of analysis.

3.2.5. The original QuEChERS extraction method

Ten grams of sediment sample were mixed with 7.5 mL of deionized water and 15 mL of acetonitrile followed by a salting-out step with 6 g of anhydrous magnesium sulfate, 1.5 g sodium chloride, 1.5 g sodium citrate tribasic dihydrate and 0.74 g sodium citrate dibasic sesquihydrate. The sample was centrifuged at 1308 x g (3000 rpm, rotational radius 13 cm) for 6 min. Subsequently, 11 ml of the organic supernatant was transferred into a polypropylene centrifuge tube to clean up with 27.5 mg Bondesil-PSA and 1.65 g anhydrous magnesium sulfate. The sample was centrifuged again for 6 min. The eluent was transferred to a conical glass flask and 100 µl of 0.05 % formic acid in acetonitrile (w/w) was added as analyte protectant for GC analysis. Two drops of toluene were added as a keeper for the pesticides

before evaporation to almost dryness. The residues were re-dissolved in 1 mL of a mixture of cyclohexane and toluene (9:1, v/v). These solutions were analyzed chromatographically.

3.2.6. Chromatographic analysis

Pesticides (chlorothalonil, chlorpyrifos, α- and β-endosulfan, cypermethrin) were analyzed by capillary gas chromatography with micro-electron capture detector (GC-μ-ECD). Dichlorvos, atrazine and dimethoate were analyzed by capillary gas chromatography with nitrogen phosphorus detector (GC-NPD). The GC-μ-ECD (Agilent Technologies 7890) was equipped with an HP-5 capillary column (length 30 m, I.D. 0.32 mm, film thickness 0.25 μm). The GC-NPD was a GC (Hewlett Packard HP 6890) equipped with an NPD manufactured by Agilent Technologies and with a capillary column especially suited for organophosphate pesticides (Rtx®-OPPesticides, Restek, USA; length 30 m, I.D. 0.25 mm, film thickness 0.25 μm). Both gas chromatographs were equipped with automatic liquid samplers (7673 Series, Agilent Technologies, USA) and with programmable temperature vaporizers (Unis PTV, JAS, Moers, Germany) operated in pulsed splitless mode. The pulsed splitless mode leads to a better response, higher resolution and diminished interferences (see, e.g., Godula et al., 1999). The PTV injection conditions were chosen as follows: injection volume 1 μL, initial temperature 125 °C, held constant for 0.2 min, and then raised to 300 °C at maximum rate of 750 °C min^{-1} (set value) for GC-μ-ECD, and 250 °C min^{-1} for GC-NPD. The final temperature of 300 °C was held constant for 25 min. Pulsed pressure and pulsed time were 207 kPa and 1.5 min, respectively. The oven temperature was initially set to 90 °C for GC-μ-ECD and 60 °C for GC-NPD, held for 2 min, and then ramped at 15 °C min^{-1} to 300 °C, where it was held for 10 min. High purity grade helium (99.999 %) was used as carrier gas in constant flow mode (2 mL min^{-1}) with both systems. Detector temperatures were set to 300 °C with μ-ECD and to 310 °C with NPD. The NPD was operated under the following conditions: H$_2$-flow: 6 mL min^{-1}, air-flow: 60 ml min^{-1}, constant make-up (N$_2$) + carrier gas flow: 12 mL min^{-1}. The bead-voltage ranged from 0.8 to 0.96 V within 4 months, which caused an offset current of approximately 10 pA. Each chromatographic measurement was done twice.

3.2.7. Optimization of the QuEChERS method

To achieve an appropriate recovery, the original QuEChERS method had to be adapted to the extraction of pesticides from sediment matrices. First, we tested an alternative solvent, ethyl acetate, against acetonitrile, the solvent used in the original QuEChERS method. Both solvents are commonly used for multi-residue analysis of pesticides from soil and sediment.

Second, we tested the effect of NaCl in the salting-out step by omitting it (0 mg NaCl) or adding the double amount (3 mg NaCl). Third, we tested the effect of PSA in the clean-up step. In recognition of the different nature of the samples, they were treated differently. With the bed samples, we tested the effect of omitting PSA. With the suspended sediment samples, which contain a higher organic matter and clay content, we tested the effect of adding 100 mg Bondesil-PSA to 27.5 mg Bondesil-PSA used in the original QuEChERS method.

All experiments were performed with three replicates. The percentage recovery is reported as average value of these replicates. Data were evaluated by a one-way analysis of variance (ANOVA). A paired t-test (α=0.05) was used to test the deviation of averages for statistical significance. All tests were performed using the statistical software package SPSS (Version 16, IBM, USA).

3.2.8. Quality assurance

With each experimental set, blanks of sediment samples (*n*=3) were extracted and cleaned up with the original QuEChERS method. The average of measured pesticide concentrations (if any) was subtracted from those of the spiked samples. The limit of detection (LOD) was calculated based on the signal-to-noise ratio approach (S/N=3).

The limit of quantification (LOQ) was determined by 6 injections of a standard solution. The relative standard deviation (RSD) of the injected concentration should be less than 20% (Armbruster and Pry, 2008). The LOD and LOQ of the analytes were derived using the pesticide standard concentrations 1μg L^{-1} and 10 μg L^{-1} for GC-μ-ECD and GD-NPD, respectively. The accuracy of the extraction method is characterized by its repeatability and its reproducibility. The spiked concentration, 30 ng g^{-1} of each pesticide, was used for both calculations. The repeatability of the method was calculated from the recoveries of the three sediment samples extracted on single days. The reproducibility was calculated from the recoveries of the sediment samples extracted on different days (n=3). Prior to this, the recoveries of the three replicates on each day were averaged.

3.3. Result and Discussion

3.3.1. Optimization of the QuEChERS method

Solvent

Acetonitrile and ethyl acetate are known to have several advantages in pesticide analysis, including good recovery, high selectivity and the ability to cover a wide analytical polarity range, which, in our case, ranged from polar (dichlorvos) to non-polar (cypermethrin). Figure

3.2 shows the pesticide recoveries from the bed samples. In general, extraction with acetonitrile gave slightly higher recoveries than ethyl acetate. Acetonitrile and water form an azeotropic mixture, which improves the recovery (Lee et al., 1991). Only in the case of cypermethrin was the difference between the recoveries significantly different from zero. This suggests that acetonitrile and ethyl acetate have similar extraction efficiencies for polar and semi-polar compounds, but that acetonitrile is more efficient in non-polar compounds. A disadvantage of acetonitrile, however, is that its use requires an additional step to evaporate it and redissolve the sample in a mixture of cyclohexane and toluene (see Section 2.5). This additional step is necessary to avoid a drawback of acetonitrile in gas chromatographic analysis, namely the larger solvent expansion volume during vaporization (Maštovská and Lehotay, 2004).

Salting out

To achieve a complete phase separation during the partitioning step, the original QuEChERS method recommends adding water to the dry sample before adding the organic solvent mixture (Anastassiades et al., 2003). The salt increases the polarity of the water phase and decreases the water fraction in the organic phase. Figure 3.3 presents the pesticide recoveries from the bed samples with different amounts of NaCl added. Upon addition of 3 g instead of 1.5 g NaCl, the recovery of all pesticides except dichlorvos increased. However, the increase was not statistically significant. In contrast, if no NaCl was added, the recovery of all pesticides except dichlorvos decreased significantly.

Clean up

The original QuEChERS method stipulates a clean-up step by dispersive SPE to eliminate lipid matrix co-extractives in the samples. Although sediment matrixes exhibit non-fatty characteristics, this is faster, cheaper and easier than by traditional SPE (Dąbrowska et al., 2003; Pinto et al., 2010). With the bed sediment samples, slightly better recoveries were obtained when PSA was used (Fig. 3.4a). However, the paired t-test shows that the difference between recoveries was not statistically significant at the confidential interval 95%.

In the case of the suspended sediment samples, with the exception of cypermethrin and α-endosulfan, all pesticide recoveries were above 100 % without clean-up (Fig. 3.4b). Some of the recoveries obtained without clean-up differed significantly from those obtained with clean-up. An important side-effect, however, is that PSA addition led to colorless sample eluates. Even if PSA addition does not decrease the interference backgrounds in the GC chromatograms, it slows down the deterioration of the capillary column and reduces maintenance costs. We therefore decided to use 27.5 mg of PSA with all samples
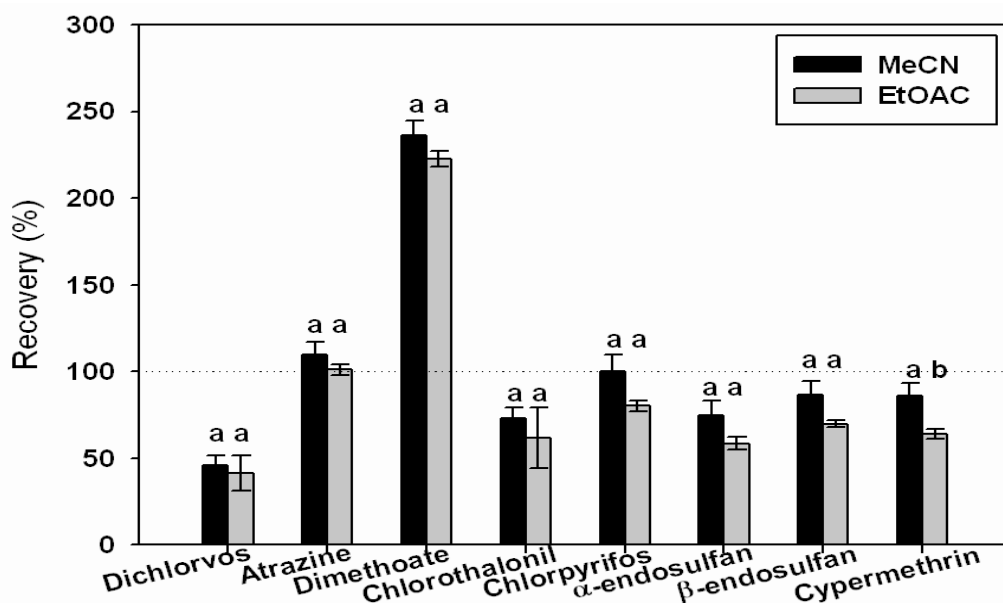
Figure 3.2: Percentage recovery of pesticides extracted from a river bed sediment sample using the QuEChERS method. Solvents: acetonitrile (MeCN) or ethyl acetate (EtOAC). The sediment samples (n=3) were spiked with 30 ng g^{-1} of the pesticides. Different indices indicate statistical differences at α= 0.05.
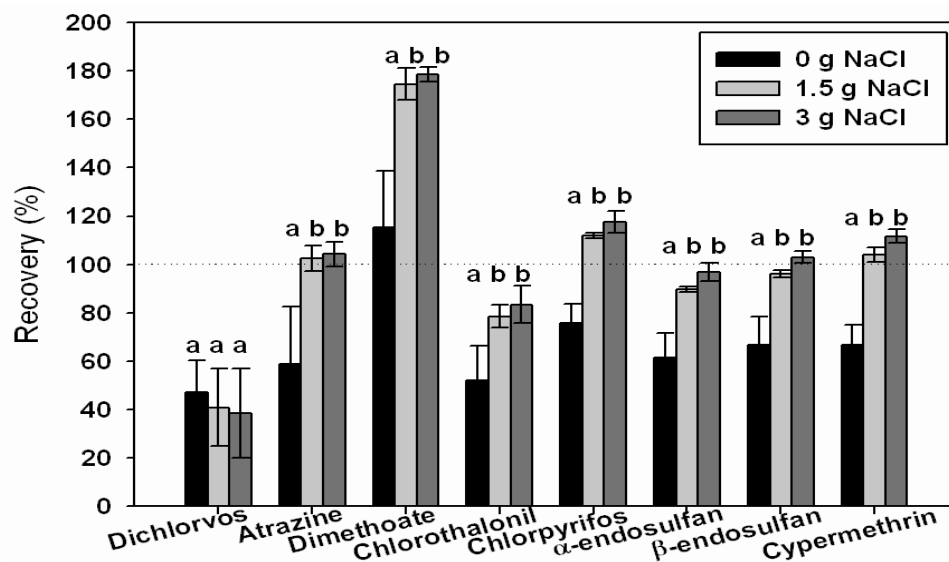
Figure 3.3: Effect adding NaCl addition on the recovery of selected pesticides in bed sediment. The sediment samples (n=3) were spiked with 30 ng g^{-1} of the pesticides. Different indices indicate statistical differences at α= 0.05.

Because PSA is a strong base, a pH buffer should be used to ensure the stability of pesticides, particularly in the case of alkaline-sensitive compounds such as chlorothalonil. To keep the extracted solution at neutral pH, we added sodium citrate dibasic sesquihydrate and sodium citrate tribasic dehydrate as a pH buffer.
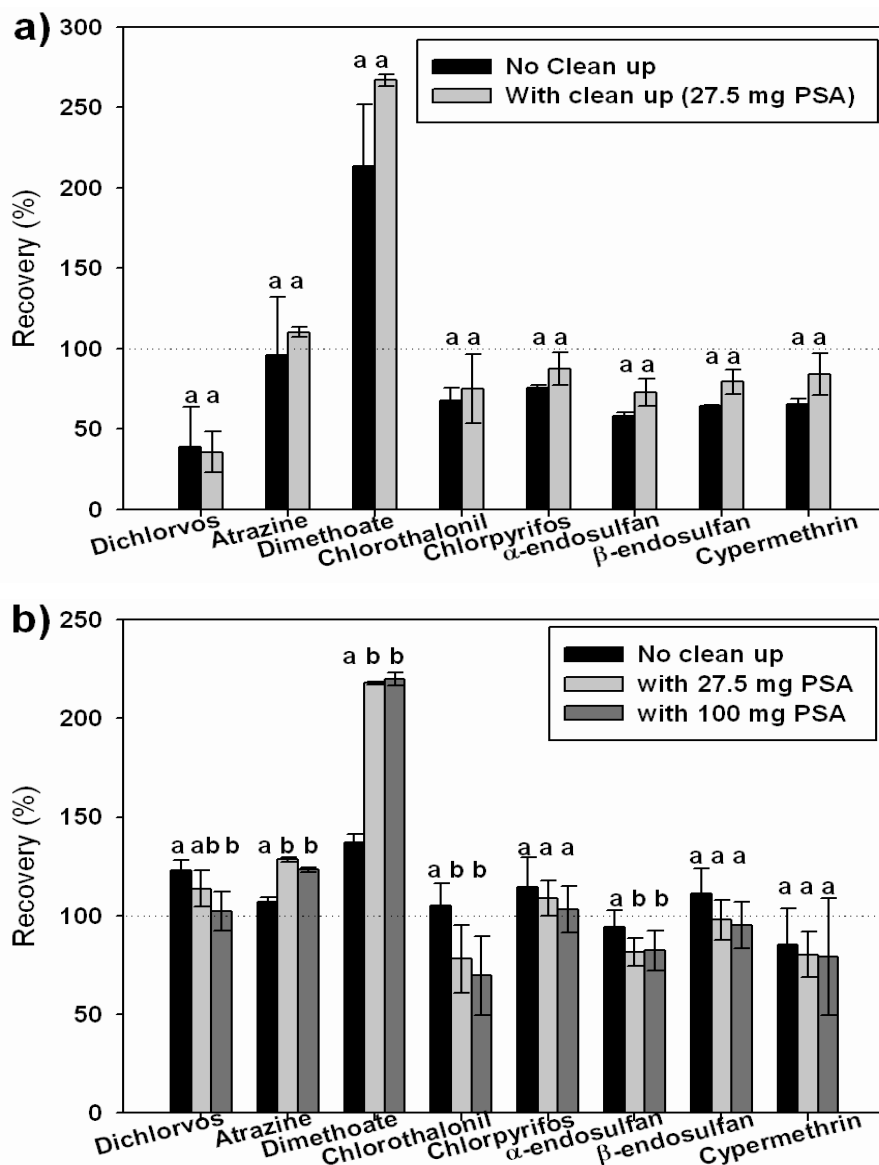
Figure 3.4: Effect of PSA clean-up in (a) bed sediment and (b) suspended sediment. The sediment samples (n=3) were spiked with 30 ng g^{-1} of the pesticides. Different indices indicate statistical differences at α= 0.05.

3.3.2. Performance data of the method

The LOD and the LOQ of all studied pesticides are presented in Table 3.3. The LOD was between 0.01 and 0.05 ng g^{-1} for GC-NPD and between 0.01 and 0.2 ng g^{-1} for GD-µECD, respectively. Concentrations 1 ng g^{-1} and 10 ng g^{-1} were quantified as LOQ of the analytical method for GD-µECD and GC-NPD, respectively. All calibration curves were linear with coefficients of determination (R^2) above 0.99. Recoveries and repeatabilities of the adapted QuEChERS method for the eight target pesticides extracted from bed and suspended sediment samples spiked with 1 ng g^{-1} and 30 ng g^{-1} of pesticides, respectively, are given in Table 3.3. Based on 2-3 spiked samples measured in triplicate, recoveries ranging from 70% to 120% are considered acceptable in pesticide residue analysis (Lehotay, 2000). In bed sediment samples, the recoveries of six of eight investigated pesticides were in the acceptable range, with a relative standard deviation (coefficient of variation) of <20 %. In the suspended sediment samples, only dimethoate was outside this range. The obtained recoveries (Table 3.3) of atrazine, chlorothalonil, chlorpyrifos, (α-, β-) endosulfan and cypermethrin were in line with the other results from (Yang et al., 2010; Brondi et al., 2011). They applied the original QuEChERs method to extract pesticides in soil and sediment samples.

There appears to be no difference in the recovery of polar, semi-polar and non-polar pesticides. The lowest recovery was recorded for the most volatile compound (dichlorvos). This finding suggests that the variation of recovery range depends on pesticide volatility. Other studies attribute the difficulty of determining dichlorvos in sediment samples to its volatility. This pesticide has been reported to be completely or partially lost during homogenization at room temperature (Vuik et al., 1992) or during sample preparation, e.g. during the evaporation step (Molina et al., 1994; Báez et al., 1997). Other environmental fate studies have shown that dichlorvos sorbs only very weakly to sediments and remains mostly in solution.

Table 3.3: Limit of detection (LOD), limit of quantification (LOQ), percentage of recovery, and relative standard deviation (RSD) of eight pesticides extracted from bed sediment and suspended sediment samples (n=3).

Pesticide	LOD (ng g^{-1})	LOQ (ng g^{-1})	Bed sediment (n=3)				Suspended sediment (n=3)			
			1 ng g^{-1} Recovery (%)	RSD (%)	30 ng g^{-1} Recovery (%)	RSD (%)	1 ng g^{-1} Recovery (%)	RSD (%)	30 ng g^{-1} Recovery (%)	RSD (%)
Dichlorvos	0.01	10	54	9.0	41	16.0	89	2.3	114	9.3
Atrazine	0.05	10	94	9.1	103	5.1	116	7.5	**128**	1.2
Dimethoate	0.05	10	**125**	0.6	**175**	6.6	**194**	7.1	**218**	0.8
Chlorothalonil	0.1	1	94	4.4	79	4.6	88	12.0	78	17.2
Chlorpyrifos	0.03	1	117	2.7	112	1.1	88	5.0	109	8.8
α-endosulfan	0.01	1	81	2.8	90	1.2	107	15.4	82	7.0
β-endosulfan	0.01	1	96	3.8	96	1.6	114	2.9	98	9.9
Cypermethrin	0.2	1	99	3.1	104	3.1	90	8.3	80	11.5

[§] Bold numbers indicate values not matching the criteria of 70–120% recovery and <20% RSD.
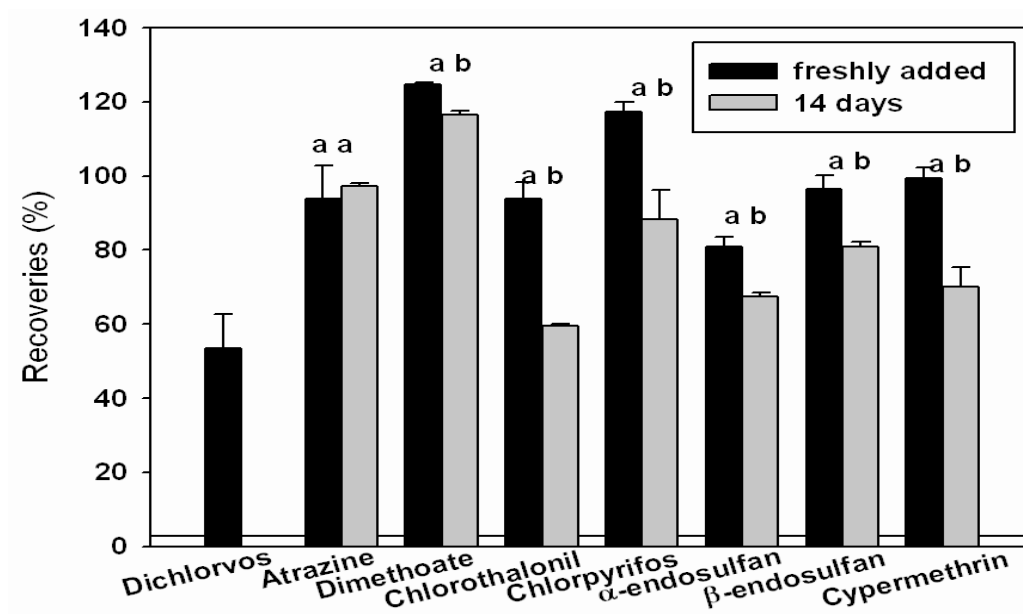
Figure 3.5: Extraction recoveries of freshly added pesticides and aged pesticide (14 days) from bed sediment samples. The samples (n=3) were spiked with 1 ng g^{-1} of the pesticides. Different indices indicate statistical differences at α= 0.05.

Regarding the different sample matrices (bed and suspended sediment samples), the efficiency of the adapted QuEChERS extraction method is generally similar. In the case of dichlorvos, however, the recoveries from the bed sediment are much lower (41-54 %) than those from the suspended sediment, which are in a satisfactory range (89-114 %). This can be explained by the lower organic matter content of the bed sediment sample. The lower the organic matter content, the fewer sorption sites and the higher the potential loss by volatilization. Moreover, the low K_{ow} of dichlorvos may have led to insufficient partitioning between aqueous and organic phases. With other sample matrices such as soil and food, however, high recoveries of dichlorvos (83-100 %) have been achieved (Lehotay et al., 2010; Yang et al., 2010; Li et al., 2011).

In the case of dimethoate, unacceptably high recoveries (above 120 %) were recorded with both sediment matrices at both concentration levels. Because dimethoate was not detected in the control (non-spiked) sediment sample, the high response probably reflects a matrix-induced chromatographic enhancement, particularly in the analysis with the GC-NPD system. This analytical problem in gas chromatography has been reported for certain compounds in

many other studies (Godula et al., 1999; Hajšlová and Zrostlíková, 2003). Dimethoate is apparently one of the analytes most sensitive to matrix effects in various commodities. For example, recovery ranges between 112 % and 296 % in foodstuffs have been widely discussed (Lee et al., 1991; Godula et al., 1999; Hajšlová et al., 1998). In surface water samples, Anyusheva et al. (2012) achieved a recovery between 123 % and 154 %.Dimethoate recoveries were higher in the suspended sediment than in the bed samples. To eliminate this analytical problem, we tried using pulsed splitless injection for GC inlet systems. This technique reduces residence time and minimizes solvent expansion volume. A variety of other measures, such as checking chromatographical response and the GC system maintenance, replacing the liner, cutting the front part of capillary column, and heating the GC systems over night were thoroughly tested, but could not eliminate matrix interference. Accordingly, we recommend using standard solutions prepared from the sample matrix for calibration, i.e. "matrix matched calibration" (Erney and Pawlowski, 1997). Anyushevaet al., (2012)] evaluated the potential analytical bias caused by matrix effect. Adopting a matrix-matched calibration technique considerably improved the recovery values of seven of the nine tested pesticides including dimethoate. From a practical point of view, however, this approach is complicated, especially in routine analysis where large numbers of samples from different sources with widely differing matrices have to be analyzed.

Table 3.4 shows the results of an intermediate precision test of the adapted QuEChERS method concerning the whole procedure of pesticide analysis in sediment samples. The method is reproducible with RSD between 5.8% and 18.8% for bed sediment and between 7.7% and 17.7% for the suspended sediment.

Table 3.4: Reproducibility of sediment extraction at a spiking level of 30 ng g^{-1} (n=3 for each day).

Relative standard deviation (RSD, %)		
Pesticide	**Bed sediment**	**Suspended sediment**
Dichlorvos	14.8	15.6
Atrazine	5.8	9.5
Dimethoate	18.8	7.7
Chlorothalonil	11.8	17.7
Chlorpyrifos	12.6	9.5
α-endosulfan	13.3	13.7
β-endosulfan	9.8	7.9
Cypermethrin	12.7	7.8

3.3.3. Application of the modified QuEChERS method

The method was applied to 176 bed sediment and 22 suspended sediment samples taken in the Mae Sa watershed in northern Thailand. The three pesticides with low K_{oc} values (dichlorvos, atrazine and dimethoate) were not detected. Table 3.5 shows the detected concentrations of pesticides in bed and suspended sediment samples in the watershed. Suspended sediment carried higher concentration range of the investigated pesticides than bed sediment. At all sampling points, pesticide hot spots of the detected pesticides were at the headwater area (S6-S7), where agricultural use is dominant. Among the detected pesticides, strong sorbing insecticides as cypermethrin had the highest concentration range, particularly in the Mae Sa Noi tributary (S3-S5) and in the Mae Sa River close to the headwater area (S6 and S7). Schulz and Liess (1999) reported transport of organic matter highly loaded with pyrethroid to the stream from an agricultural field. The associated particles of pyrethroid accumulate on bed and suspended sediments, where they act like a sink of pyrethroid. Chlorpyrifos was detected at moderate concentrations in the Mae Sa Noi tributary (S4). Chlorothalonil concentrations were higher around the headwater area (S7).

Table 3.5: Pesticides detected in sediment samples of the Mae Sa River (Thailand) in 2007-2008.

Site	Sedment sample	Chlorothalonil Detection (%)	Concentration range (ng g^{-1})	Chlorpyrifos Detection (%)	Concentration range (ng g^{-1})	Endosulfan* Detection (%)	Concentration range (ng g^{-1})	Cypermethrin Detection (%)	Concentration range (ng g^{-1})
S1	BS (n=22)	9	0.92-8.3	77	0.49-2.7	18	0.65-1.9	82	3.4-12.8
	SS (n=10)	70	1.4-28.3	100	3.1-28.3	50	0.46-3.2	70	21.5-184.1
S2	BS (n=22)	23	0.72-9.7	82	0.65-5.1	32	0.37-1.5	82	1.3-20.8
S3	BS (n=22)	41	0.74-13.7	95	0.38-5.3	32	0.27-2.8	95	1.8-26.9
S4	BS (n=22)	4	<LOQ-2.2	82	0.66-12.4	18	0.46-1.0	82	2.1-35.2
	SS (n=6)	nd	nd	67	5.0-6.4	nd	nd	100	32.7-82.5
S5	BS (n=22)	14	1.7-17.1	82	0.43-3.3	18	0.24-5.0	82	2.2-33.1
S6	BS (n=22)	45	0.91-9.7	73	0.46-6.5	9	0.86-2.0	86	3.2-32.0
S7	BS (n=22)	45	0.92-30.4	91	0.63-3.4	4	<LOQ-0.42	96	2.2-32.6
	SS (n=6)	71	11.3-68.0	100	5.1-37.1	42	1.1-4.2	100	35.9-249.7
S8	BS (n=22)	9	2.3-6.3	36	0.58-2.2	18	0.090-099	68	0.50-21.6

Note * The reported data were sum of (α- and β-) endosulfan concentrations.

** BS= bed sediment, SS= suspended sediment, n= number of samples, nd = not detected.

Comparing pesticide concentrations with literature values yields a varying picture. For example, the maximum concentrations of cypermethrin and chlorothalonil in the bed sediments are lower than the maximum concentrations detected in the Ebro River, Spain (0.1-71.9 ng g^{-1}) (Feo et al., 2010). In the San Joaquin River (USA) the detected chlorpyrifos in suspended sediments was lower, but in the bed sediment was higher than the present study (1.5-2.4 ng g^{-1} for suspended sediment and 0.4-62.2 ng g^{-1} for bed sediment) (Smalling and Kuivila, 2008). The maximum concentration of sum of (α- and β-) endosulfan in bed sediment is in line with the measured concentration in Wu-Shi River, Taiwan (<0.2-7.4 ng g^{-1}) (Doong et al., 2012).

3.4. Conclusion

A simple and rapid modified QuEChRES method was developed to determine 8 residue pesticides in bed and suspended sediment samples. Both acetonitrile and ethyl acetate can be used for analytical extraction of the polar and the semi-polar compounds, but to extract the non-polar compounds acetonitrile is more preferable. Addition of salt improved partitioning of the analytes into organic fraction. Although the clean-up step with PSA is not obligatory, this step is recommended in order to reduce the maintenance costs and to prolong the performance of the GC instrument. The modified method could be successfully applied to determine pesticides in bed and suspended sediment samples from a tropical river in Northern of Thailand.

3.5. Acknowledgements

3.6. References

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4. Publication 2

Short-term dynamics of pesticide concentrations and loads in a river of an agricultural watershed in the outer tropics

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4.0. Abstract

The intensification of agriculture in the mountainous regions of northern Thailand has led to an increased input of agrochemicals, which may be lost to streams and contaminate the surface water of the lowlands. The present study quantifies the dynamics of pesticide loads in a tropical river during three runoff events. To elucidate the processes involved in pesticide transport from agricultural fields to the stream water we used a high temporal resolution of sampling (1 h) and applied a time series analysis. Water samples were analyzed for seven pesticides (atrazine, chlorothalonil, chlorpyrifos, cypermethrin, dichlorvos, α- and β-endosulfan). Six of the seven pesticides were detected in the river water. Only dichlorvos was below the detection limit in all samples. In particular, pesticides with low K_{oc} value such as atrazine and dimethoate were transported during the runoff peaks. In case of chlorothalonil, chlorpyrifos, α- and β-endosulfan and cypermethrin, short concentration peaks lasting about 1 h were detected during the falling limbs of the runoff peaks, indicating that a fast and sporadic sub-surface flow component (e.g., preferential interflow) plays an important role as a transport pathway. Our study demonstrates that in tropical areas sampling schemes with a high temporal resolution are needed to adequately assess the pesticide contamination of rivers. Otherwise, extreme situations may remain unsampled.

Keywords: atrazine, dimethoate, chlorothalonil, chlorpyrifos, α- endosulfan, β-endosulfan, cypermethrin, pesticides in surface water, pesticide load, sub-surface transport, mountainous watershed, Thailand.

4.1. Introduction

The increasing demand for agricultural products and the urbanization in lowland areas has led to the expansion of permanent cultivation to the vulnerable slopes of the mountainous areas in northern Thailand. To protect crops from diseases and to increase crop yields, the application of pesticides has been intensified during the last decades. The intensive and/or careless use of pesticides may contaminate soil and water, causing environmental problems and posing a risk to human health, both in the uplands and lowlands (Stuetz et al., 2001; Kruawal et al., 2005; Panuwet et al., 2008).

The environmental fate of pesticides has been extensively studied in temperate zones (e.g., Kreuger, 1998; Riise et al. 2004; Müller et al., 2006) and Mediterranean zones (e.g., Louchart et al., 2004; Oliver et al., 2012). However, little is known about pesticide dynamics in tropical regions (Reichenberger et al., 2002; Castillo et al., 2000; Polidoro et al., 2009). To our knowledge, only few studies have investigated the transport of pesticides in the tropics in real field situations. In northern Thailand, the climate is characterized by the sequence of distinct rainy and dry seasons. Crops are grown and pesticides sprayed in the rainy season with heavy rainfalls and runoff. Thus, pesticide contamination in water resources is a relevant environmental issue in this region. Understanding dynamics of pesticides in agricultural watersheds is crucial for working out effective mitigation and management strategies.

Rainfall-induced surface runoff is considered an important transport pathway of pesticide loss from agricultural fields. Ng and Clegg (1997) analyzed the contribution of different flow components to the transport of atrazine in the Nissouri Creek in Canada. The loss with surface runoff was about twice that of interflow and baseflow. Sub-surface transport, however, may also considerably contribute to total loss. Kladivko et al. (1991) and Brown et al. (1995) found that pesticide concentrations increased at the start of discharge events, and that they rapidly decreased with the recession limb of hydrograph. This type of transport is often called "event-driven". It is hypothesized that the early part of an event is dominated by rapid flow processes such as surface runoff and sub-surface transport by preferential water flow. Later, matrix flow becomes more important, so that solutes are retarded in soil, and thus pesticide concentrations in leachate are much lower (Kladivko et al, 1991).

The present study was conducted in the Mae Sa watershed in northern Thailand. In previous studies within the Mae Sa watershed the fate of pesticides after application to a sloped litchi orchard was investigated at the plot and at the hillslope scale. The results show that macropores caused significant preferential transport in vertical (Ciglasch et al., 2005) and

lateral direction (Kahl et al., 2008). The extent of preferential flow and transport strongly depended on rainfall and antecedent soil moisture (Kahl et al., 2007, 2008). Additionally, simulations based on a two-domain reservoir model indicate that under wet soil conditions, "old" water may be pressed into the preferential flow pathways by very small rainfall events, leading to desorption of pesticides from the pore walls. Therefore, preferential interflow must be considered as an important transport process for pesticides in the mountainous areas of northern Thailand (Kahl et al. 2010).

Studies on the plot and field scale under relatively well defined conditions allow to investigate in detail the influence of selected factors such as application time, rainfall intensity or antecedent soil wetness on pesticide loss. These studies, however, can give only a limited picture of the real situation at the catchment scale. At this scale, additional factors control transport and loss of pesticides from the application area to water bodies. Differences in agricultural practices and cropping systems create a large variability of a pesticide application in time and space. Moussa et al. (2003), for example, reported that ditch networks may play an important role for water flow characteristics such as runoff volume, lag time, and form of runoff peak. The spatial distribution of the agriculturally used areas may also influence pesticide losses during flood events (Frey et al., 2009; Wohlfahrt et al., 2010).

The aim of our study was to gain a better understanding of the transport of seven pesticides with widely differing physicochemical properties (log K_{oc} 1.5-4.9) under wet-dry tropical conditions at the catchment scale. The watershed under study can be regarded as representative for agricultural mountainous watersheds in northern Thailand and elsewhere with similar climatic conditions. Based on a high-resolution sampling scheme and a time series analysis, we deduced potential transport pathways from observed pesticide concentration patterns. We investigated three rainfall events: one event at the beginning of the rainy season when soils were dry and two events in the middle and towards the end of the rainy season when soil moisture was high.

4.2. Materials and methods

4.2.1. Description of the study area

The Mae Sa watershed is located 30 km northwest of Chiang Mai in northern Thailand. The total area of the watershed is 77 km^2 (Fig. 4.1). The agricultural land use in the catchment was mapped based on a SPOT 5 image centered at N19°1'4" E98°49'24" taken on 6 November 2006 (Fig. 2) (GISTDA 2007). About 24 % of the watershed is in agricultural use, whereby

this land use class covers also a small fraction of settlements. The remaining 76 % is covered by deciduous, evergreen forest and mixed forests (Fig. 4.2). The fraction of agricultural area in the headwater sub-catchment was 28.5 %. This area is mainly used for growing vegetables (cabbage, bean, chayote, etc.), fruit (litchi) and flower production (gerbera, chrysanthemum, etc.). In the headwater area (28 km^2), the proportion of agricultural area and particularly the number of greenhouses is higher than in the lower parts of the watershed. Dominant soil types in the watershed are Acrisols and Cambisols, with a highly developed macropore network (Schuler, 2008). Top soil texture of the Acrisols (0.0-0.2 m) is clay loam, while that of the Cambisols varies from clay loam to sandy clay loam (Schuler, 2008; Spohrer et al., 2006). The parent material is mainly granite and paragneiss. The catchment is characterized by steep slopes and narrow valleys. The altitude ranges from 350 to 1540 m above sea level (a.s.l.). The average slope is 36 %, with large differences from the headwater (HW) towards the outlet (OL). The climate is tropical with distinct rainy (May to October) and dry seasons (November to April). Mean annual air temperature and mean annual rainfall in 2004-2010 were 21.0 ^{o}C and 1250 mm, respectively (Thai Meteorological Department, 2011). The total rainfall in 2008 was 1236 mm which is close to the average annual rainfall between 2004-2010. The typical crops are grown in the rainy season (June to September). Off-season fruits, such as Litchi, and temperate crops, such as carrot, white radish etc., are cultivated in winter (November to February). Most agricultural areas are located in the valleys following the river network (see Fig. 4.2). The occurrence of surface runoff is typical for the rainy season. In 2008, the average discharge of the HW and the entire watershed was 2.34 and 1.36 mm d^{-1}, respectively. The maximum flow rate at the HW station was 14.6 mm d^{-1} (with a peak of 14.0 m^3 s^{-1}), which occurred on 21 August 2008. At the OL station, the maximum flow was recorded as 8.5 mm d^{-1} (with a peak of 21.5 m^3 s^{-1}) on 6 September 2008.
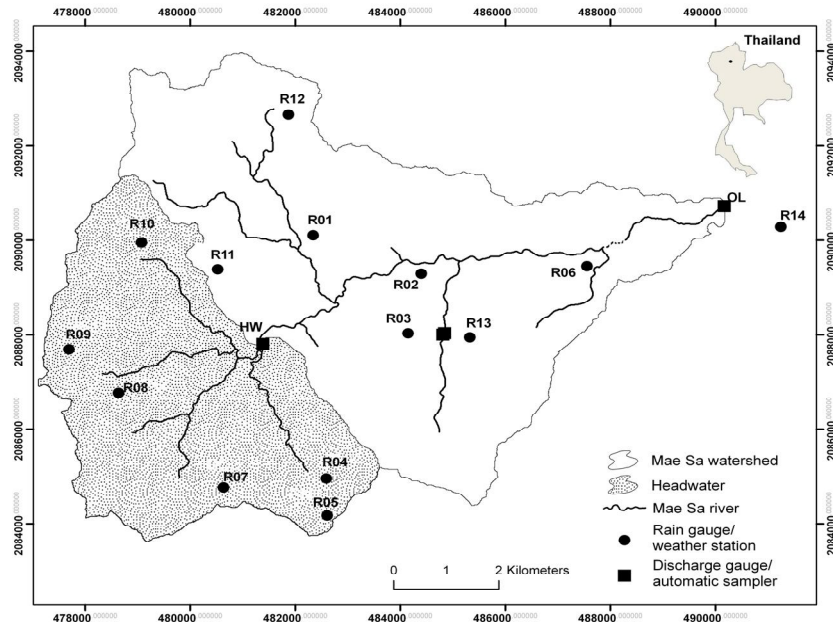
Figure 4.1: Mae Sa watershed (North Thailand) with sampling locations and measurement network
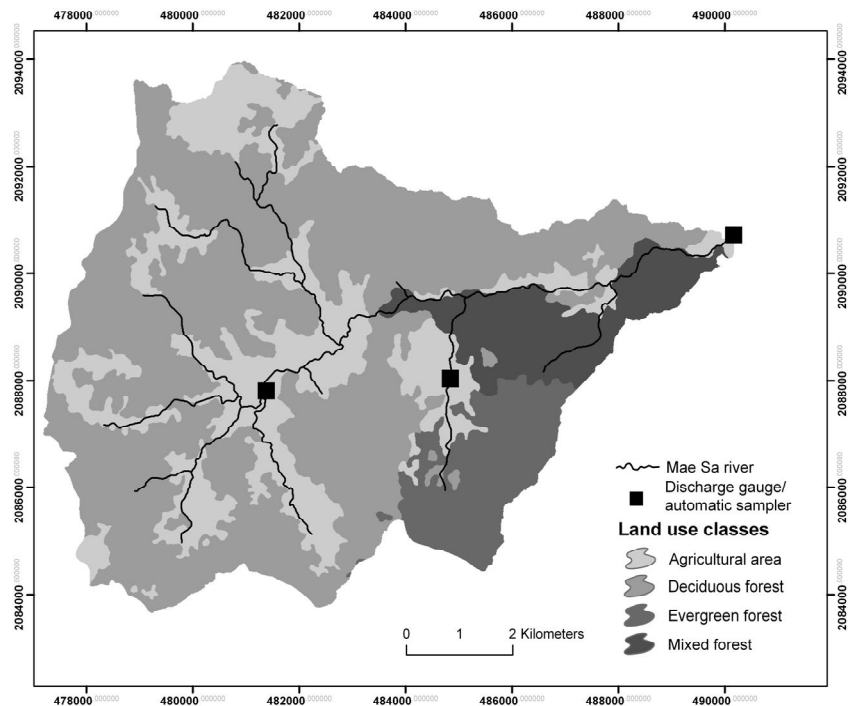
Figure 4.2: Land use Map of the Mae Sa watershed, 2006

4.2.2. Pesticide selection

We selected seven pesticides frequently applied by the farmers in the Mae Sa watershed. Their properties are given in Table 4.1. According to a survey by Schreinemachers and Sirijinda (2008), dichlorvos, chlorpyrifos, cypermethrin, and chlorothalonil are intensively used in bell pepper, chrysanthemum, and white cabbage production (Table 4.2). Endosulfan and dimethoate were included because they had been detected in a previous study in the Mae Sa River (Ciglasch et al., 2006). Although not mentioned in Schreinemacher's survey, atrazine was included because we had found significant concentrations in preliminary investigations.

Table 4.1: Physico-chemical properties of the investigated pesticides.

Pesticide	Water solubility[a]	Log K_{oc} [b]	Half life in water
	(mg L^{-1})	(L kg^{-1})	(days)
Dichlorvos	10,000	1.7	7[c]
Atrazine	28	2.0	30[c]
Dimethoate	25,000	1.5	8[d]
Chlorothalonil	0.6	2.9	49[c]
Chlorpyrifos	2	3.9	35-78[d]
Endosulfan	0.32	4.1	28[d]
Cypermethrin	0.01	4.9	> 50[e]

Data from [a]EXTOXNET (1996), [b]Footprint PPDB (2011), [c]PAN database (2008), [d]Howard (1991) and [e]EPA (1989)

Table 4.2: Major crops and usage of investigated pesticide in the Mae Sa watershed 2007 (Schreinemachers and Sirijinda, 2008).

Crop	Insecticide					Fungicide
	Dichlorvos	Dimethoate	Chlorpyrifos	Endosulfan	Cypermethrin	Chlorothalonil
Bell pepper	X		X		X	X
Chrysanthemum	X		X		X	X
White cabbage	X		X	X	X	
Bush bean	X					X
Chinese cabbage	X		X		X	
Litchi	X		X		X	X
Chayote	X					X
Potato		X				
Paddy rice			X		X	

4.2.3. Field measurements and data analysis

4.2.3.1. Sampling and stream flow measurement

Stream flow and pesticide loads originating from the headwater catchment were measured at the HW gauge (767 m a.s.l.; 28 km^2), those originating from the entire watershed at the OL gauge (345 m a.s.l.; 77 km^2). At each station, the water level was continuously recorded using an ultra sonic water level sensor (710 Ultrasonic module, Teledyne ISCO Inc., USA). The conversion into discharge volume was based on calibration data taken by an acoustic flow meter (OTT ADC, Germany). Discharge data were recorded in 10-min intervals.

Each gauging station was equipped with an automatic water sampler (6712 Portable sampler, Teledyne ISCO Inc., USA). The first runoff event was sampled on the beginning of the rainy season from 2 May to 7 May 2008. Two further events were sampled in the middle and close to the end of the rainy season. The second campaign was conducted from 20 to 24 August and the third event was sampled from 13 to 17 September 2008.

During the sampling campaigns (each 3-4 days long), composite samples were taken at hourly resolution. Each composite sample (300 mL) was mixed from six 50 mL samples drawn from the river every 10 min. The decision of which samples to use for analysis was made later in the lab, based on measured discharge. To characterise the background concentrations before the discharge peak (16 h in case of the May event, and 8 h in case of the August and September event), samples were selected with a 4 hourly resolution. The beginning of increasing discharge was determined visually. In the automatic sampler and later, sampling bottles were cooled with ice. Within one day, they were transported to the lab. Samples were stored in a refrigerator at 4 °C in the lab and processed during the following two to three days.

4.2.3.2. Rainfall data

To quantify the rainfall within the watershed, a network of twelve automatic rain gauges (Typ 441301, 0.2 mm resolution, Fischer GmbH, Germany) was installed (Fig. 1). The rain gauges were distributed over the whole catchment area and cover the major elevation levels. Additionally, the rainfall data of two neighboring weather stations were included. All stations were operated with 10 min resolution. The average rainfall within the catchment was computed after Shaw (1988):

$$\bar{R} = \frac{1}{A} \sum_{i=1}^{n} R_i A_i$$

Here, R_i (mm) is the rainfall measured at the i-th rain gauge, the symbol n stands for the number of rain gauges, A (km^2) is the total area of the catchment and A_i (km^2) is the Thiessen polygon area of the i-th gauge. In the case of HW rainfall, only the parts of the Thiessen polygons located in the headwater area were used to calculate the amount of rainfall.

4.2.3.3. Runoff coefficient

The runoff coefficient (RC) is defined here as the percentage of rainfall that appears as runoff during an event. Rainfall related to a particular flood event was included from the point in time when discharge started to rise until it started to fall again. Runoff volume directly generated by rainfall was determined by using an automated two-component hydrograph separation method separating baseflow and direct flow (Arnold et al., 1995; Arnold and Allen, 1999). This Baseflow Filter Program is also available from http://swatmodel.tamu.edu/software/baseflow-filter-program. The RC was calculated from the quotient between direct flow and rainfall.

4.2.3.4. Time series analysis

To relate rainfall, discharge and pesticide concentrations in the stream to each other, a time series analysis was conducted. Cross-correlation coefficients (CCC) between variables x and y were computed as

$$CCC = \frac{\sum_t (x_{t+\tau} - \bar{x})(y_t - \bar{y})}{\sqrt{\sum_t (x_{t+\tau} - \bar{x})^2 \sum (y_t - \bar{y})^2}}$$

where τ is the time lag in hours, and x_t and y_t are the values of the correlation variables at time t. The symbols $\bar{x}$ and $\bar{y}$ denote the means of x and y, respectively. CCCs were calculated for rainfall and stream discharge, rainfall and pesticide concentration in stream water, and stream discharge and pesticide concentration with $0 \leq \tau \leq 300$ min (HW, May: 565 data points; OL, May: 708 data points; HW, August: 346 data points; OL, August: 417 data points). The time series analysis was performed with the statistical software package SPSS (Version 16.0, SPSS Inc., USA) using 95% confidence intervals.

4.2.3.5. Pesticide extraction and analysis

Pesticides were concentrated from water samples by solid phase extraction (SPE) (Supelclean^{TM} Envi-Carb, *Graphitized Non-Porous Caron,* surface area 100 m^2 g^{-1}, particle size 120/400 mesh, 0.5 g, 6 mL; Supelco, USA). Prior to extraction, all samples were filtered

through a glass fiber filter (GF/F, 0.45µm; Whatman Inc., USA) to remove suspended particle material. To condition and deactivate the sorbent, the cartridges were rinsed with 8 mL of a dichloromethane:methanol mixture (9:1, v/v), 3 mL methanol, and 25 mL of ascorbic acid (γ = 10 g L^{-1}; this solution was brought to pH 2 using hydrochloric acid). After this conditioning step, 400 mL of the filtered water samples were sucked through a SPE cartridge at a flow rate of about 5 mL min^{-1} using a vacuum pump. After the sample load, air was sucked through the cartridges for approximately 5 min. At the end, the cartridges were packed in bags, sealed, and stored in the freezer (-18 °C). As shown by Anyusheva et al. (2012), samples processed in this way can be stored without significant pesticide loss for up to nine months. After having been prepared as described above, the samples were shipped to Germany within approximately 24 h using solid carbon dioxide as cooling agent. They were stored at -20 °C until extraction and analysis.

To remove possible water from the sample, air was again sucked through the sorbent for 5 min followed by rinsing with 1.5 mL of methanol. Subsequently, the SPE cartridges were eluted with 10 mL of acetone, 15 mL of a dichloromethane: methanol mixture (9:1, v/v), and 30 mL of tert-butyl methyl ether (TBME). The flow-rate of all solvents was restricted to less than 2 mL min^{-1}. The eluted solutions were collected in conical flasks, and two drops of toluene were added as a keeper before evaporating to almost dryness. The residues were re-dissolved in 1 mL of a mixture of cyclohexane and toluene (9:1, v/v). These solutions were used for analysis.

4.2.3.6. Analytical procedure

The elutes were analyzed by capillary-GC and partly by GC-MS. For capillary-GC analysis, two differently equipped GCs were operated: Firstly, a Hewlett Packard HP 6890 gas chromatograph equipped with an organophosphate pesticide capillary column, Rtx[®]-OPPesticides (length 30 m, I.D. 0.25 mm, film thickness 0.25 µm; Restek, USA), and a nitrogen-phosphorus detector (NPD, with Blos-bead; Agilent Technologies, USA), and secondly, an Agilent Technologies 7890 GC equipped with an HP-5 capillary column (length 30 m, I.D. 0.32 mm, film thickness 0.25 µm) and a micro-electron capture detector (µ-ECD). Dichlorvos, dimethoate, and atrazine were analyzed by GC-NPD. Chlorothalonil, chlorpyrifos, (α, β) endosulfan, and cypermethrin were analyzed by GC-µ-ECD.

The inlets of both GCs were programmable temperature vaporization (PTV) injectors (Model UNIS; Joint Analytical Systems GmbH, Germany), which were operated in the pulsed splitless mode. The advantage of this pulsed splitless mode is better resolution and response

(e.g., Godula et al., 1999). The starting temperature in PTV was 125 °C. The temperature was held constant for 0.2 min and then raised to 300 °C at a rate of 250 °C min^{-1} with GG-NPD or 750 °C min^{-1} with GC-µECD. Here, temperature was held constant for 25 min. The PTV inlet pressure in the beginning was set to 159 kPa and pressure was increased during the pulsed splitless mode for 1.5 min to 207 kPa. The injection volume was 1 µL. The temperature of the GC oven was initially set to 90 °C, held constant for 2 min, ramped to 300 °C at 15 °C min^{-1} and then held constant for 10 min. High purity grade helium was used as carrier gas in constant flow mode (2 mL min^{-1}). The NPD temperature was set to 310 °C and operated at the following gas flows. H$_2$-flow: 3 mL min^{-1}, air-flow: 60 mL min^{-1}, constant make-up (N$_2$) + carrier gas flow: 20 mL min^{-1}. The bead-voltage ranged from 0.8 to 0.96 V within 4 months, which caused an offset current of approximately 10 pA. The µ-ECD temperature was also set to 300 °C.

Capillary-GC results of selected samples, i.e. samples with outstanding high peak concentrations, were confirmed by GC-MS (GCQ; Finnigan MAT, USA). The MS was equipped with capillary column FactorFour VF-5MS (length 30 m, I.D. 0.25 mm, film thickness 0.25 µm; Varian, USA). The injector of the GC-MS system was operated in the splitless mode (-0.2 to 1.5 min) at constant inlet temperature of 230 °C. As carrier gas, helium was used in constant flow mode at 40 cm s^{-1}. At the beginning the GC oven temperature was set to 90 °C, held for 2 min and raised to 290 °C at a rate of 15 °C min^{-1}. Then, temperature was held constant for 10 min. The temperature of the transfer line between the GC and ion trap detector was set to 300 °C. Electron impact ionization (EI) was performed at 70 eV. Fragments within the m/z (mass-to-charge ratio) range from 75 to 430 atomic mass units (amu) were collected and analyzed. Mass spectra from the sample chromatograms were compared to mass spectra of the pure substances measured with the same instrument and under the same operating conditions and to mass spectra published in literature, e.g. from the NIST Chemistry WebBook. Limits of detection (LOD), recoveries, and relative standard deviations (RSD) of the pesticide analysis are given in Table 4.3.

Table 4.3: Limit of detection (LOD) and recoveries of pesticides in water

Pesticide	LOD (ng L^{-1})	% Recovery (RSD) (n=3)
Dichlorvos[a]	0.1	60 (8)
Dimethoate[a]	0.5	117 (16)
Atrazine[a]	2	113 (7)
Chlorothalonil[b]	1	58 (27)
Chlorpyrifos[b]	0.3	106 (5)
α-Endosulfan[b]	0.1	91 (9)
β-Endosulfan[b]	0.1	101 (7)
Cypermethrin[b]	2	69 (4)

[§]RSD = relative standard deviation, [a] Analyzed by GC-NPD, [b] Analyzed by GC-μECD.

4.2.3.7. Pesticide load calculation

Pesticide loads were calculated by multiplying the hourly stream flow volume with the average pesticide concentration of stream water of that period. Concentrations below the detection limit were set to zero. At both gauging stations, the average areal pesticide loads (g km^{-2}) were computed to compare the pesticide losses between the two catchments. For that, the cumulative pesticide loads were divided by the catchment area of arable land (km^2) assigned to each gauging station.

4.3. Results

4.3.1. Hydrological event characterization

The response of runoff to rainfall varied remarkably between the sampling events (Fig. 4.3). The first event, a minor discharge peak, was sampled at the beginning of the rainy season in May. The HW sub-catchment received 56 mm rainfall during 44 h, which led to two runoff peaks, one after about 1 h with a maximum flow of 2.5 m^3 s^{-1} and a smaller one with a maximum flow of 1.9 m^3 s^{-1} which followed 7 h later. The RC of the event was 0.8 % (Table 4.4). On average, the rainfall in the whole catchment was 45 mm during a period of 48 h. The peak flow at the OL station occurred about 4 h later with a smaller peak flow of 2.8 m^3 s^{-1}. A larger peak, with a flow rate of 3.8 m^3 s^{-1}, appeared about 14 h later. The RC was also 0.8 % (Table 4.4). The in-stream travel time between the main runoff peaks between HW and OL station was about 4 h.

The second and the third events were sampled in the middle and towards the end of the rainy season in August and September. Other than with the first event, sharp discharge peaks were observed at both stations. At HW, the event sampled in August was the highest runoff event in 2008 (Fig. 4.3). A total rainfall of 9.9 mm over a period of 7 h initiated runoff within 1 h. Peak flow was 14 m^3 s^{-1}. With 13.1 %, the RC was considerably higher than that of the first event (Table 4.4). In the whole catchment, total rainfall was slightly higher (10.9 mm). Peak flow amounted to 12.4 m^3 s^{-1}, 3 h after the start of rainfall. RC was 4.8 %. The in-stream travel time between both stations was 3 h (see below) and hence shorter than in May. Because of a technical failure at the OL station, in September the pesticide data are only available at the HW station. Five runoff peaks were observed during the sampling campaign. In this study, we will only consider the hydrological characteristics of the three main events. On the first main event, the total rainfall amounted to 13.7 mm. It resulted in a discharge peak of 7.6 m^3 s^{-1} within 50 min (Fig. 4.6). A slightly lower discharge peak (7.1 m^3 s^{-1}) was observed on 15 September triggered by a total rainfall of 11.7 mm. The highest discharge peak (7.9 m^3 s^{-1}) was measured on 16 September. It was initiated by a relatively lower rainfall amount (5.2 mm). The RCs of the three September events was 7.3, 10.2 and 12.7 %.
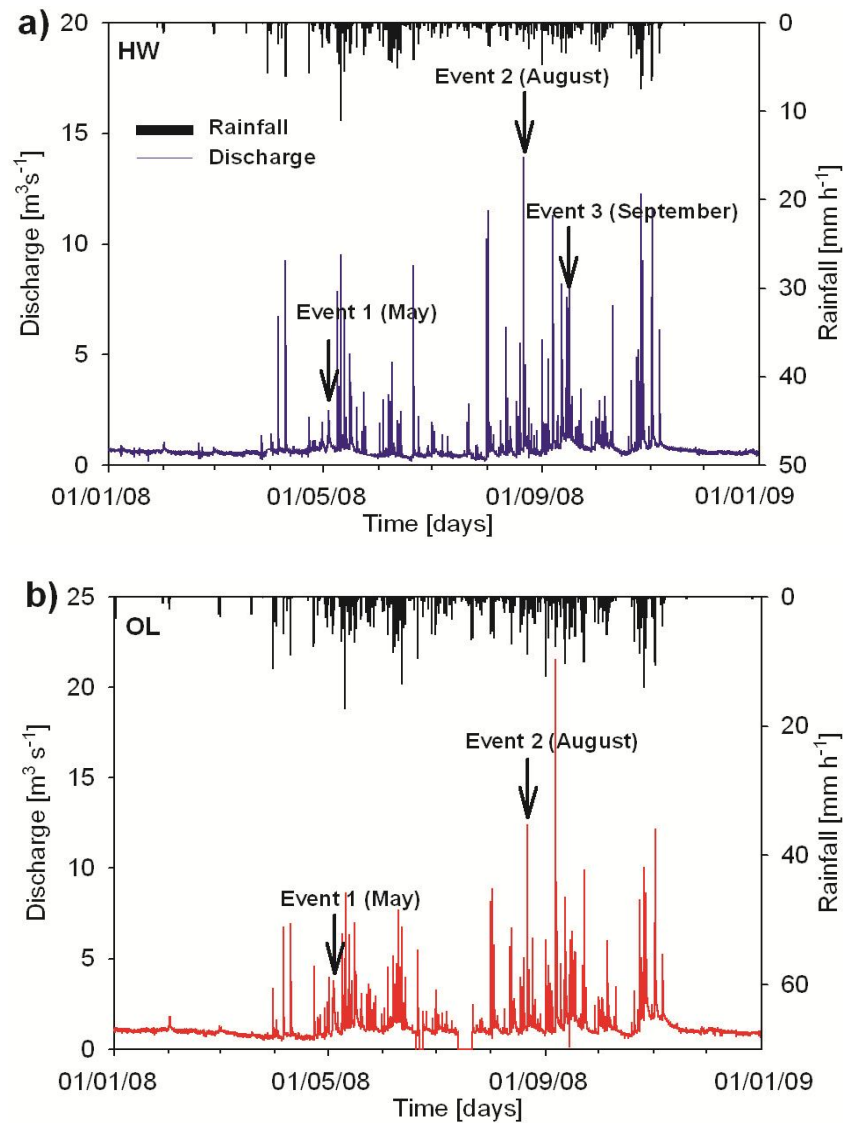
Figure 4.3: Time-series of rainfall and discharge in 2008 and three sampling events at (a) the headwater (HW) station and (b) the outlet (OL) station.

Table 4.4: Hydrological characteristics of the runoff events monitored at the headwater (HW) and the outlet (OL) station.

Hydrological characteristics	Event 1 (2.-7.05.08)		Event 2 (20.-24.08.08)		Event 3 (13.-17.09.08)		
	HW1	OL1	HW2	OL2	HW3[a]	HW3[b]	HW3[c]
Rainfall (mm)	56	45	9.9	10.9	13.7	11.7	5.2
Mean rainfall intensity (mm h^{-1})	1.3	0.89	1.4	1.1	1.9	1.5	0.52
Maximum rainfall intensity (mm h^{-1})	6.5	5.7	5.6	7.1	8.4	3.2	4.6
Total runoff (mm)	6.6	6.7	4.7	2.2	5.7	9.2	1.7
Direct flow (mm)	0.44	0.36	1.3	0.52	1.0	1.2	0.66
Runoff coefficient (%)	0.8	0.8	13.1	4.8	7.3	10.2	12.7
Peak discharge (m^3 s^{-1})	2.5	3.8	14.0	12.4	7.6	7.1	7.9

§ The three main runoff peaks during the HW3 event: [a] 14 September 2008, [b] 15 September 2008 and [c] 16 September 2008.

4.3.2. Pesticide concentrations in the stream

Table 4.5 summarises the range of pesticide concentrations and their frequency of detection (measured concentration > LOD) in stream samples taken at the HW and OL stations. The number of detected pesticides was highest during the May event. Six out of seven pesticides analysed were detected in the Mae Sa River (exception: dichlorvos). The dynamics of rainfall, stream discharge, and pesticide concentrations for the three events are shown on chemographs in Figure 4.4-4.6.

At the HW station, the concentration of atrazine increased with increasing discharge and peaked to 0.12 µg L^{-1} between the two runoff peaks (Fig. 4.4a). After rainfall had ended, several smaller atrazine peaks were observed on the falling limb of the recession curve. At the OL station, with the beginning of the rain event, atrazine concentrations in stream water closely followed the runoff curve with a delay of about 3 h to reach a maximum of 0.4 µg L^{-1} (Fig. 4.4b). After the first runoff peak, atrazine concentrations declined gradually to a low level, but concentrations remained higher than before the event. In the course of the second runoff peak and the following recession phase, no significant additional concentration peaks were observed.

Dimethoate peaked within the same time frame as atrazine, with a maximum concentration of 0.6 µg L^{-1} at the HW station (Fig. 4.4c). Several post-event concentration peaks were detected during the following recession phase. At the OL station, dimethoate concentration also increased after the first runoff peak but not as pronounced as atrazine. Similar to HW, smaller post-event peaks (<0.2 µg L^{-1}) were also observed at the OL station.

With chlorpyrifos, a single peak (0.6 µg L^{-1}) was detected before the runoff peak at the HW station. Additional chlorpyrifos peaks occurred after the runoff peak during the following phase of increasing discharge. No clear post-event concentration peaks were observed at that station (Fig. 4.4e). At the OL station, chlorpyrifos increased only slightly with the onset of increasing discharge. Three concentration peaks in the range of 0.1 µg L^{-1} were sporadically observed along the recession limb of the runoff curve (Fig. 4.4f).

Table 4.5: Ranges and mean of pesticide concentrations, and frequency of detection (concentration > LOD) measured at headwater (HW) and outlet (OL) stations during three rain events.

Pesticide	Pesticide concentration in water														
	Headwater station (HW)									Outlet station (OL)					
	May event			August event			September event			May event			August event		
	Range	Mean	Samples >LOD	Range	Mean	Samples >LOD	Range	Mean	Samples >LOD	Range	Mean	Samples >LOD	Range	Mean	Samples >LOD
	$\mu g\ kg^{-1}$	$\mu g\ kg^{-1}$	%	$\mu g\ kg^{-1}$	$\mu g\ kg^{-1}$	%	$\mu g\ kg^{-1}$	$\mu g\ kg^{-1}$	%	$\mu g\ kg^{-1}$	$\mu g\ kg^{-1}$	%	$\mu g\ kg^{-1}$	$\mu g\ kg^{-1}$	%
Atrazine	0.01 - 0.1	0.03	42	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.004-0.4	0.07	96	n.d.	n.d.	n.d.
Dimethoate	0.003 - 0.6	0.10	93	0.07-0.3	0.07	67	n.d.	n.d.	n.d.	0.005-0.2	0.06	89	0.06-0.4	0.07	69
Chlorothalonil	0.01 - 0.6	0.04	98	n.d.	n.d.	n.d.	0.01-0.07	0.01	38	0.003-0.07	0.02	87	n.d.	n.d.	n.d.
Chlorpyrifos	0.008 - 0.5	0.08	98	0.04-9.7	0.65	95	0.01-0.04	0.01	38	0.002-0.1	0.04	90	0.04-0.9	0.2	94
Endosulfan	0.002 - 0.09	0.02	95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.006-0.05	0.01	91	n.d.	n.d.	n.d.
Cypermethrin	0.008 - 0.2	0.06	82	0.002-0.05	0.01	44	n.d.	n.d.	n.d.	0.01-0.2	0.02	39	0.003-0.008	0.004	79

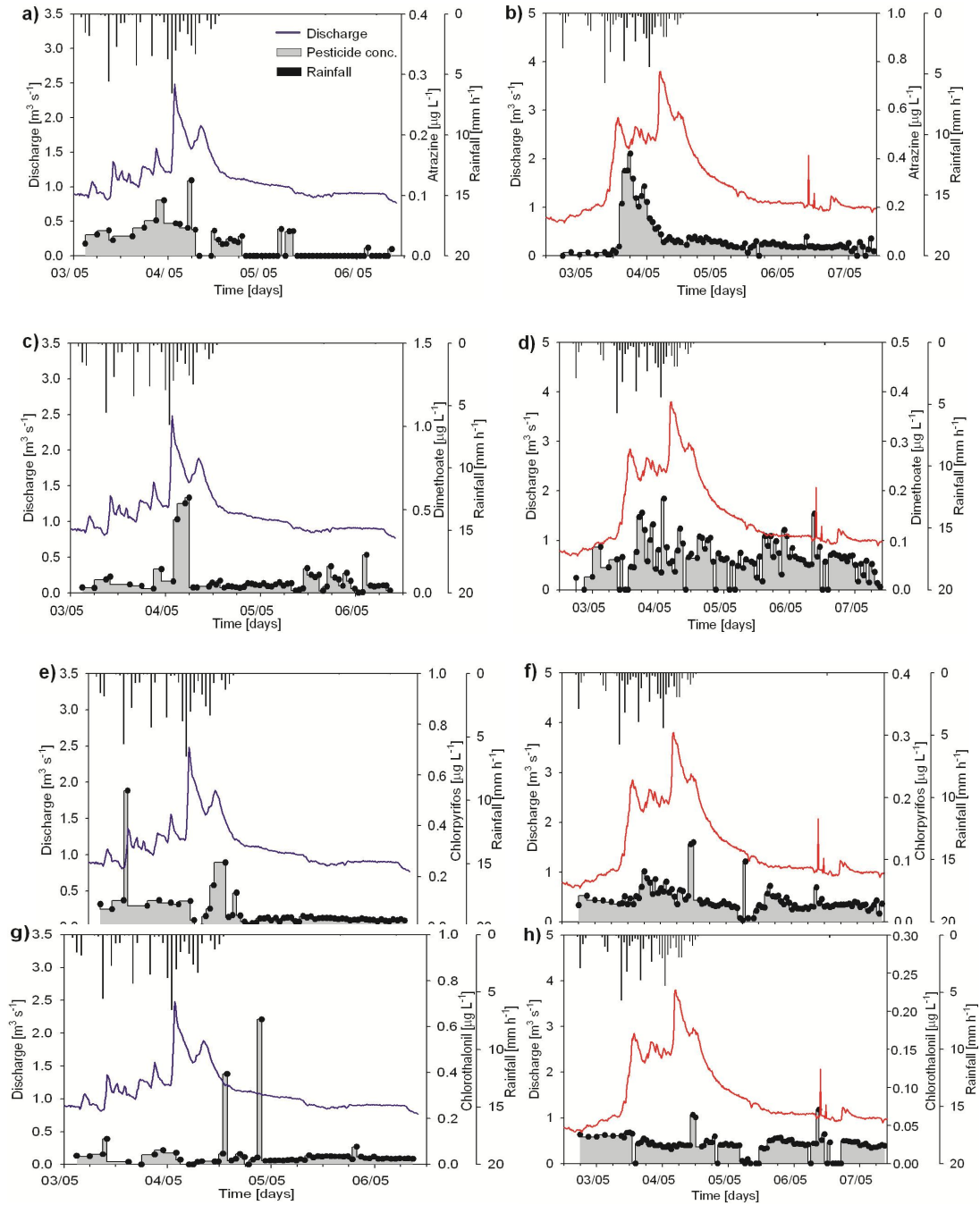[§] n.d. = not detected; LOD: limit of detection

Figure 4.4: Concentrations of six pesticides, discharge, and rainfall data during the May event. Left column: headwater (HW) station. Right column: outlet (OL) station. Pesticides: (a, b) atrazine, (c, d) dimethoate, (e, f) chlorpyrifos, (g, h) chlorothalonil, (i, j) (α, β)-endosulfan, (k, l) cypermethrin. Dichlorvos was not detected.
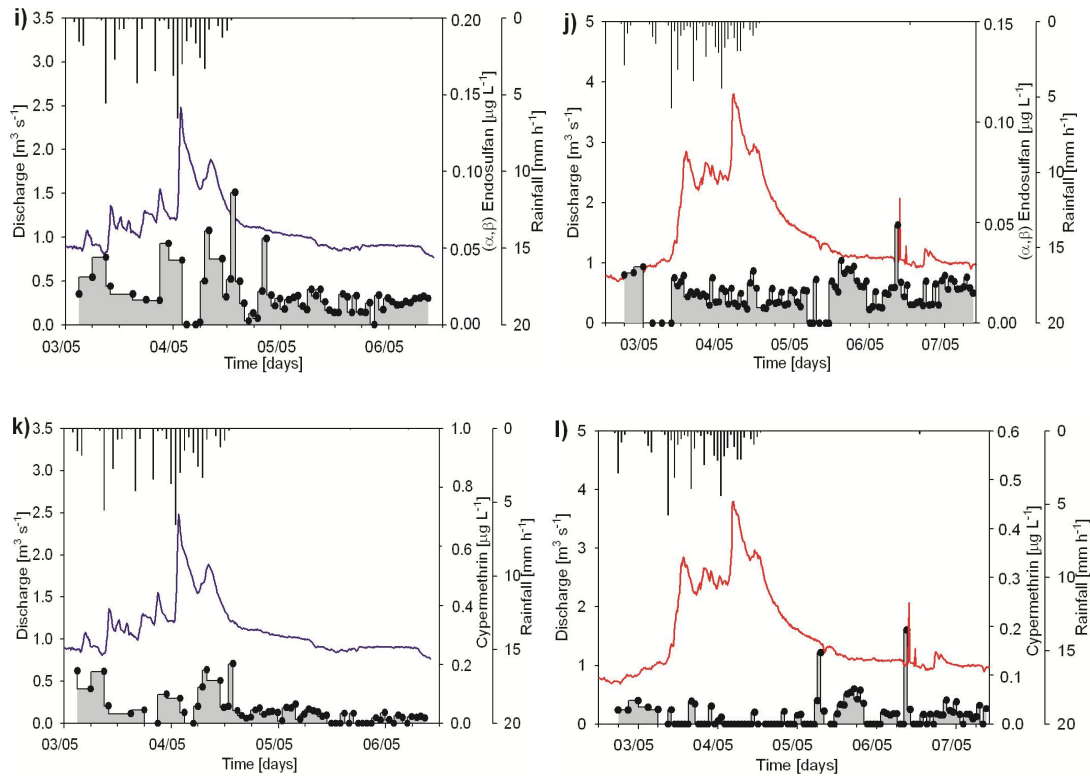
Figure 4.4. *(continued).*

Concentrations of chlorothalonil remained at a low level before and during the increase of discharge, but two remarkable concentrations peaks were detected along the recession limb, with a maximum concentration of 0.6 µg L^{-1} at the HW station (Fig. 4.4g). Also at the OL station the concentrations of chlorothalonil were quite constant during the entire event. Only three samples showed concentrations above 0.05 µg L^{-1} during the phase of decreasing discharge (Fig. 4.4h).

The endosulfan concentrations reported in Fig. 4 are the sum of the isomers α- and β-endosulfan. Concentrations peaked at the initial phase of the event. The highest concentration was found later during the falling limb of the runoff curve (Fig. 4.4i). At the OL station, most concentrations of endosulfan were below 0.03 µg L^{-1}. They were approximately constant during the event. Only one concentration peak of 0.05 µg L^{-1} was observed on the falling limb of the hydrograph.

Cypermethrin concentrations at the HW station were already as high as 0.2 µg L^{-1} before the discharge distinctly increased. Slightly lower concentrations were measured during the increase of the runoff peak. Close to the end of the main decrease, cypermethrin peaked again

at 0.2 µg L^{-1} (Fig. 4.4k). At the OL station, the concentration pattern was similar to that at the HW station. Only some small peaks of cypermethrin were detected during the discharge increase, whereas the main peaks appeared sporadically during the recession phase of the runoff, with a maximum concentration of 0.2 µg L^{-1} (Fig. 4.4l).

Note that the concentrations of all pesticides increased remarkably with the steep, but small runoff peak on 6 May.

Pesticide dynamics during the mid-rainy season event in August are shown in Figure 5. Only three of the seven pesticides investigated, namely dimethoate, chlorpyrifos and cypermethrin, were detected in the water samples. At the HW station, dimethoate concentrations increased as discharge increased peaked at 0.3 µg L^{-1} shortly after the runoff peak, and gradually declined during recession (Fig. 4.5a). At the OL station, only dimethoate showed this pattern (Fig 4.5b).

Extremely high concentrations of chlorpyrifos (up to 9.7 µg L^{-1}) were detected at the HW station during the recession. The concentration peak showed up later in stream water than in the case of dimethoate (Fig. 4.5c). During the runoff peak, only very low concentrations of chlorpyrifos were found. The concentration pattern at the OL station was very similar to that of the HW station, but the concentration peak was broader and the maximum concentration (0.9 µg L^{-1}) was much lower than at the HW station (Fig. 4.5d).

Cypermethrin values reached 0.05 µg L^{-1} prior the runoff event at the HW station. The pesticide concentration decreased during the runoff peak and increased again to a maximum of 0.1 µg L^{-1} at the end of recession limb (Fig. 4.5e). No clear post-event peak of cypermethrin was detected. The cypermethrin concentration at the OL station showed no significant peaks. During the entire event, the concentrations of this pesticide were low (0.003-0.008 µg L^{-1}) (Fig. 4.5f).

In September, only chlorothalonil and chlopyrifos were detected at the HW station during the sampled runoff events. Similarly to the previous event, we found a delay between peak concentration and peak flow. Chlorothalonil peaked with 0.05 µg L^{-1} the first time during the small runoff peak that preceded the main runoff event on 14 September (Fig. 4.6a). It peaked the second time with 0.07 µg L^{-1}, 14 h after the discharge peak of the runoff event (on 14 September). Similar to chlorothalonil, several concentration peaks of chlorpyrifos were detected sporadically between the peak flows of 14 and 15 September. The highest

concentrations of this insecticide (0.04 µg L^{-1}) were measured during the discharge peak of 16 September (Fig. 4.6b).
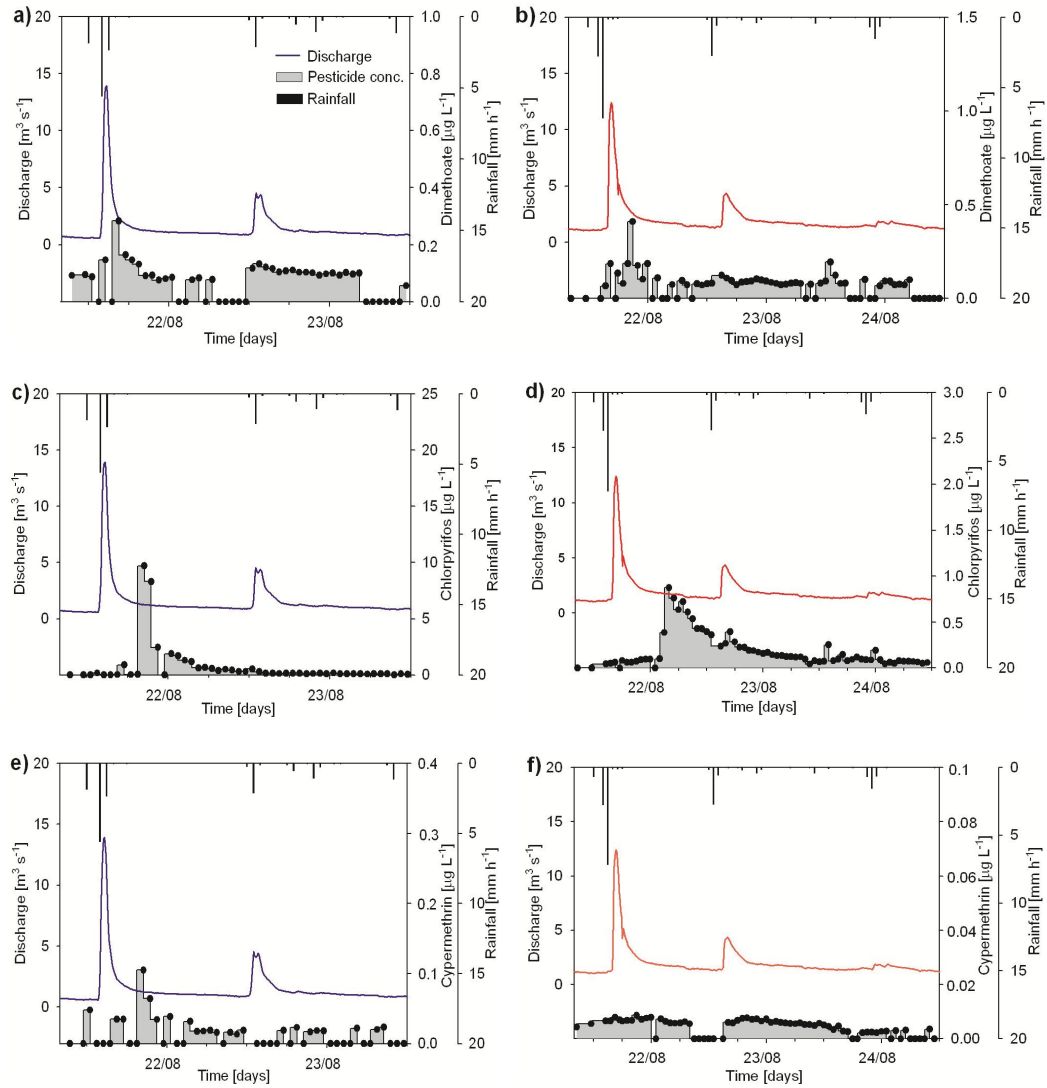
Figure 4.5: Concentrations of three pesticides, discharge, and rainfall data during the August event. Left column: headwater (HW) station. Right column: outlet (OL) station. Pesticides: (a, b) dimethoate, (c, d) chlorpyrifos, and (e, f) cypermethrin. The other pesticides were not detected.
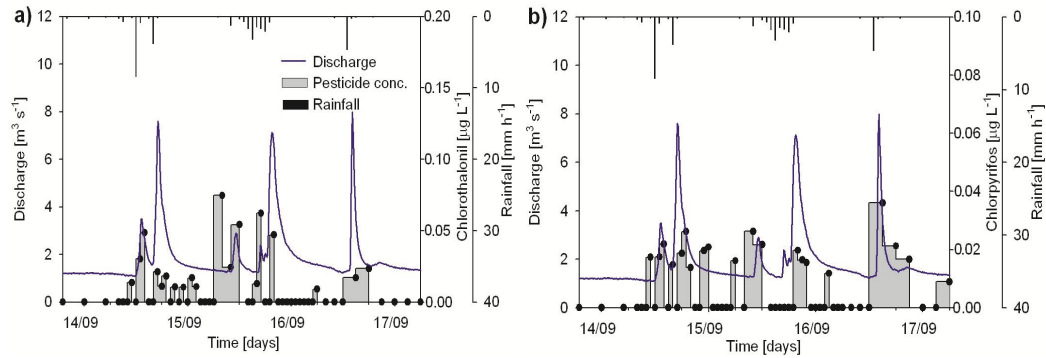
Figure 4.6: Concentrations of two pesticides, discharge, and rainfall data during the September event at headwater (HW) station. Pesticides: (a) chlorothalonil (b) chlorpyrifos. The other pesticides were not detected.

4.3.3. Pesticide loads

Table 6 gives total (mass) and average areal (mass per unit area) loads of dissolved pesticides at both gauge stations. During the May event at the OL station, the total load of most pesticides was higher than at the HW station, in case of atrazine by a factor of ten. Only in case of cypermethrin, the total load at OL was lower than at HW. At OL, the highest average areal loads were those of atrazine and dimethoate. At HW, the loads of dimethoate and chlorpyrifos were the highest. In August, a very high load of chlorpyrifos (20.1 g km^{-2}) was observed at the HW station. The average areal loads of all investigated pesticides were higher than at OL. In September, when pesticide loads were determined only at HW, the loads were generally lower (Table 4.6).

Table 4.6: Pesticide load at headwater (HW) and outlet (OL) stations during three runoff events.

Pesticide	Headwater station						Outlet station			
	May event		August event		September event		May event		August event	
	Total load	Areal load	Total load	Areal load	Total load	Areal load	Total load	Areal load	Total load	Areal load
	(g)	(g km^{-2})	(g)	(g km^{-2})	(g)	(g km^{-2})	(g)	(g km^{-2})	(g)	(g km^{-2})
Atrazine	4.9	0.62	n.d.	n.d.	n.d.	n.d.	50.5	2.7	n.d.	n.d.
Dimethoate	21.4	2.7	24.6	3.1	n.d.	n.d.	37.9	2.0	43.9	2.4
Chlorothalonil	10.2	1.3	n.d.	n.d.	4.4	0.55	14.8	0.80	n.d.	n.d.
Chlorpyrifos	14.5	1.8	159.3	20.1	3.2	0.41	23.0	1.2	84.7	4.5
Endosulfan	5.0	0.63	n.d.	n.d.	n.d.	n.d.	8.0	0.43	n.d.	n.d.
Cypermethrin	11.4	1.4	3.1	0.39	n.d.	n.d.	7.9	0.43	2.5	0.1

[§] Agricultural land use in 2006: headwater catchment 7.9 km^2, entire catchment 18.5 km^2 (GISTDA, 2007)

4.3.4. Time series analysis

To better understand the observed pesticide concentration patterns, we performed a time series analysis with atrazine and cypermethrin, atrazine being a weakly-sorbing, cypermethrin being strongly sorbing pesticide. The analysis was carried out for the May event.

At HW, the highest CCC between rainfall and discharge occurs at about one hour (Fig 4.7a and c). At OL, the time lag is 4 h (Fig. 4.7b and d). At HW, the CCC between discharge and atrazine concentration is highest at zero time lag, implying quick transport of atrazine. At OL, the highest cross-correlation between discharge and atrazine concentration occurs at a time lag of 3 h. In May, no significant correlation between atrazine and discharge was found at time lags > 14 h.

Cypermethrin shows a different pattern. At HW, the maximum CCC between discharge and cypermethrin concentration was found at a time lag of 11 h (Fig. 4.7c). At OL, the cross-correlation between discharge and concentration was even zero at time lags of up to 18 h (Fig. 4.7d). Here, highest CCCs between discharge and cypermethrin concentration were found at time lags of 26 and 33 h.

Figure 8 compares cross-correlations involving chlorpyrifos during the three events. During the May event, at HW several peaks of CCCs between discharge and chlorpyrifos concentration appeared at the early part of the event (Fig. 4.8a). At OL, chlorpyrifos showed a continuous response to discharge, with largest CCC between time lags 0 and 6 h (Fig. 4.8b). During the August event, the rainfall-runoff response at HW occured within one hour. Chlorpyrifos was not observed during the recession limb. The CCC of chlorpyrifos was highest at a 6 h lag time (Fig. 4.8c). At OL, the in-stream pattern of chlorpyrifos during discharge was similar as that observed at HW with the peak of chlorpyrifos at a lag time of 12 h after the discharge peak (Fig. 4.8d). During the September event, at HW the two rainfall-runoff responses peaked at time lag 1 and 5 h (Fig. 4.8e). An additional pronounced CCC between rainfall and runoff was found at a time lag of 23 and 31 h. Discharge and chlorpyrifos are correlated at very small time-lags and at time lags of 17, 20 and 27 h. The latter CCC peaks do not coincide with highest rainfall-runoff cross-correlations (Fig. 4.8e).

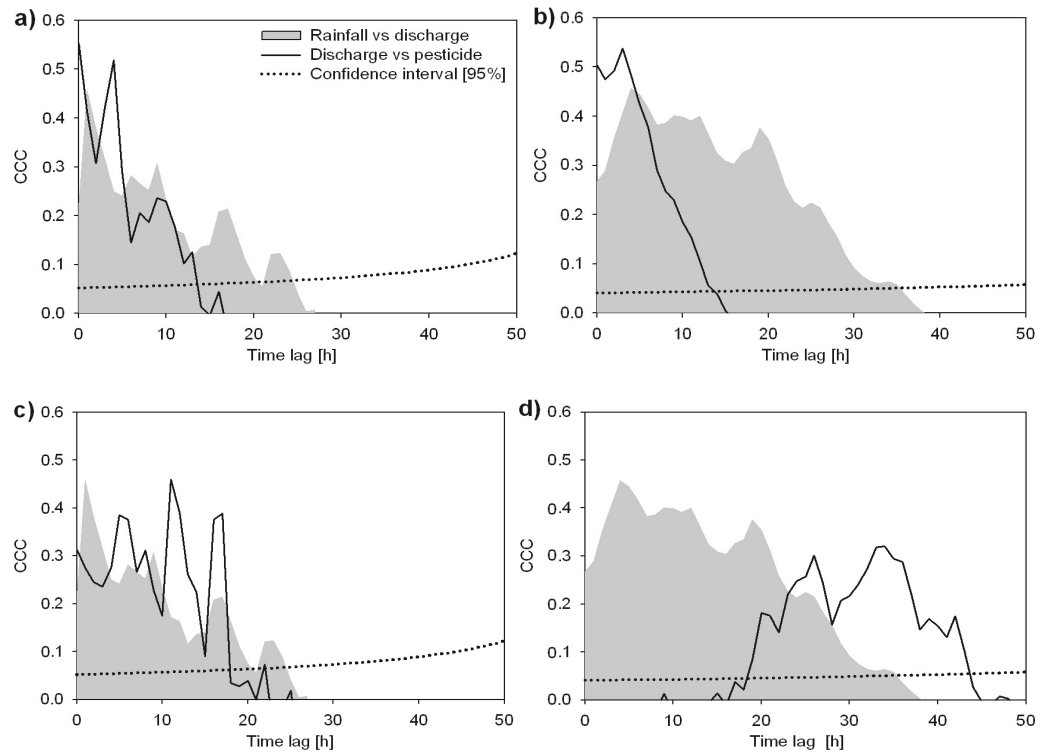Figure 4.7: Cross-correlograms of rainfall, discharge and pesticide concentration at the HW (left panel) and OL (right panel) stations in May: (a, b) atrazine, and (c, d) cypermethrin.
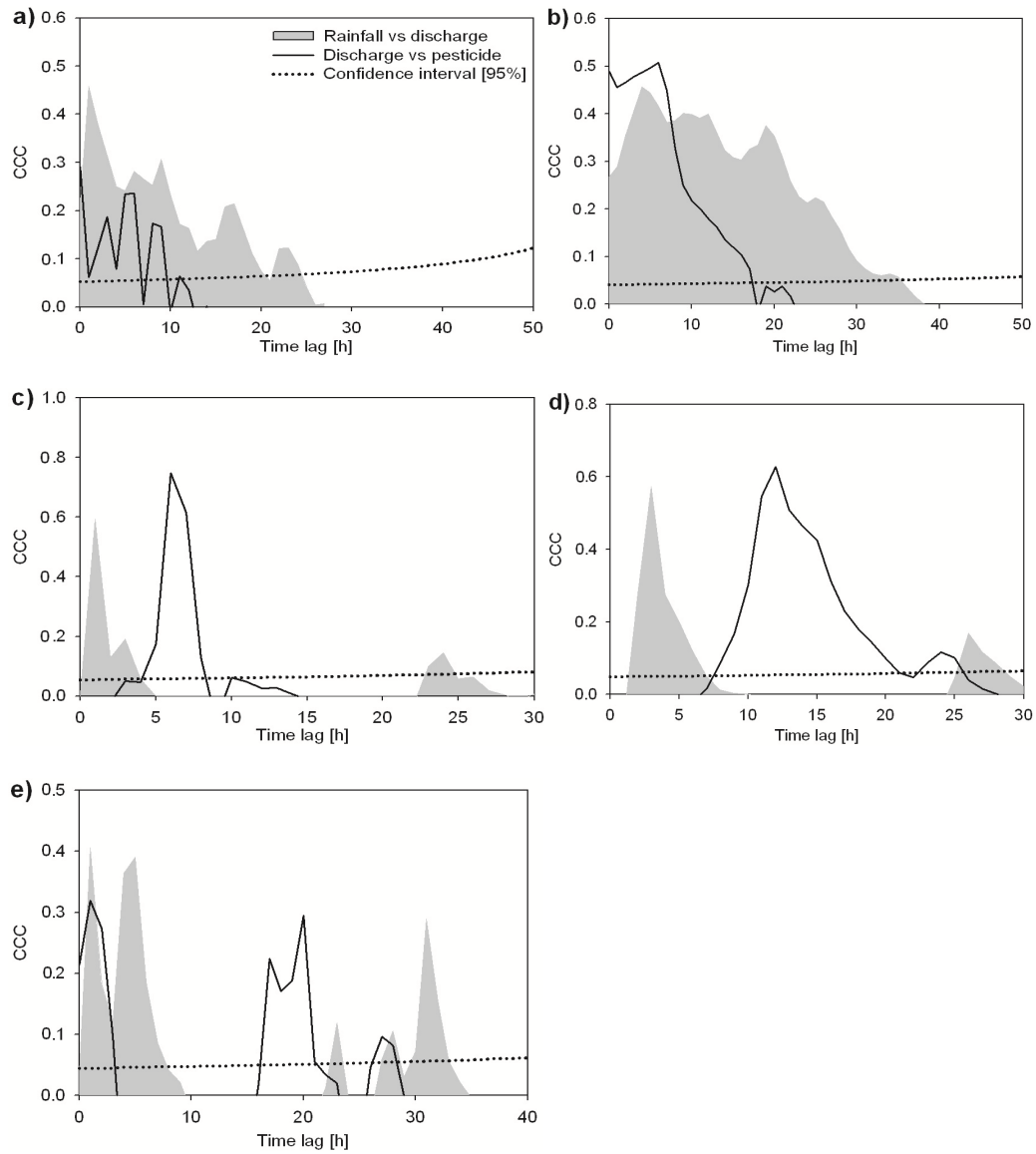
Figure 4.8: Cross-correlograms of rainfall, discharge and pesticide concentration: for HW (left panel) and OL (right panel): (a, b) chlorpyrifos in May, (c, d) chlorpyrifos in August, (e) chlorpyrifos in September.

4.4. Discussion

4.4.1. Pesticide concentration patterns

Transport mechanisms and pathways of pesticides form a central link between agro-ecosystems and their surrounding environmental compartments. We observed three different concentration patterns of pesticides: (a) increase during the rainfall events as discharge increases, (b) sporadic high values during the falling limb of the runoff peak, and (c) low but more or less continuous values on a baseline level.

On the May event, the first pattern cannot be clearly attributed to a specific transport pathway because the processes contributing to discharge are too complex: several rain events caused overlapping hydrographs. Our time series analysis suggests that a fast flow component, such as surface runoff, which, in some areas, may contribute up to 75 % of the total pesticide load (Ng and Clegg, 1997), significantly contributed to the total pesticide load. The highest cross-correlations between discharge and pesticide concentration were observed at short time lags. For example, the highest cross-correlation between atrazine concentration and discharge occurred at time lags between 0 and 3 h at OL; at larger time lags (>14 h) it vanished (Fig. 4.7b). In addition, however, the concentration peaks of more strongly sorbing pesticides such as chlorpyrifos were somewhat delayed to those of less strongly sorbing pesticides such as dimethoate (see Fig. 4.4c and e on 4 May). This chromatographic behaviour points to an interaction with a matrix, probably during transport along a sub-surface pathway (Kahl et al., 2010). Hence, during the May event the pesticide transport was probably controlled by both surface runoff and sub-surface flow.

Our findings agree well with the results of previous studies. Leu et al. (2004) and Duffner (2010) reported that in agricultural catchments atrazine losses were event-driven with concentrations increasing almost simultaneously with increasing discharge and peaking with peak flow. Oliver et al. (2012) also found a strong relationship between peak concentrations of pesticides and peak flow during runoff events, particularly when log K_{oc} < 3. In case of chlorpyrifos (log K_{oc} 3.9), however, they found that the concentration in stream water increased as the hydrograph increased, but it did not decrease as the hydrograph decreased.

The second concentration pattern, the appearance of sporadic post-event pesticide peaks on the falling limb of the runoff curve, was most clearly observed with the more strongly sorbing pesticides such as chlorpyrifos (Fig. 4.4e and f), chlorothalonil (Fig. 4.4g and h), endosulfan (Fig. 4.4i and j), and cypermethrin (Fig. 4.4k and l). This incidence is even clearer

in the August event, where the hydrograph consisted of two clearly separated runoff peaks, simplifying interpretation. Chlorpyrifos did not peak with the runoff peak but appeared in the river water about 6 h later at the HW station and 12 h later at the OL station (Fig. 4.5c and d). Moreover, in the third event in September, the sporadic appearance of chlorothalonil and chlorpyrifos after the peak flows confirmed this type of input pattern (Fig. 4.6a and b). In a study of pesticide transport at the hillslope scale in the Mae Sa watershed Kahl et al. (2008) found a similar concentration pattern. Supported by a modelling study, they attributed the appearance of the pesticide peaks at the falling limbs of the runoff curve to preferential subsurface flow (Kahl et al., 2010). Because in the present study the pesticides were not applied under controlled conditions, we can not fully exclude that the observed sporadic pesticide peaks are the result of point sources or local spills. However, we are convinced that the low concentrations in between the sporadic peaks are not an artefact due to sampling, sample preparation or analysis errors. The sampling volume was always determined with a graduated cylinder. A failure of the sampling unit would have been detected immediately. All water samples were prepared and analysed under exact the same standard conditions. For six of the seven pesticides the analytical method had a high reproducibility (RSD<20 %). Only in case of chlorothalonil, the variability of the method was somewhat higher (RSD=27 %).

The third concentration pattern, steady, but low pesticide concentrations, cannot be explained by the fast transport mechanisms mentioned above. Instead, it points to a continuous leaching of pesticides with the base flow, especially during periods after rainfall. The atrazine concentrations during the recession phase in May at the OL station (Fig. 4.4b) are a good example for this pattern.

Our observations agree well with the results of Leu et al. (2004). These authors also observed sustained elevated atrazine concentrations during the long-lasting tailing of discharge after a heavy rainfall. They assigned this finding to a pesticide pool in the saturated zone, which was filled up by vertical fast components during the rain event and subsequently leached to the river over a longer period.

4.4.2. Hydrological implications

Provided that transport is chromatographical, strongly sorbing pesticides should have longer travel times and appear at lower concentrations compared to weakly sorbing pesticides. This holds true when there is sufficient time for interaction between pesticides and soil. In case of a preferential transport, however, the time available for sorption and degradation is

drastically reduced, which may lead to an almost direct transfer of pesticides to surface waters (Müller et al., 2003).

At the beginning of the rainy season in May, soils were still rather dry. At low water content, the preferential flow paths are not well connected and the potential of pesticide leaching is low. The detection of high K_{oc} substances, i.e. chlorpyrifos (Fig. 4.4e), endosulfan (Fig 4.4i) and cypermethrin (Fig. 4.4g) at the HW station shows that retardation did not have a major impact on the loss rates of the pesticides and their temporal dynamics.

As indicated by the higher RCs in August and September the soils in the catchment were wetter as a consequence of the cumulated high rainfalls in the previous months. Antecedent rainfall has an important role in that it increases soil water content which may trigger preferential flow (Kahl et al., 2007) and the leaching of pesticides (Flury, 1986; Lewan et al., 2009). Pesticides may be dissolved in pre-event water and sorb to walls of macropores. Later during a rainfall event, water may travel within macropores through the soil and leach previously sorbed pesticides to the river. Pesticide peaks will be caused by the drainage of a mixture of old and new water. This process is significantly delayed in comparison to surface runoff because the travel distance in the pores is larger and the travel velocity lower (Duffner, 2010; Kahl et al., 2010).

4.4.3. Comparison of pesticide loads between HW and OL gauge

The pesticide concentration patterns as well as the set of detected pesticides were similar at both stations. The fast increase of discharge during rainfall and the appearance of pesticide peaks shortly thereafter (see e.g., atrazine (Fig. 4.4a and b), dimethoate (Fig. 4.4c and d) and chlorpyrifos (Fig. 4.4c and d)) at the HW station, however, indicate a quicker and more sensitive hydrological response at HW than at OL. The steep slopes of the headwater area foster the rapid transfer of water to the stream network. The longer delay between rainfall, discharge and pesticide peaks at the OL station reflects the travel distance from precipitation and application area.

Other than at the HW station, at the OL station two smooth pesticide curves were obtained for atrazine in May and chlorpyrifos in August. A possible explanation is that pesticide losses at the outlet of the catchment are an integral from spatially distributed pesticide sources over the fields located upstream. The larger the upstream area, the more fields contribute to the pesticide load and the smoother is the integrated concentration curve. Obviously, the smoothness of the signal will also depend on the uniformity of application time and rates.

The average areal pesticides loads can tentatively be used to trace back pesticide use in the watershed. Average areal loads of atrazine and dimethoate were highest at the OL gauge. While at HW dimethoate was also lost at high quantities, the average areal load of atrazine was much lower, suggesting that the major atrazine sources were located downstream of the HW gauge. The average areal losses of chlorpyrifos, dimethoate and cypermethrin in the headwater area were higher than those in the whole watershed. This finding suggests that the three pesticides were mainly applied within the HW area, where around 471 greenhouses were in operation (Schreinemachers et. al., 2009). The cultivation per cropping cycle of bell pepper and chrysanthemum under greenhouses requires intensive use of pesticides. The environmental impacts of pesticide used with these two crops are relatively high compared to the other field crops (Schreinemachers et al., 2009).

4.4.4. Implications for the design of appropriate sampling schemes

During rainfall and several hours after rainfall, maximum concentrations of many pesticides such as chlorpyrifos (9.7 µg L^{-1}), chlorothalonil (0.6 µg L^{-1}), and endosulfan (0.09 µg L^{-1}) exceeded the European limits for pesticides in surface water (chlorpyrifos: 0.03 µg L^{-1}; endosulfan: 0.005 µg L^{-1}) and/or the Canadian water quality guidelines for protection of aquatic life (chlorothalonil: 0.18 µg L^{-1}; chlorpyrifos: 0.0035 µg L^{-1}; endosulfan 0.02 µg L^{-1}). However, they do not exceed the limit of the Thai quality standard of surface water issued by the National Environmental Board (1994) of 50 µg L^{-1} for total organochlorines.

Most of the pesticides showed highly dynamic concentration patterns. Highest concentrations were detected both during initiation of runoff and during the longer recession phase. These extreme events were shortly pulsed and lasted less than one hour. This highly dynamic nature of pesticide input to surface waters should have consequences for monitoring schemes and ecotoxicological tests. In our study we took samples every 10 minutes and mixed six samples to one composite sample, ending up with an hourly resolution. Using a monitoring strategy with a lower temporal resolution would lead to an erroneous assessment of the water quality status. This point was stressed by Holvoet et al. (2007). They stated that the current ecotoxicological testing and risk assessment approaches need to be tuned to the specific dynamics of pesticides in surface waters. While conventional ecotoxicological tests assume a constant dose of a contaminant to an organism, the stress of the aquatic ecosystem induced by pesticides is characterized by short and multiple-pulsed extreme events.

Pesticide monitoring can be used to strengthen confidence in environmental and ecological exposure estimates. Understanding the fate of pesticides in aquatic environments and assessing their potential effects on non-target organisms are important for protecting environmental and human health. During single rainfall events, the transport pattern of pesticides is highly complex. This must be considered in the design of sampling schemes for pesticide monitoring and ecological risk assessment. To ensure accurate monitoring, high-resolution sampling schemes are needed. Using a too low temporal resolution would result in a biased assessment of the water quality status (see also Holvoet et al., 2007). Also Reinert et al. (2002) pointed to the importance of pulsed concentrations of pesticides and time varying exposure for ecotoxicological testing and risk assessment approaches. Moreover, the average exposure may not lead to an adequate estimate of toxic effects. Pesticide properties and input patterns must be taken into account for choosing an adequate sampling period. We observed a high pesticide exposure during the initiation of rainfall and runoff peak but also during the later recession phase.

4.5. Summary and conclusions

Six out of seven pesticides applied by local farmers were detected in the Mae Sa River. Measured concentrations exceeded European Union and Canadian limits for pesticides in surface water but were far below the Thai limits. Pesticide loss was related to sorption strength, but other factors interfered. We identified three different pesticide input patterns. The first pattern – increasing concentrations during the rainfall events as discharge increases – suggests transport with surface runoff. The second pattern – sporadic high concentrations during the falling limb of the runoff peaks – was mostly observed with pesticides of medium to high K_{oc} ($2.5 < \log K_{oc} < 5$) such as chlorpyrifos, chlorothalonil, endosulfan, and cypermetrin. It points to a sporadic sub-surface flow component (e.g., preferential interflow). The third pattern – low but more or less continuous concentrations on a baseline level – is probably related to some long-term storage in the underground.

The highly dynamic nature of pesticide input into surface water has important implications for the design of representative monitoring schemes and ecotoxicological risk assessment. The sampling scheme must be set up in a way to capture the peaks during the rain events and peak runoffs, but also the short and pulsed peaks during the following recession phases. Sampling schemes with a high temporal resolution are therefore advisable.

4.6. Acknowledgements

4.7. References

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5. Publication 3

Monitoring and risk assessment of pesticides in a tropical river of a mountainous watershed in Northern Thailand

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5.0. Abstract

The increasing application of pesticides in the uplands of northern Thailand has increased the transfer of pesticides to surface water. To assess the risk of pesticide use for stream water quality we monitored the concentrations of seven pesticides (atrazine, dichlorvos, chlorpyrifos, dimethoate, chlorolothalonil, (α-, β-) endosulfan, cypermethrin) frequently used in the Mae Sa watershed (77 km^2) in water and sediment samples over a period of one and a half years (2007-2008). All investigatedpesticideswere recorded in the river. Chlorpyrifos was detected most often in water samples (75% at the headwater station), while cypermethrin was most often found in bed (86%) and in all suspended sediment samples.Highest concentrations of the pesticides were detected during the rainy season. About 0.002% to 4.1% by mass of the applied pesticides was lost to surface water. The risk assessment was based on the risk characterization ratio (RCR). The RCRs of dichlorvos in water, (α-, β-) endosulfan, and cypermethrin in water and sediments were higher than unity indicating that they are likely to pose a threat to aquatic ecosystem. Finally, we discuss the role of sampling design on ecotoxicological risk assessment. Our study shows that pesticide contamination of surface waters is an environmental issue in the Mae Sa watershed and that measures need to be undertaken to reduce the loss of pesticides from soil to surface waters.

Keywords: surface water, agricultural watershed, risk assessment, risk characterization ratio.

5.1. Introduction

The mountainous area of northern Thailand is dominated by market-driven crop production. Highland agriculture uses intensive agrochemical inputs to increase farm productivity and to improve incomes and food provision. Due to climatic and environmental factors, soil, ground- and surface waters may be contaminated with pesticides, posing a risk for human health (Kruawal et al., 2005; Stuetz et al., 2001).

Ideally, a pesticide should achieve its intended effect specifically without harming the environment or ecosystem (Snelder et al., 2008). In practice, however, pesticides are not deposited exclusively on the target object and may thus contaminate groundwater, rivers, lakes etc. (Schulz, 2001; Müller et al., 2006; Vryzas et al., 2011 and 2012). Pesticides associated with sediment may be an important source of water contamination after resuspension of particulate matter (Müller et al., 2000; Commission of European Communities, 2003).

Numerous factors such as rainfall, slope, soil type, and physio-chemical properties of the pesticides (water solubility, partitioning coefficients, etc.) affect pesticide loss from soil to surface waters (Flury, 1996; Dabrowski et al., 2002). Mountainous areas under intensive agricultural use are specifically vulnerable (i.e. shallow soils, steep slopes). The Mae Sa watershed in northern Thailand has been used to study the fate of pesticides for a decade. Ciglasch et al. (2005) investigated leaching of several pesticides, among others malathion, chlorpyrifos, endosulfan, in a litchi orchard. Kahl et al. (2008) reported that between 1.6% and 11.4% of applied mass of a fungicide (chlorothalonil) and an insecticide (methomyl), respectively, were lost to the adjacent river within one month after application. At the same study site, Duffner et al. (2012) found that about 0.4% and 0.01% of the applied mass of atrazine and chlorpyrifos, respectively, were detected in the streamwithin one month after application.

At this and other sites in the Mae Sa watershed, Sangchan et al. (2012) detected chlorpyrifos concentrations that exceeded both the European and Canadian water quality guidelines by two order of magnitude after single rainfall events. Tapunya (2000) indicated that pesticide use here could unbalance the ecosystem by reducing the population density of macro-invertebrates and changing the benthic community structure.

To assess the risk of pesticides for aquatic ecosystems, several risk indices have been proposed (Kovach et al., 1992; Levitan, 1997; Finizio et al., 2001). Among them, the ratio of predicted environmental concentration (PEC) to predicted no-effect concentration (PNEC) has been frequently applied(Commission of European Communities, 2003; Palma et al., 2004; Vryzas et al., 2009; 2011), and it is termed the risk characterization ratio (RCR) (European

Chemical Agency, 2008). The calculation method combines environmental exposure and ecotoxicological effects. The method is applied for all toxic chemicals including plant production products. A RCR value higher than unity indicates a likely significant risk to the aquatic environment. PEC values can be derived either from monitoring or from modeling considering application rate, persistence, leaching, sorption etc. Measured data are favored because they are considered more reliable than modeling results (Commission of European Communities, 2003; ECOFRAM, 1999). PNEC values can be calculated from short-term exposure concentrations, e.g. the median lethal concentration (LC_{50}), the median effect concentration (EC_{50}),or long-term exposure concentration, i.e. the no observed effect concentration (NOEC).The methodologies for deriving PNECs for the freshwater and sediment environments are based on the Technical Guidance Document of the European Commission (Commission of European Communities, 2003) and recently, European Chemical Agency (2008).The RCR provides the basis for regulatory decisions and further steps in the risk assessment procedure, such as the classification as a mutagen, toxic or harmful chemical and/or the minimization of chemical input.

The aims of this study are 1) to monitor pesticide residues in a tropical river basin of an intensive agricultural area, 2) to investigate the influence of sampling frequency on the detected compounds and concentrations, and 3) to elucidate the relation between pesticide properties, agricultural practice and the observed concentrations and RCR values.

5.2. Materials and Methods

5.2.1. Study area

The study area has been described in detail elsewhere (Sangchan et al., 2012). In brief, the Mae Sa watershed is located northwest of Chiang Mai in northern Thailand. The total area amounts to 77 km^2 (Fig. 5.1) and is characterized by steep slopes. The average slope is 36%, with large differences from the headwater towards the outlet. The result is higher discharge rates of the headwater stream compared with close to the outlet. Predominant soils are acrisols and cambisols with a highly developed macropore network (Schuler, 2008).The climate is wet-dry tropical. From 2004 to 2010, the mean annual air temperature was 21.0^{o}C, mean annual rainfall 1250 mm. The rainy season starts in late May and ends in mid-October followed by a cooler dry season from late October to February and a hotter dry season from March to mid-May (Thai Meteorological Department, 2011).
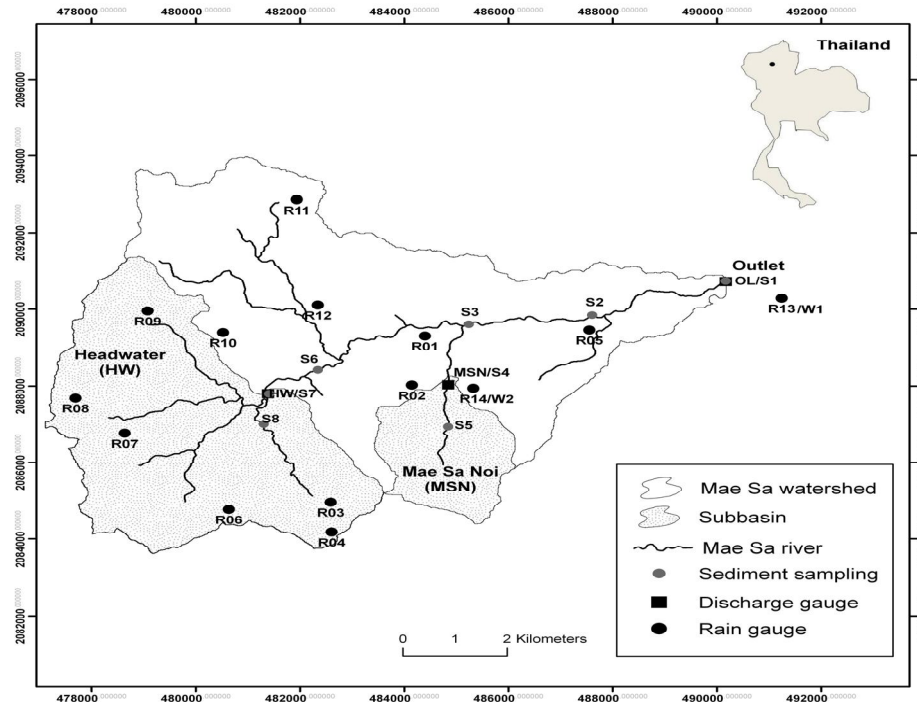
Figure 5.1: Map of Mae Sa watershed showing the positions of rain and discharge gauges as well as the sediment sampling sites. The two sub-catchments "Headwater" (HW) and "Mae Sa Noi" (MSN) are marked in grey.

Land use in the catchment was mapped based on a SPOT 5 image (Fig. 5.2) provided by the Geo-Information and Space Technology Agency (GISTDA, 2007). This image was taken on 6 November 2006. The scene center was N19°1'4" E98°49'24". About 76% of the catchment area is covered by forest, the remainder area is used for agriculture or settlement. In the headwater catchment (28 km^2) and the Mae Sa Noi sub-catchment (7.5 km^2), agriculture and settlements cover 28.5% and 15% of the area, respectively.

In 2006, 268 local farmers corresponding to about 25% of the total households within the watershed were interviewed regarding their land use and pest protection activities (Schreinemachers et al., 2006; Schreinemachers and Sirijinda, 2008) for the recall period from November 2005 to October 2006. At this time, the agricultural area was used to produce field crops (cabbage, bell pepper, chayote etc.), fruits (e.g. litchi), and flowers (gerbera, chrysanthemum etc.). The typical crops are grown in the rainy season. Off-season fruits, such as Litchi, and temperate crops, such as carrot, white radish etc., are cultivated in winter. The headwater catchment is characterized by abundant greenhouses with an intensive production of vegetables and flowers. These two production types are typically associated with high pesticide application rates (Schreinemachers et al., 2009).
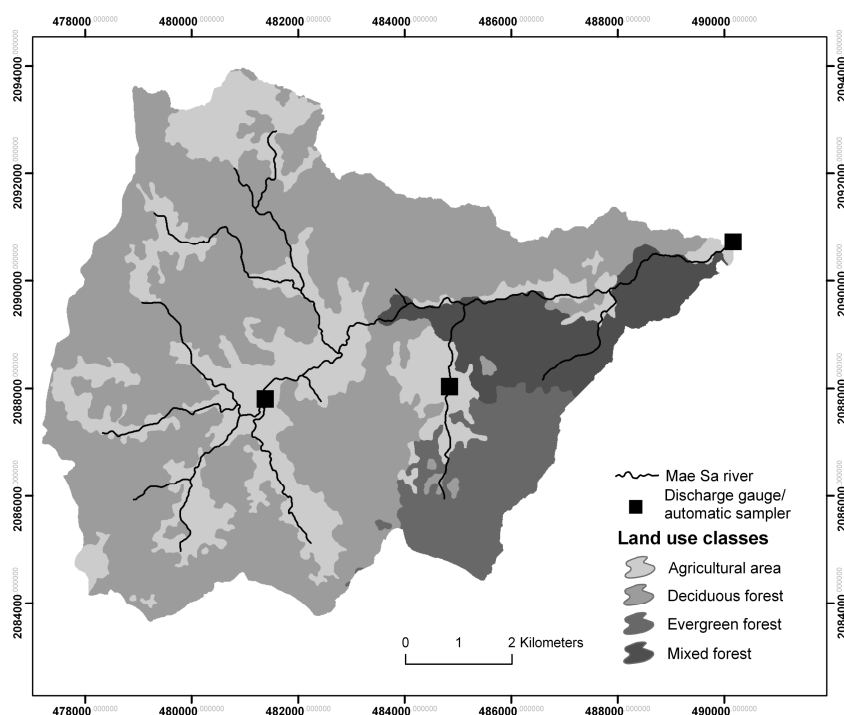
Figure 5.2: Land use map in the Mae Sa watershed in 2006

5.2.2. Selection of investigated pesticides and estimation of their amounts applied

Based on the survey of Schreinemachers and Sirijinda (2008), we selected the four pesticides most frequently applied during that period. Dichlorvos, chlorpyrifos, cypermethrin and chlorothalonil were used intensively on bell pepper, chrysanthemum and white cabbage. We further included (α-, β-) endosulfan and dimethoate, because they had been detected in the Mae Sa River in a previous study of Ciglasch (2006). In addition, we monitored atrazine, which had not been mentioned by the farmers but detected in significant concentrations in a screening pre-test of the stream water. The pesticide usage, toxicity and physico-chemical properties of the seven pesticides considered in our monitoring program are given in Table 5.1.

Table 5.1: Pesticide usage, toxicity and physico-chemical properties of the investigated pesticides (Source: Footprint PPDB, 2011).

Pesticide	Pesticide usage	Toxicity[a]	S [b] $(mg\ L^{-1})$	log K_{ow} [c]	log K_{oc} [d] $(L\ kg^{-1})$
Dichlorvos	Insecticide	I	18000	1.9	1.7
Atrazine	Herbicide	III	1	2.7	2.0
Dimethoate	Insecticide	II	39800	0.7	1.5
Chlorothalonil	Fungicide	II	1.05	2.9	2.9
Chlorpyrifos	Insecticide	II	0.81	4.7	3.9
Endosulfan	Insecticide	I	0.32	4.7	4.1
Cypermethrin	Insecticide	II	0.009	5.3	4.9

[a] US-EPA toxicity category: I = danger (highly toxic), II = warning (moderately toxic), III = caution (slightly toxic) [b] Solubility in water, [c] Octanol-water partition coefficient, [d] Organic-carbon sorption coefficient.

5.2.3. Field measurements and data analysis

5.2.3.1. Rainfall

A network of fourteen tipping-bucket rain gauges (resolution: 0.2 mm per tip) was installed in the watershed (Fig. 5.1). Rainfall was recorded in a 10 min resolution. The positions were arranged to cover the major elevation levels of the watershed.

5.2.3.2. Stream flow and pesticide measurements

Stream flow and pesticide concentrations were measured at three gauging stations within the watershed. The first station was set up in a headwater position (HW, 767 m. a.s.l., 28 km^2), the second in the Mae Sa Noi tributary (MSN, 805 m. a.s.l., 7 km^2), and the third at the outlet of the watershed (OL, 345 m. a.s.l.) (Fig. 5.1). Each gauging station was equipped with an ultrasonic water level sensor and an automatic water sampler (710 Ultrasonic module, 6712 Portable sampler, Teledyne ISCO Inc., USA).Water levels were converted into discharge volumes based on stage-discharge calibration curves measured with an OTT acoustic digital current meter (ADC; OTT Hydromet, Germany). Discharge data were recorded in 10-min intervals. Water samples were taken daily from July 2007 to November 2008. From July to August 2007, sampling was performed time-proportionally because the water level-discharge relationship was not yet available. Thirty milliliters of water were taken every 40 min. Ten 30-mL samples were collected into one sampling bottle (300 mL). Four sampling bottles were combined to one composite sample. Hence, one composite sample represents a time interval of 26.7 h. After calibration of the discharge measurements, water samples were taken volume-

proportionally, that is, the sampling interval was made proportional to measured discharge. In the dry season, samples were taken every 1000, 120 and 2000 m^{3}at the HW, MSN and OL stations, respectively. In the rainy season, the respective volumes were 2000, 200 and 3000 m^3. Because at each station the average discharge level is different and daily composite samples were required, water samples were collected with different volume thresholds among the seasons and sampling sites.

During the rainy season (May to October),176 bed sediment samples were collected bi-weekly by grab sampling (USEPA, 1989) at 6 points in the Mae Sa River (S1-S3, S6-S8) and at 2 points (S4 and S5) in the Mae Sa Noi tributary (Fig. 1). From July to September 2008, total suspended sediment samples were collected to monitor sorbed pesticide concentration. Samples were taken as suggested by Liess et al. (1996). The sampler consisted of a 3-L collection vessel mounted on a concrete box in the bed. The upper inlet tube and the lower outlet tube were located 0.1 m above the stream bed. One suspended sediment sample was taken at each storm event. The sample was removed from the collection vessel one day after each storm event. In total, 7 samples were taken at the HW gauge (4 and 24 July, 4, 12, 20, and 23 August, and 9 September 2008), 6 samples at the MSN station (4 and 21 July, 4, 12, 20 and 23 August 2008) and 10 samples at the OL gauge (4 and 21 July, 19, 20, 21, and 22 August, and 7, 917, and 18 September 2008).

During sample transport to the lab, sediment samples were cooled by ice. In the lab, the samples were stored at 4°C until further treatment. On average, storage time was one week. Then, bed sediment and suspended sediment samples were dried in the dark at 20-25 $^{\circ}$C and stored at -18°C until extraction.

5.2.4. Pesticide extraction and analysis

Pesticide extraction and stream water analysis were performed as described in Sangchan et al. (2012). In brief, water samples were filtered through glass fiber filters (GF/F, 0.7µm; Whatman Inc.,USA). Pesticides were extracted from water by solid phase extraction (SPE) using graphitized non-porous carbon (500 mg, Envi-Carb, Supelco, Germany). The cartridges were preconditioned by sequentially rinsing a dichloromethan:methanol mixture (9:1, v/v) followed by methanol and ascorbic acid (pH 2). Subsequently, one litre of water sample was sucked through the conditioned cartridge under vacuum at a flow rate of about 5 mL min^{-1}. Afterwards the cartridges were dried, packed in bags, and stored in a freezer (-18°C) until further treatment in Germany.

The SPE cartridges were rinsed and discarded with methanol to remove residue water. Subsequently, they were eluted with acetone, dichloromethane:methanol mixture (9:1, v/v), and tert-butyl methyl ether (TBME). Two drops of toluene were added as a keeper before evaporation almost to dryness. The residues were re-dissolved in 1 mL of a mixture of cyclohexane and toluene (9:1, v/v). These solutions were used for analysis.

The method for pesticide extraction from the sediment samples was adapted from the QuEChERS method (Anastassiades et al., 2003). 7.5 mL of deionized water and 15 mL of acetonitrile were added to 10 g of sediment sample (dry weight), followed by a salting-out step using 6 g magnesium sulphate anhydrous, 1.5 g sodium chloride, 1.5 g sodium citrate tribasic dehydrate and 0.74 g sodium citrate dibasic sesquihydrate. The sample tube was shaken immediately for 2 min and then it was centrifuged at 1308 g (3000 rpm, rotational radius 0.13 m) for 6 min. Eleven milliliters of organic layer was transferred into a small tube and cleaned up by dispersive SPE with a mixture of 27.5 mg bondesil-primary secondary amine (PSA, Varian, Germany) and 1.65 g magnesium sulphate anhydrous. After centrifugation, the eluent was transferred to a conical flask, and 100 µL of 0.05%w/w of formic acid in acetonitrile were quickly added as analytical protectant for GC analysis. Two drops of toluene were added as a keeper before evaporation to almost dryness. The residues were re-dissolved in 1 mL of a mixture of cyclohexane and toluene (9:1, v/v). This solution was used for analysis.

5.2.5. Analytical procedure

In brief, eluents were analyzed by capillary gas chromatography (capillary-GC) and partly by gas chromatography mass spectrometry (GC-MS). For capillary-GC two different gas chromatographs were applied:(a) a Hewlett Packard HP 6890 equipped with an organophosphate pesticide capillary column, Rtx®-OPPesticides (length 30 m, I.D. 0.25 mm, film thickness 0.25 µm; Restek, USA), and a nitrogen-phosphorus detector (NPD, with Blos-bead; Agilent Technologies, USA), and (b) an Agilent Technologies 7890 GC equipped with an HP-5 capillary column (length 30 m, I.D. 0.32 mm, film thickness 0.25 µm) and micro-electron capture detector (µ-ECD). The inlets of both GCs were programmable temperature vaporization (PTV) injectors (Model UNIS; Joint Analytical Systems GmbH, Germany) operated in the pulsed splitless mode. The analyses were carried out with 1 µL injection. The temperature programs of the GC ovens are described in Sangchan et al. (2012). Extraordinarily high peak concentrations were confirmed by GC-MS (GCQ; Finnigan MAT, USA). A capillary column (FactorFour VF-5MS, length 30 m, I.D. 0.25 mm, film thickness

0.25 µm; Varian, USA) was installed into the mass spectrometer (MS). The injection was operated in splitless mode. Electron impact ionization (EI) was performed at 70 eV. Fragments within m/z (mass-to-charge ratio) range from 75 to 430 atom mass unit were collected and analyzed. Limits of detection (LOD), recoveries and relative standard deviations (RSD) of the pesticide analysis are given in Table 5.2. It should be noted that with the method of analysis described in this study, the determination of α and β endosulfan can be recorded separately, but this benefit could not be tested with cypermethrin in time. Endosulfan and cypermethrin were reported as sums of concentrations of the isomers.

Table 5.2: Limit of detection (LOD) and recoveries of pesticides in water and sediment samples.

Pesticide	LOD (ng L^{-1})	% Recovery (RSD[§])		
		Water (n=3)	Bed sediment (n=3)	Suspended sediment (n=3)
Dichlorvos[a]	0.1	60 (8)	54 (9)	89 (2)
Dimethoate[a]	0.5	117 (16)	94 (9)	116 (7)
Atrazine[a]	2	113 (7)	125 (0.6)	194 (7)
Chlorothalonil[b]	1	58 (27)	94 (4)	88 (12)
Chlorpyrifos[b]	0.3	106 (5)	117 (3)	88 (5)
α-endosulfan[b]	0.1	91 (9)	81 (3)	107 (15)
β-endosulfan[b]	0.1	101 (7)	96 (4)	114 (3)
Cypermethrin[b]	2	69 (4)	99 (3)	90 (8)

[§]RSD = relative standard deviation, [a] analyzed by GC-NPD, [b] analyzed by GC-µECD.

5.2.6. Calculation of pesticide loads

Based on the interview data (Schreinemachers and Sirijinda, 2008), the annual application rate of each active ingredient during the investigated period was estimated. The amount of pesticide use per crop, time of application and cropping were asked. The daily load of a pesticide was calculated by multiplying the daily stream flow volume ($Q(t)$) with the daily stream pesticide concentration ($C(t)$) measured at the station. Concentrations below the detection limit (see Table 5.2) were set to zero. The monthly pesticide load was calculated by multiplying the average daily load with length of the month. The annual pesticide load was calculated as the sum of monthly pesticide loads. The total pesticide losses for the entire catchment in (July-December) 2007 and 2008 were calculated. To compare pesticide losses between the three stations, the areal pesticide loss (g km^{-2}) was computed. For that, the annual

pesticide load recorded at a station was divided by the agriculturally used area located upstream.

5.2.7. Risk assessment

The aquatic risk associated with the pesticides was assessed using the approach proposed by European Chemical Agency (2008). It builds upon the risk characterization ratio (RCR): the ratio between predicted environmental concentration (PEC) and predicted no effect concentration (PNEC). For PEC, the mean and the maximum of the measured pesticide concentrations were used as measures for chronic and acute impacts of the respective pesticide on the aquatic ecosystem. The PNEC value of a pesticide was derived from its toxicity data, namely the LC_{50}, EC_{50} and NOEC values referring to three highly sensitive species (*Scenedesmussubspicatus* (algae), *Daphnia magna* (aquatic invertebrates), or *Oncorhynchusmykiss* (fish)). Each species represents one trophic level (Table 5.3). The toxicity data were taken from the Pesticide Properties Database (PPDB), which has been developed by the Agriculture and Environment Research Unit at the University of Hertfordshire funded by the European Union FOOTPRINT project (see http://sitem.herts.ac.uk/aeru/footprint), among others. If available, NOECs, a measure for chronic toxicity, are used as the risk indicator rather than LC_{50} or EC_{50} values. If chronic toxicity data were not available, acute toxicity data were used.

To take into account (a) the uncertainty in extrapolation from laboratory toxicity tests for a limited number of species to the real environment, and (b) the quality of the database used, toxicity data are divided by an assessment factor (AF) (European Chemical Agency, 2008). The AF depends on the number and the type of available toxicity data. A factor 10 is used if NOECs are available for all three trophic levels. This criterion was fulfilled with atrazine, dimethoate, chlorothalonil, chlorpyrifos and cypermethrin. The PNEC value is then calculated by taking the lowest available NOEC and dividing it by the AF. In the case of dichlorvos, only two NOECs were available. In general, in such a situation an AF of 50 is used. Because the most sensitive species (*Daphina magna*) has an EC_{50} value lower than the lowest NOEC, the PNEC was calculated by using an AF of 100 to the EC_{50} (European Chemical Agency, 2008, p. 19). For (α-, β-) endosulfan, only a single long-term NOEC for fish (*Oncorhynchusmykiss*) is available; an AF of 100 was therefore applied (European Chemical Agency, 2008, p. 19).

Because the toxicity data on benthic organisms are limited, the $PNEC_{sed}$ for exposure via water from sediment was calculated based on the assumption of linear equilibrium sorption. This calculation is used only in screenings (European Chemical Agency, 2008).

$$PNEC_{sed} = \frac{K_{susp-water}}{RHO_{susp}} \cdot PNEC_{water} \cdot 1000$$

Here, $PNEC_{sed}$ is the predicted no effect concentration in sediment (mg kg^{-1}), $K_{susp-water}$ denotes the partition coefficient between the water and the suspended matter phase (m^3 m^{-3}), RHO_{susp} is the bulk density of wet suspended matter (kg m^{-3}), and $PNEC_{water}$ stands for the predicted no effect concentration in water (mg L^{-1}). For further details on the calculation of RHO_{susp} and $K_{susp-water}$ we refer to European Chemical Agency (2008). The method only considers uptake via the water phase. Uptake by benthic organisms, however, may also occur via other exposure pathways such as ingestion of sediment and direct contact with sediment. For this reason, it is recommended to increase the PEC_{sed}/$PNEC_{sed}$ ratio (RCR) by a factor of 10 for compound where log K_{ow}>5 (i.e. cypermethrin) (European Chemical Agency, 2008, p 40).

Table 5.3: Toxicity data for the selected pesticides in water.

Pesticide	Algae*		Zooplankton*		Fish*		Critical concentration ($\mu g\ L^{-1}$)	AF	$PNEC_{water}$ ($\mu g\ L^{-1}$)
	EC_{50} ($\mu g\ L^{-1}$)	NOEC ($\mu g\ L^{-1}$)	EC_{50} ($\mu g\ L^{-1}$)	NOEC ($\mu g\ L^{-1}$)	LC_{50} ($\mu g\ L^{-1}$)	NOEC ($\mu g\ L^{-1}$)			
Dichlorvos	52800	4730	0.19	-	550	110	EC_{50}:0.19	100	0.0019
Atrazine	59	100	85000	250	4500	2000	NOEC:100	10	10
Dimethoate	90400	3200	2000	40	30200	400	NOEC:40	10	4
Chlorothalonil	210	33	84	9	38	3	NOEC:3	10	0.3
Chlorpyrifos	480	43	0.1	4.6	1.3	0.14	NOEC:0.14	10	0.014
Endosulfan (α, β)	2150	-	440	-	2	0.0001	NOEC:0.0001	100	0.000001
Cypermethrin	>100	1300	0.3	0.04	2.8	0.03	NOEC:0.04	10	0.003

LC_{50}: median lethal concentration, EC_{50}: median effect concentration; NOEC: no observed effect concentration; PNEC: predicted no effect concentration. * The toxicity data of the three trophic organism groups obtained from Footprint PPDB, 2011.

5.3. Results

5.3.1. Rainfall and stream discharge

Table 5.4 summarizes the average monthly rainfall from the fourteen rain gauges and monthly discharges measured at the three gauging stations (HW, MSN, OL). In 2007, rainfall was about 10% higher than in 2008. Fourteen moderate rainfall events (20-35 mm d^{-1}) and two high-intensity rainfall events (>35 mm d^{-1}) were recorded in 2007. In 2008, there were only eleven moderate rainfall events and no high intensity rainfall. In both years, May and September were the two months with highest rainfall. Lowest rainfall was measured in December and January. Lowest monthly discharge at OL occurred in March 2008, that is, about three months after lowest rainfall. During the rainy season the discharge was more than twice as high as during the dry season. As expected, the total discharge volume was highest at OL. Relative to the respective catchment area, however, discharge was highest at HW.

5.3.2. Pesticide concentrations

5.3.2.1. Stream water samples

During the investigation period, in total 370 composite samples were collected and analyzed for the seven pesticides which consist of one triazine (atrazine), two organochlorines ((α-, β-) endosulfan, chlorothalonil), three organophosphates (dichlorvos, chlorpyrifos, dimethoate) and one pyrethroid (cypermethrin). Table 5.5 summarizes the statistics of the measured concentrations as well as the frequency of detection (FD) at the three gauging stations. All seven pesticides were detected at all discharge gauges, at least occasionally. Most endosulfan was detected in the α form. Chlorpyrifos was the most frequently detected pesticide at HW and OL stations, whereas atrazine (66%) was the most frequently one detected at MSN. Except for (α-, β-) endosulfan, maximum concentrations of pesticides ranged between 0.1 and 1 μg L^{-1}. The maximum (α-, β-) endosulfan concentration was 0.06 μg L^{-1}.

Fig. 5.3 shows the seasonal variation of pesticide concentrations in the Mae Sa River. The figure combines the pesticide data from all three gauging stations from July 2007 to November 2008. High concentrations were recorded mainly during the rainy season (May to October).

To assess the current contamination level of the Mae Sa River, we compared the measured concentrations with the respective environmental quality standards of the European Union

(European Council, 2008) and Canada (Canadian Council of Ministers of the Environment, 2004). Note that both guidelines do not set a limit value for dichlorvos and cypermethrin. The peak concentrations of atrazine, chlorothalonil, chlorpyrifos and (α-, β-) endosulfan exceeded one of these two limits or both, particularly often in the case of chlorpyrifos. About 8% of the measured chlorpyrifos concentrations exceeded the EU limit (0.03 μgL^{-1}) and about 48% the Canadian limit (0.0035 μgL^{-1}). The maximum detected concentration of chlorpyrifos was 0.2 μgL^{-1} at the HW station. Although (α-, β-) endosulfan concentrations were in general low, the EU limit (0.005 μgL^{-1}) was exceeded in about 4% of the samples with a peak value 0.06 μgL^{-1} at the OL station. In only two samples (α-, β-) endosulfan concentrations were higher than the Canadian limit (0.02 μgL^{-1}). Only in one case the atrazine concentration (0.8 μgL^{-1}) exceeded the respective EU limit (0.6 μgL^{-1}).Two percent of the samples exceeded the Canadian limit (0.18 μgL^{-1}) for chlorothalonil. None of detected dimethoate concentrations were above the Canadian limit (0.62 μgL^{-1}).
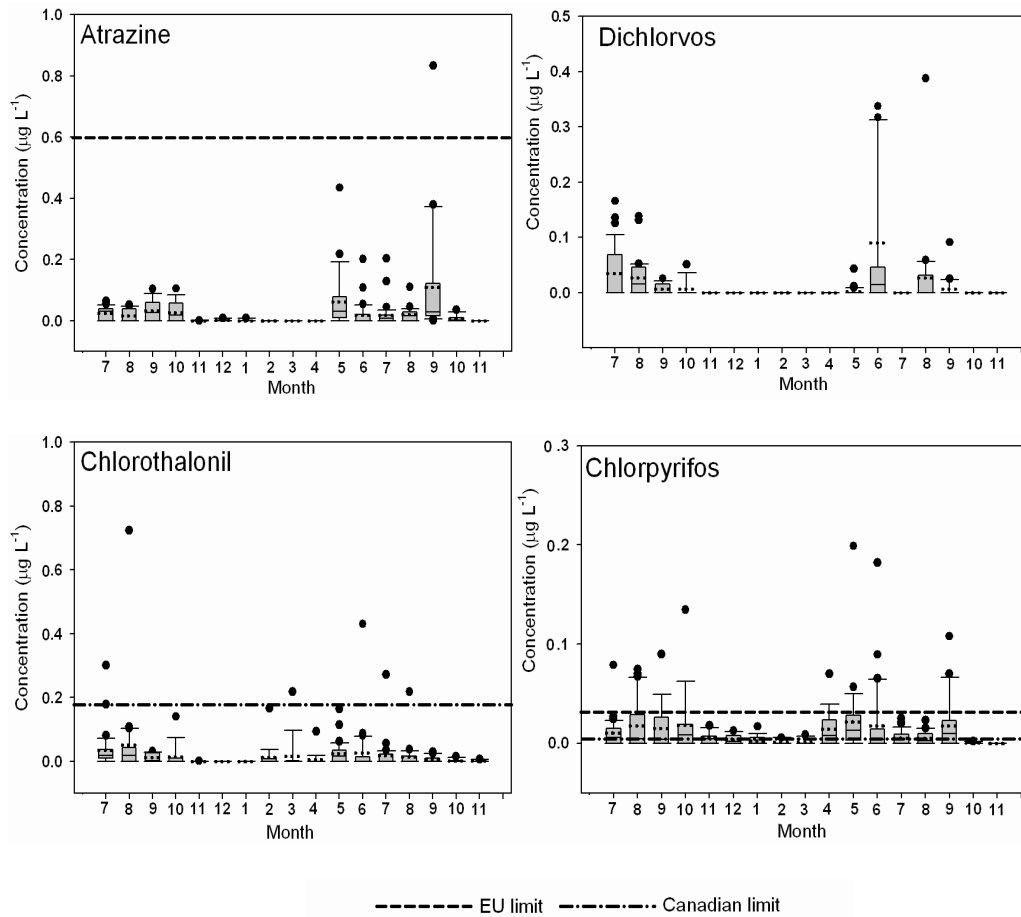
Figure 5.3: Box-plots of monthly pesticide concentrations from July 2007 to November 2008 showing data of all three discharge gauge. Means are indicated by the dashed. Boxes indicate the 25th-75th percentiles, whiskers show the 10th and 90th percentiles and outliers are indicated by dots. Note that a limit value for dichlorvos is defined neither by the EU nor by the Canadian quality standard guideline in surface water.

Table 5.4: Monthly rainfall and discharge at the three gauging stations in 2007 and 2008.

Month	2007 Rainfall	Discharge HW		MSN		OL		2008 Rainfall	Discharge HW		MSN		OL	
	(mm)	(m^3x10^6)	(mm)	(m^3x10^5)	(mm)	(m^3x10^6)	(mm)	(mm)	(m^3x10^6)	(mm)	(m^3x10^5)	(mm)	(m^3x10^6)	(mm)
Jan	-	-	-	-	-	-	-	11	1.77	63	1.44	21	1.67	22
Feb	-	-	-	-	-	-	-	16	1.49	53	0.99	14	1.13	15
Mar	-	-	-	-	-	-	-	27	1.57	56	0.86	12	0.92	12
Apr	60	-	-	-	-	-	-	95	2.00	72	0.99	14	1.22	16
May	298	-	-	-	-	-	-	201	2.32	83	1.84	26	2.56	33
Jun	142	-	-	-	-	-	-	153	1.50	53	2.05	29	2.96	38
Jul	132	2.36	84	2.85	41	2.18	28	86	1.44	51	1.39	20	1.63	21
Aug	191	2.60	93	4.14	59	3.30	43	149	2.21	79	3.22	46	2.89	38
Sep	271	3.71	133	7.67	110	7.54	98	224	3.05	109	4.99	71	4.17	54
Oct	130	3.29	117	4.06	58	4.47	58	210	2.78	99	4.76	68	3.76	49
Nov	73	2.68	96	3.14	45	3.16	41	58	2.31	82	4.42	63	3.84	50
Dec	3	2.11	75	1.97	28	2.20	29	5	1.60	57	2.58	37	2.57	33
Total	**1299**	**16.75**	**598**	**23.83**	**341**	**22.86**	**297**	**1236**	**24.04**	**857**	**29.53**	**422**	**29.32**	**381**

Table 5.5: Mean and maximum concentrations of pesticides in surface water at each gauging station in the Mae Sa watershed from 2007 to 2008.

Pesticide	HW (N=130)				MSN (N=119)				OL (N=121)			
	Mean ($\mu g\ L^{-1}$)	Max. ($\mu g\ L^{-1}$)	RSD (%)	FD (%)	Mean ($\mu g\ L^{-1}$)	Max. ($\mu g\ L^{-1)}$)	RSD (%)	FD (%)	Mean ($\mu g\ L^{-1}$)	Max. ($\mu g\ L^{-1)}$)	RSD (%)	FD (%)
Dichlorvos	0.008	0.3	25	19	0.04	1.1	31	37	0.006	0.3	16	13
Atrazine	0.01	0.1	60	37	0.05	0.8	45	66	0.01	0.2	50	36
Dimethoate	0.01	0.2	43	29	0.02	0.4	31	18	0.009	0.2	37	26
Chlorothalonil	0.03	0.7	39	58	0.01	0.2	44	33	0.006	0.2	27	26
Chlorpyrifos	0.02	0.2	59	75	0.004	0.1	30	18	0.008	0.06	76	60
Endosulfan (α,β)	0.001	0.02	40	32	0.0003	0.01	21	6	0.002	0.06	31	49
Cypermethrin	0.01	0.5	23	15	0.004	0.1	23	6	0.008	0.1	40	18

Max.: maximum; RSD: Relative standard deviation; FD: frequency of detection

5.3.2.2. Sediment samples

In total, 176 samples of bed sediment and 23 samples of suspended sediment were collected. The mean organic matter content of the bed sediment was 8.8 ± 7 gkg^{-1} of dry weight. Higher organic matter contents were found in suspended sediment (mean 27.0 ± 13.9 gkg^{-1} of dry weight). The concentrations in bed sediment and suspended sediment samples are given in Table 5.6. In all detected cases, suspended sediment contained more pesticides than bed sediment. In both years, above average concentrations of pesticides in bed sediments were detected between June and August. Cypermethrin and chlorpyrifos were significantly detected pesticides in the bed and suspended sediments. The three pesticides with the lowest K_{oc} values (dichlorvos, atrazine, dimethoate) were not detected in the sediment samples. The cypermethrin concentrations in bed sediment ranged from 0.2 µg kg^{-1} (detection limit) to 52.9 µg kg^{-1}. The concentrations in the upper range were found in the Mae Sa Noi tributary (S3, S4, S5, see Fig. 5.1) and in the Mae Sa River close to the HW station (S6 and S7). Slightly higher concentrations of chlorpyrifos were found in the Mae Sa Noi tributary (S4) and at sampling point S3, where the Mae Sa Noi tributary discharges into the main river.

The headwater was a hot spot for pesticides in suspended sediments: we found the highest contents of cypermethrin, chlorothalonil, chlorpyrifos and (α-, β-) endosulfan at HW. Neither atrazine nor dimethoate was detected in the sediment samples.

Table 5.6: Measured pesticide concentrations in bed and suspended sediment of the Mae Sa River.

Pesticide	Bed sediment (N=176)				Suspended sediment (N=23)			
	Mean (μg kg^{-1})	Max. (μg kg^{-1})	RSD (%)	FD (%)	Mean (μg kg^{-1})	Max. (μg kg^{-1})	RSD (%)	FD (%)
Chlorothalonil	1.5	27.7	293	24	10.3	68.0	147	71
Chlorpyrifos	2.0	18.6	105	78	11.2	37.1	72	100
Endosulfan (α, β)	0.4	7.5	250	48	0.6	4.2	171	47
Cypermethrin	10.5	52.9	100	86	82.8	239.7	76	100

Max.: maximum; RSD: Relative standard deviation; FD: frequency of detection

5.3.3. Pesticide loss

We estimated the fractional loss of pesticides from the catchments by relating the detected loads to the estimated applications rates, assuming that agriculture activities, i.e. cropping and pesticide use, were similar in 2007 and 2008 (Table 5.7). In 2007, pesticide loss per unit area ranged from 0.002% (chlorothalonil) to 1.0% (dimethoate), and in 2008 from 0.003% (chlorothalonil) to 4.1% (dimethoate). Although atrazine had the high loss at all stations (atrazine $0.01\text{-}0.1 \text{kg km}^{-2}$), the loss of atrazine could not be computed because the application rate of this herbicide had not been queried in the survey.

To compare the change of pesticide loss between the rainy season (May to October) and the dry season (November to April), we used the data from November 2007 to November 2008. During the rainy season the pesticide loss monitored at OL was around 7 times higher than during the dry season (dry season: 8.7 g km^{-2}; rainy season: 60.5 g km^{-2}).

The spectrum of pesticides in river water differed considerably between the gauging stations (Table 5.7). While at HW chlorothalonil and chlorpyrifos exhibited the highest losses, at MSN atrazine and dichlorvos losses were highest. The highest total loss was observed at the HW station. In 2007, for example, at HW the total pesticide loss amounted to 0.3 kg km^{-2} of arable land. At the OL gauge this value reached only 0.04kg km^{-2} in that year. The inter-annual variability of pesticide losses was substantial. At all stations, (α-, β-) endosulfan was found in the lowest quantities.

Table 5.7: Measured pesticide loads at the three gauges in 2007-2008. Measured loads at OL are given as percentages of the annual application rate as estimated by Schreinemachers and Sirijinda (2008).

Pesticide	Application rate		Pesticide load							Pesticides load at OL as percentage of applied mass	
			HW		MSN		OL				
	$kg\ km^{-2}$		$kg\ km^{-2}$		$kg\ km^{-2}$		$kg\ km^{-2}$				
	(Jul-Dec)									(Jul-Dec)	
	2007	2008	2007	2008	2007	2008	2007	2008		2007	2008
Dichlorvos	14.2	36.0	0.01	0.02	0.07	0.07	0.002	0.01		0.01	0.04
Atrazine	n.a.	n.a.	0.04	0.03	0.08	0.1	0.02	0.02		n.a.	n.a.
Dimethoate	0.2	0.4	0.007	0.04	n.d.	0.06	0.005	0.02		2.6	4.8
Chlorothalonil	155.8	259.9	0.09	0.06	0.03	0.02	0.006	0.01		0.004	0.004
Chlorpyrifos	25.3	60.1	0.05	0.03	0.0002	0.01	0.01	0.009		0.05	0.02
Endosulfan (α, β)	0.3	0.3	0.0005	0.003	n.d.	0.0009	0.001	0.003		0.3	1.0
Cypermethrin	112.4	185.2	0.02	0.03	0.004	0.006	0.008	0.01		0.007	0.005
Total	**308.2**	**541.8**	**0.2**	**0.2**	**0.2**	**0.3**	**0.05**	**0.08**		**3.03**	**5.85**

n.a. = not available, n.d. = not detected

5.3.4. Aquatic risk assessment

Table 5.8 shows the RCR of pesticide surface water concentrations. The RCR values of mean and maximum concentrations of dichlorvos, (α-, β-) endosulfan, and cypermethrin are larger than unity at all three monitoring stations. This indicates that these three pesticides act as chronic stressors for aquatic life in the Mae Sa catchment. Based on their maximum concentrations, chlorpyrifos also posed a risk to the environment in the catchment. Chlorothalonil had the RCR above unity only for its maximum concentrations at HW. The RCR values of atrazine and dimethoate were one to three orders of magnitude lower than unity, indicating that these two pesticides are currently not of ecotoxicological concern in the Mae Sa catchment.

Due to the lack of the respective toxicity data, the risk assessment for the bed sediment was based on a simplified approach using the sorption isotherm. As explained in the Material and Methods section, the approach is only suited for screening purposes (Table9). The RCRs of both mean and maximum concentrations of chlorpyrifos, (α-, β-) endosulfan, cypermethrinand chlorothalonil exceeded the threshold value threshold unity value, in case of (α-, β-) endosulfan by several orders of magnitude. Atrazine, dichlorvos and dimethoate contents were below the detection limit.

Table 5.8: Ecotoxicological risk assessment of pesticides detected in the Mae Sa River. Risk assessment was based on the risk characterization ratio (RRC) . For details see section 5.4.2.

Pesticide	RCR_{water}					
	HW		**MSN**		**OL**	
	Mean	**Max.**	**Mean**	**Max.**	**Mean**	**Max.**
Dichlorvos	4.0	167	18.8	600	3.2	178
Atrazine	0.001	0.01	0.005	0.08	0.001	0.02
Dimethoate	0.004	0.05	0.005	0.09	0.002	0.05
Chlorothalonil	0.1	2.4	0.04	0.7	0.02	0.7
Chlorpyrifos	1.3	14.2	0.3	7.7	0.6	4.4
Endosulfan (α, β)	921	16003	298	11268	1880	57687
Cypermethrin	4.21	158	9.1	209	2.7	50.8
Total	**931**	**16344**	**326**	**12086**	**1886**	**57920**

Table 5.9: Ecotoxicological risk assessment of pesticides detected in bed sediment of Mae Sa River.

Pesticide	$PNEC_{sed}$[a] $(mg\ kg^{-1})$	RCR_{sed}	
		Mean	**Max.**
Chlorothalonil	0.011	0.1	2.4
Chlorpyrifos	0.005	0.4	3.7
Endosulfan (α, β)	0.000001	773	14976
Cypermethrin	0.015	7.1	35.5

[a] Calculated with the equilibrium partitioning method (European Chemical Agency, 2008).

5.4. Discussion

5.4.1. Seasonal variation and spatial distribution of pesticides

Ciglasch et al. (2006) analyzed grab samples taken in 2002 at three different positions in the Mae Sa watershed for 24 pesticides. They did not measure discharge and were therefore unable to determine the respective loads. Chlorothalonil (0.02-0.41 µg L^{-1}) and chlorpyrifos (0.05-0.16 µg L^{-1}) concentrations were in the same range as in our study (chlorothalonil: 0.0002-0.7 µg L^{-1}, chlorpyrifos: 0.0007-0.2 µg L^{-1}). (α-, β-) endosulfan concentrations in water (0.09 to 0.43 µg L^{-1}) and sediments, however, were much higher in 2007-2008 (0.0009-0.06 µg L^{-1}), and so was its frequency of detection, suggesting that its use has been reduced in the recent years.

Although atrazine was not listed by farmers in the Schreinemachers and Sirijinda (2008) survey, it was detected over water quality guidelines (0.6 µgL^{-1} by EU limit). On average, values were in the range of concentrations (0.058-0.086 µgL^{-1}) reported from the Chao Praya River, Central Thailand (Kruawal et al., 2005). In that study, samples had been taken in July 2003 at the entry point into a raw water canal for drinking water and at the outlet into the Gulf of Thailand.

During the rainy season (May to October) the detected concentrations of the pesticides in surface water were higher than the dry season (November to April).This could be explained by the outbreak of pests and diseases due to the high humidity. The application of insecticides (e.g. chlorpyrifos and cypermethrin) and fungicides (e.g. chlorothalonil) is typically increased in this period (Schreinemachers et al., 2009). In addition, the intensive rainfall causes surface runoff and subsurface flow and increases the transport of pesticides (Kahl et al., 2008, Dam and Van den Brink, 2010). According to Schreinemachers and Sirijinda (2008), cypermethrin and chlorothalonil are also intensively applied in Mae Sa, but in the cooler dry season (late

October to February). Because of low and less intensive rainfall during this period, concentrations and loads of cypermethrin and chlorothalonil were very low.

The wide spectrum of pesticide residues detected in the Mae Sa River reflects the very diverse agricultural production in Mae Sa. Farmers grow flowers, vegetables, fruits and crops. At MSN, 58% of the area is used for litchi and 30% for field crops (Schreinemachers and Sirijinda, 2008). Here, the losses of dichlorvos (1.1 μgL^{-1}) and atrazine (0.8 μgL^{-1}) were highest. This finding is consistent with that of a previous study on short-term pesticide dynamics in which the major source of atrazine was suspected downstream of HW (Sangchan et al., 2012). In the headwater, where the production of fruits (e.g. litchi), vegetables (e.g. bell pepper, cabbage) and flowers (e.g. chrysanthemum, roses) prevails, the losses of chlorothalonil and chlorpyrifos were relatively high.

The insecticide cypermethrin is extensively used on many crops (Schreinemachers et al., 2009). It has low water solubility and strongly sorbs to soil; it is therefore unsurprising that its loss was very low. The concentrations of cypermethrin in sediments were significantly higher than the detected concentrations in water, particularly at the HW station and at several sampling points along the Mae Sa River and the Mae Sa Noi tributary (sampling sites 3-7).

The fractional losses of pesticides in this study agree with results from other studies. Müller et al. (2003), for example, reported yearly pesticide losses from an agricultural catchment (Zwester Ohm, 49.7 km^2) located in a low mountain range in Germany. The values ranged from 0.0004% (fenpropimorph, k_{oc}=3400 L kg^{-1}) to 0.16% (metamitron, k_{oc}=156 L kg^{-1}). Wauchope (1978) reviewed the annual losses from agricultural fields and concluded that they are usually between <0.1 and 1%. Note, however, that some of our application rates are somewhat uncertain because Schreinemachers and Sirijinda (2008) had interviewed only few farmers applying dimethoate and a mixture of endosulfan (α-, β- endosulfan and endosulfan sulfate) and none who admitted to have applied atrazine.

At OL, the losses of all pesticides per agricultural area were lower than at the other two stations. In the upstream areas of HW and MSN, agricultural production is highly intensive. OL is located about 10 km downstream of HW. On the way from HW to OL, the water passes longer sections where the catchment is not used for agriculture but covered by forest (Fig. 5.2). During its passage through this area, the river water is diluted by pesticide-free or less contaminated water. Moreover, on their way downstream, pesticides may sorb to particulate and suspended sediments and be degraded. Hence, natural attenuation facilitated by buffering and filtering zones along forested areas is important process to lower the pesticide

contamination level of river water on its way to the lowlands, where the water is used as drinking water.

5.4.2. Risk assessment

Three of the studied pesticides, namely atrazine, chlorpyrifos and endosulfan are included in the list of the 33 priority substances in surface water defined in the Annex II of the Directive 2008/105/EC. Particularly endosulfan is defined as priority hazardous substance. Aquatic organisms of three taxonomic groups – algae, zooplankton and fish – were considered representative to assess the ecological risk in the Mae Sa River. Generally, the herbicide atrazine is more toxic to algae than to zooplankton or fish (Table 5.3) because its active ingredients act on the photosynthesis system. Dichlorvos is toxic mainly to zooplankton. The insecticides namely chlorpyrifos, endosulfan, cypermethrin and the fungicide chlorothalonil, that accumulated in the sediments, are toxic to both zooplankton and fish. In particular, the concentrations of chlorpyrifos and cypermethrin were distinctly higher than the acute toxicity levels to zooplankton such as *Daphnia magna* (Table 5.3).

Dichlorvos, (α-, β-) endosulfan, and cypermethrin are likely to cause adverse affect to aquatic organism in the catchment. Although the absolute concentration of (α-, β-) endosulfan were low (see Table 5.5), its RCR value was the highest due to the extreme toxicity of theis pesticide to aquatic invertebrates and fish, yielding very low PNEC values (Table 5.3). Although the total pesticide loss at the outlet was lower than at the other two stations, the RCR cumulated over all pesticides was higher due to the higher concentration of the hazardous substance (α-, β-) endosulfan. The highest RCR of dichlorvos was found at MSN because of the high concentration detected there. Its contribution to the cumulated RCR, however, is moderate because of the dominating role of (α-, β-) endosulfan.

The PNECs of chlorpyrifos and chlorothalonil are relatively low as well. The risks with regard to their mean concentrations are acceptable, however, because they strongly sorb to soils and sediments and their concentrations in the water phase are low. Regarding the maximum concentrations of these insecticides, however, the risk is significant. Whereas atrazine was frequently detected in the water, the RCR indicates an acceptable risk due to the low PNEC value. Similarly, dimethoate mean and maximum concentrations are of little concern in the catchment.

Dichlorvos, atrazine and dimethoate have a relatively high mobility because of their high solubility and low k_{oc} value. Because of the latter, they were not detected in bed and suspended sediments. The RCRs of (α-, β-) endosulfan and cypermethrin in bed sediment

were higher than unity, in particular that of (α-, β-) endosulfan. These pesticides adversely affect aquatic organisms such as invertebrates and fish, and their sediment concentrations are a cause for concern. Their application should be reduced. (α-, β-) endosulfan, dichlorvos, and cypermethrin should be substituted by less toxic products.

The risk assessment results are in accordance with the studies of Vryzas et al. (2011). Cypermethrin, chlorpyrifos and endosulfan were reported as non-acceptable aquatic risk in surface water in the riparian drainage canals in northeastern Greece. The high PEC/PNEC ratios were mainly due to their relatively high toxicity to fish, algae or aquatic invertebrates. Moreover, atrazine and dimethoate posed an acceptable risk when the median and maximum concentrations were used for the risk calculation.

5.4.3 The effect of sampling resolution

In mountainous tropics, many factors such as high and intensive rainfalls, poor soils with a low sorption capacity increase the loss of pesticides into surface and groundwater during runoff events and causes high input levels of the toxicants with ashort exposure duration due to the fast dissipation rate in tropic environment. These aspects must be considered in the design of an appropriate sampling scheme for pesticide monitoring and ecological risk assessment in mountainous tropical regions.

The effect of sampling resolution is illustrated in Table 10, which compares RCR values calculated from concentrations measured at low and high temporal resolution. The high-resolution data are from the study of Sangchan et al. (2012). Those authors collected water samples every 10 min. Because six samples were mixed to one composite sample, the temporal resolution was 1 h. Note that the temporal resolution in the present study was 1 d.

At the 1-h resolution, mean and maximum pesticide concentrations were generally higher than at the 1-d resolution. As a consequence, the RCR values were also higher. Hence, the sampling scheme with the lower resolution underestimates the ecological risk because peak concentrations were averaged out. In contrast, sampling scheme with high temporal resolution will usually be kept shorter to avoid excessive analyses. This entails the risk of missing pesticide losses that occur only occasionally. For example, while Sangchan et al. (2012) did not detect dichlorvos, our study has revealed that this pesticide is of ecotoxicological concern in the Mae Sa watershed. Yet, the overall rank of the pesticides is similar between the two sampling schemes. (α-, β-) endosulfan exhibits the highest RCR, and atrazine and dimethoate the lowest.

Table 10: Comparison of RCR values of pesticides in surface water at the headwater station collected with two different monitoring schemes.

Pesticide	RCR_{water}			
	Long-term monitoring (2007-2008; N=130)		Short-term monitoring (2-7 May 2008; N=61)[a]	
	Mean	**Max.**	**Mean**	**Max.**
Dichlorvos	4.0	167	n.d.	n.d.
Atrazine	0.001	0.01	0.001	0.005
Dimethoate	0.004	0.05	0.02	0.1
Chlorothalonil	0.1	2.4	0.1	2.1
Chlorpyrifos	1.3	14.2	5.7	38.6
Endosulfan (α, β)	921	16003	20000	90000
Cypermethrin	3.1	118	15.0	50.0
Total	**930**	**16305**	**20021**	**90090**

[a] Data from Sangchan et al., 2012, n.d. = not detected

5.5. Summary and conclusions

Among the pesticides detected in the Mae Sa river water, chlorpyrifos was most frequently detected, particularly at the HW station. Atrazine and dichlorvos were mainly found in the Mae Sa Noi tributary. Cypermethrin was the most frequently detected pesticide in both the bed and suspended sediment samples.

The risk assessment revealed that (α-, β-) endosulfan, dichlorvos, and cypermethrin are the main ecotoxicological stressors in the river water. The sediment contents of (α-, β-) endosulfan and cypermethrin suggest that these pesticides adversely affect aquatic organisms. In conjunction with a previous study, our results point to the challenge of designing a proper sampling scheme for ecotoxicological risk assessment. Depending on observation period and temporal resolution, short-term ecological stresses may be overlooked by smoothing of peak concentrations. On the other side, the pesticides may go undetected. A possible solution is to employ a nested scheme that means sampling at two or more time scales.

5.6. Acknowledgement

5.7. References

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6. Final discussion

6.1. Analysis of pesticides in water and sediment

Before the monitoring program could begin, the extraction methods and analytical procedures of the pesticides in the water and sediment samples had to be established. Generally, physicochemical properties such as polarity, solubility in water and/or octanol-water partition coefficient (K_{ow}), volatility, and stability are important aspects to be considered in pesticide analysis. In multi-residue analysis, however, determining pesticides with a wide range of properties at the same time typically results in more problems. Several extraction methods for single groups of pesticides, i.e. polar or non-polar compounds, may be best suited. However, in a routine studies it is commonly not possible due to increased efforts and costs. To reduce constraints in the analysis compromises are necessary, while an acceptable result should still be achievable. Not all analysts will have 100 % recovery for detection at low levels in all matrices. In general, for the multi-residue analysis of pesticides, a recovery ranging between 70 % and 120 % and relative standard deviation (RSD) less than 20 % are sufficient.

From the bed sediment, five of the seven investigated pesticides, but not dichlorvos and dimethoate, were recovered at acceptable ranges. With the suspended sediment, only dimethoate was outside of the upper acceptable range. The low recovery of dichlorvos is most probably due to the high volatility of this insecticide. Dimethoate recoveries of above 120 % were found in both sediment matrices. A matrix-induced chromatographic enhancement was suspected to increase the analytical signal of extracted samples, particularly with the GC-NPD system.

Additional information on how the extraction and analytical methods for the water samples were set up was presented in Chapters 4 and 5. The recoveries of the seven investigated pesticides ranged between 58 % and 117 % with high repeatability (RSD<20 %), except for chlorothalonil. Dichlorvos, chlorothalonil, and cypermethrin were troublesome pesticides with recoveries below the lower acceptable range of 70 %. Dichlorvos is a highly volatile pesticide. Evaporation is reported to be the main reason for low recoveries (Anyusheva et al., 2012). In contrast, the low extraction efficiency (58 %) and high variation (RSD=27 %) of chlorothalonil can be explained by the strong retention of chlorothalonil by the graphitized carbon black (GCB) sorbent. The high affinity of the planar molecule

chlorothalonil can provoke effects of chemisorption for particular adsorbents. In order to eliminate this undesirable effect, the sorbent was deactivated by washing the cartridge with ascorbic acid (Di Corcia et al., 1993). In our study, however, the recovery of chlorothalonil was high compared to literature values (0-46 %, Tolosa et al., 1999). The recovery of cypermethrin (69 %) was slightly below the acceptable range, because of the strong sorption of the pesticide (Log K_{oc} 4.9) in the cartridge (Tolosa et al., 1999).

6.2. Comparison of pesticide losses during single runoff events versus long-term monitoring data

Pesticide monitoring was conducted on two different time scales: on the scale of a runoff event and on a seasonal time scale. The results from both monitoring regimes supplement each other. Short-term monitoring during the single runoff events allows for a comprehensive investigation of the input patterns of pesticides in the watershed. Additionally it uncovers occasional extremely high runoff concentrations. The long-term monitoring provides the seasonal variation and spatial distribution of the pesticides depending on the climate, pesticide use, and agricultural practices used within the watershed.

During the single runoff events, our results showed that some high mobility pesticides (log K_{oc}<2.5), such as atrazine and dimethoate, were characterized by a close relationship between the peak concentration and peak flow at the early part of the runoff hydrograph, indicating transport by fast flow components. However, other strongly sorbing pesticides, such as chlorpyrifos, chlorothalonil, (α, β) endosulfan, and cypermethrin, behaved inconsistently. These pesticides were sporadically detected in high concentrations during the falling limb of the runoff peak, indicating a fast and sporadic sub-surface flow component. After recession, many pesticide concentrations remained low and fairly constant on a baseline level until the end of the sampling course. Similar findings were reported by many studies. Pedersen et al. (2006) found that the maximum concentration of some organophosphorus insecticides occurred sometimes near the beginning of an event (e.g. malathion and diazinon) but chlorpyrifos remained fairly constant throughout the hydrograph. Oliver et al. (2012) reported that during the runoff event the concentration of chlorpyrifos increased with increasing peak flow, but did not decrease with the descending limb of the hydrograph.

In the long-term monitoring study, pesticide concentrations and loads in surface water show a marked increase during the rainy season (May to October when the use of insecticides (e.g., chlorpyrifos and cypermethrin) and fungicides (e.g. chlorothalonil) is typically high (Schreinemachers and Sirijinda, 2008). The pesticide load monitored at the outlet station

during the rainy season was more than 10 times higher than during the dry season (Chapter 5). In general, mean and maximum concentrations of pesticides obtained from the long-term monitoring, were lower than pesticide concentrations determined during single rainfall events. During one single runoff event in August 2008, chlorpyrifos concentration reached up to 9.7 μg L^{-1} at the headwater catchment of Mae Sa River. This concentration is clearly higher than the limit of EU (>0.03 μg L^{-1}) for chlorpyrifos in surface water and it is much higher than the Canadian limit (>0.0035 μg L^{-1}). Nevertheless, although the short-term monitoring scheme provides a better picture of maximum concentration and load of pesticides due to high resolution sampling, it runs the risk of not detecting the pesticides that show up only sporadically in river waters. For example, dichlorvos was detected in none of the three single rainfall events in May, August and September 2008. However, with long term monitoring, dichlorvos was detected several times during the rainy season in 2007 and 2008. The maximum concentration of dichlorvos at the MSN station was as high as 1.1 μg L^{-1}.

7. Final conclusions and Perspectives

7.1. Key results

The contamination by pesticides raises concerns about water quality and environmental risk regulation. To minimize agricultural impacts on surface water quality, detailed knowledge of the behavior and fate of pesticides in surface water is required. The present dissertation combines comprehensive investigations of pesticide transport during several single runoff events, seasonal variation and spatial distribution of pesticides over the year within an agriculturally used catchment in the outer tropics.

In the short-term study, the dynamics of seven pesticides with physico-chemical properties varying of a wide range (log K_{oc} 1.5-4.9) were investigated at the beginning and mid of rainy season. Three input patterns of the pesticides were identified. The first input pattern – increasing concentrations during the rainfall events as discharge increases – suggests transport with surface runoff. Strong relationships between pesticide concentration peak and peak flow were found for highly mobile pesticides (log K_{oc}<2.5), such as atrazine and dimethoate. The second pattern – sporadic high concentrations during the falling limb of the runoff peaks – was mostly observed with pesticides of medium to high K_{oc} (2.5<log K_{oc}<5), such as chlorpyrifos, chlorothalonil, endosulfan, and cypermethrin. It points to a sporadic sub-surface flow component (e.g. preferential interflow). This process is significantly delayed in comparison to the surface runoff because the distance travelled in the pores is larger and the travel velocity is lower. Obviously strong relationships between antecedent rainfall and pesticide transport, with delay preferential process, were found in mid of rainy season events. The third pattern – low but more or less continuous leaching of pesticides at concentrations on a baseline level, especially during periods of rainfall – is probably related to some long-term underground storage.

Long-term monitoring of the 2007-2008 pesticides shows that all seven investigated pesticides were detected in the Mae Sa River. The seasonal dynamics of pesticides show that pesticide concentrations and loads markedly increased during the rainy season (May to October), which is the period of the main pesticide application in the study area. Additionally, during this period, antecedent rainfall caused an increased transport of pesticides from agriculture sites by surface runoff and subsurface flow. Pesticide use and agricultural activities, particularly during the rainy season, dramatically increased the transport of the

chemicals in the watershed area. Chlorpyrifos was most frequently detected in the headwater area. Atrazine and dichlorvos were mainly found in the Mae Sa Noi tributary. While cypermethrin was not often detected in the water samples, it was the most frequently detected pesticide with high concentrations in sediment samples at the Mae Sa Noi tributary and nearby the headwater station.

The ecological risk assessment revealed that contamination of pesticides in surface water and sediment is a serious environmental issue. At all stations, endosulfan and dichlorvos were the main stressors in the water phase. Strongly sorbed pesticides, such as endosulfan and cypermethrin, have a high potential to cause adverse effects on aquatic organisms in the sediment phase.

7.2. Implication of research results

7.2.1. Monitoring strategies for pesticide studies and ecological risk assessment

Pesticide monitoring can be used to strengthen confidence in environmental and ecological exposure estimates. Understanding the fate of pesticides in aquatic environments and assessing their potential effects on non target organisms are important for protecting environmental and human health and for product use registration. In the aquatic risk assessment, the concentration (i.e. mass per volume), not the load (i.e. mass per area) is the most common quantity used because it correlates with ecotoxicological effects.

During single runoff events, the transport patterns of pesticides with respect to hydrological processes open insights into the optimal design for an appropriate sampling scheme for pesticide monitoring and ecological risk assessment. To ensure that monitoring requirements are achieved, high-resolution sampling schemes are suggested. Additionally, to gain more realistic worst-case exposure for the risk assessment, the input patterns of pesticides must be taken into account when choosing the sampling period. For instance, to quantify the short-term exposure during the single runoff events, significant concentrations of pesticides during initiation of rainfall and runoff peak and the longer period of the recession phase must be considered.

In addition, to illustrate the effect of sampling resolution of monitoring the outcome of a risk assessment, the RCRs of the two monitoring schemes were compared. In general, the short-term monitoring scheme delivers higher mean and maximum exposure concentrations. This means that pesticide risk of the aquatic environment during the short-term event was higher than from the long-term period. It also indicates that the data from the long-term

monitoring scheme are likely to underestimate the ecological risk because high concentration peaks are averaged out. On the other hand, using a sampling scheme with a high-temporal resolution, but with a short observation period, runs the risk of missing a pesticide with a significant ecological impact.

7.2.2. Strategies for pesticide use and mitigation

As mentioned in Chapters 4 and 5, the Mae Sa watershed may be regarded as representative for the agriculturally used mountainous watersheds in northern Thailand. It is located in monsoon tropical climate with high intensive rainfall during rainy seasons. The watershed characteristics, e.g. soil properties, intensively agricultural land use, and steep slope, influence the seasonal and spatial distribution of pesticides.

The input patterns of pesticides during the single runoff events reveal that surface runoff, fast and delayed preferential flow and baseflow, are key contributors of pesticide losses in the watershed. The results from the long-term monitoring show that mainly atrazine, dichlorvos and chlorpyrifos were detected in the water samples. Moreover, in the sediment samples, cypermethrin and chlorpyrifos were mainly found. In addition, the risk assessment shows that the contamination of pesticides in the surface water is a serious environmental issue. Many pesticides in the study program, i.e. endosulfan, dichlorvos, chlorpyrifos and cypermethrin, have the potential to cause adverse effects in both water and sediment compartments. To reduce pesticide loss from fields and to diminish the ecological impact, implicit measures such as pesticide selection, soil preparation and vegetative buffer areas are reviewed as follows.

Pesticide selection

It is important to provide basic knowledge to farmers on how to select the right pesticide. In general the chemical should be effective with a low application rate and low impact on human health and the environment.

The mobility of a pesticide depends on its properties, i.e. solubility in water, sorption and persistence in soil. These properties can be used to estimate susceptible loss of pesticides through leaching, surface runoff and a potential to pollute groundwater. Low mobility of a pesticide will reduce transport of the pesticide through soil matrix, but it may not effectively be eliminated because of surface runoff and preferential flow transports (Flury, 1996). In soil, pesticides can be degraded by combined chemical and biological processes. Fast degradation of pesticides reduces pesticide transport by fast flow components, but it is favorable for slow leaching through soil (Flury, 1996). Formulations of a pesticide (as liquid, solid, gas

formulations) and application methods (e.g. aerial or canopy spraying, incorporation or injection into the soil, and with water) can influence the efficiency of pesticide use and loss. For example, controlled release formulations are recognized as effective methods that diminish the adverse effects and increase the efficiency of active ingredient. The formulations allow the release of the active ingredient to the target at the control rate. This can maintain its concentration in the environment within a lower limit over a specific period of time (Gish et al., 1994; Buhler et al., 1994). Several studies showed that the use of controlled release formulations can reduce the losses of highly mobile pesticides such as atrazine, alachlor and metolachlor in surface runoff and leachate (Buhler et al., 1994; Hermosin et al., 2001; Fernández-Pérez et al., 2011). Although the use of endosulfan has been reduced in the Mae Sa watershed during the last few years, the results from the present study show that endosulfan still has an outstandingly high adverse impact on the aquatic ecosystem due to its severe toxicity. The use of an effective but highly toxic substance should be diminished or it should be replaced by less toxic chemicals. Farmers must carefully read and follow the labels containing the pesticide information.

Application time and rainfall event

In the Mae Sa watershed, cropping period and application time of pesticides mainly occur during the rainy season when intensive rainfall occurs nearly every day. The time between pesticide application and rainfall is one promising factor that may reduce pesticide loss in this area. After pesticides are applied to soil, they interact with organic matter and soil particles through many processes. Adsorption of pesticide in soil may be a rate-limited process (Fortin et al., 1997). It is known to increase with time after application (Arias-Estévez et al., 2008). To reduce the risk of pesticide transport by runoff and leaching processes, as they have little time for movement and interaction into the soil, therefore, an application of pesticides shortly before rain should be avoided. Moreover, in tropical areas where it rains nearly every day during rainy seasons, using a pesticide in an oil-based mixture is better than using a water-based mixture. The oil carrier acts as a sticker-spreader helping to improve the coverage and adsorption of the pesticide. This results in a decreased loss of pesticides from the application area. The relation between application time and pesticide loss in runoff and leaching event has been observed in many studies (Wauchope, 1978; Leonard, 1990). They reported that concentrations of pesticides in runoff and leaching increased shortly after application. Soil properties and topography of the fields are dominant factors of pesticide losses in both pathways.

Soil preparation

In many studies, it was found that conservation tillage was able to greatly reduce pesticide loss in runoff by decreasing the runoff volume due to increasing the infiltration capacity of soil (Holvoet et al., 2007) and decreasing the detachment effect of raindrop impact (Ritter, 2001). Minimal cultivation systems leave crop residues near the surface protecting soil from erosion by increasing organic matter content and structural stability in the top few centimeters. This increases adsorption of strongly sorbing pesticides on soil organic matter and reduces the loss of chemicals sorbed to sediment in runoff. Isensee and Sadeghi (1994) reported that in the conservation practices with no-tillage, organic carbon content was four times larger than in the conventional tillage practice. Moreover, conservation tillage can be utilized to increase crop yield by improving soil fertility.

Vegetative buffer strips

Vegetative buffer strips have received the largest attention in mitigation of pesticide and sediment transport by surface runoff. The application of this method has been suggested particularly for steep slopes and for lower edges of fields. Buffer strips reduce the velocity of runoff, increase infiltration and deposit sediment, which reduces the concentration of contaminants in runoff. The working group on landscape and mitigation factors in ecological risk assessment (FOCUS, 2007) evaluated potential reduction efficiencies of various mitigation measures for runoff losses to surface water. They found that vegetative filter strips can retain 20-60 % of strongly sorbing pesticides. For highly mobile pesticides such as atrazine, Popv et al. (2006) reported that the total load of atrazine could be reduced by grassed buffer strips on cracking vertisol soil by up to 85 %. In buffer strips, a relatively large amount of the coarser fractions will be trapped compared to the clay fraction. Ziegler et al. (2006) studied the effectiveness of buffer strips in a hilly watershed in northern Vietnam. Many factors, such as topography (slope angle), buffer strip geometry (size and length), and type and volume of surface runoff, influenced the effectiveness of the buffers. These results suggest that multiple and staggered buffers might be required in case the surface runoff is generated from large hillslope areas.

7.2.3 Implications for modeling

In future, the hydrological data and monitoring results of pesticide concentrations from the previous study will be used for computer modeling. The Soil and Water Assessment Tool (SWAT) is a distributed hydrological model that has been verified and used for assessing non-

point source pollutant loading across large catchment areas (Ramanarayanan et al., 2005; Luo et al., 2008). The model is capable to simulate complex land management and pesticide transport at the watershed scale. Accuracy of the simulation depends on quality of input spatial parameters describe the characteristics of the watershed. To predict the environmental fate of pesticide and its behavior, hydrological characteristics, soil properties, climate information, land use, pesticide concentration, chemical properties, etc. are needed for modeling. The temporal trend and spatial distribution of dissolved pesticide can be intensively investigated by the model (Luo et al., 2008). Moreover, sensitivity analysis of hydrology and pesticide transport supplied by SWAT will provide useful support and will give an insight into which parameters are most sensitive concerning pesticide transport towards rivers (Holvoet et al., 2005). To assist decision making for mitigation strategies, the SWAT model was applied to quantify the effectiveness of agricultural practices to reduce pesticide loss in surface runoff at the watershed scale (Zhang and Zhang, 2011). The results show that the combination of vegetated ditches, buffer strips and reduction of pesticide use can decrease load of diazinon and chlorpyrifos by up to 94 %.

8. Summary

Transport of pesticides in a river of a tropical mountainous watershed in northern Thailand

In the northern region of Thailand, in the upland areas population growth and migration of people from the lowlands have rapidly driven land use changes. The expansion of cultivation to increasingly vulnerable areas such as the slopes of mountainous watersheds has led to increasingly adverse impacts on the environment. In particular, intensive application of pesticides poses a contamination risk for stream water and the aquatic ecosystem. This thesis identified the transport patterns of pesticides with different physico-chemical properties during single runoff events under farmer's practice conditions on the catchment scale. Moreover, the exposure concentrations of frequently used pesticides in surface water and sediment in the watershed were measured in the frame of long-term monitoring. The data were used to calculate pesticide loads in the Mae Sa watershed (Chiang Mai, Thailand) and to assess the ecological risk of pesticides for the aquatic ecosystems.

Prior to start of the monitoring program, methods to extract and analyze pesticides in the surface water and sediment samples were established. The pesticides in water samples were extracted by solid phase extraction with a graphitized carbon black sorbent. The recoveries of pesticides in a simultaneous analysis ranged from 58 % to 117 % for the seven pesticides (dichlorvos, atrazine, dimethoate, chlorothalonil, chlorpyrifos, (α, β) endosulfan, cypermethrin) with a high repeatability of the method (Relative Standard Deviation, (RSD)<20 %), except for chlorothalonil (RSD=27 %). For analysis of sediments, the QuEChERS method was adapted. Extraction conditions such as solvent, partitioning of pesticide due to salt effect and clean up step with dispersive solid phase extraction were optimized. Except for dichlorvos in the bed sediment sample and for dimethoate in bed and suspended sediments, recoveries were between 81 % and 116 %. The results show that the QuEChERS method is a valuable method for extracting pesticides from sediment samples.

To identify the transport pathways contributing to pesticide losses from soil to the Mae Sa River, automatic gauging stations were installed at the headwater (HW) and outlet (OL) of the watershed to measure discharge and to collect water samples for pesticide analysis. During three runoff events in May, August and September 2008, water samples were collected in a high temporal resolution (1 hour). The potential transport pathways of pesticides were

elucidated by time series analysis. Three different input patterns of pesticides were observed: (a) pesticide peaks during the rainfall events as discharge increased, (b) sporadic high concentrations of pesticides during the falling limb of the runoff peak, and (c) low concentrations but more or less continuous values on a baseline level. A chromatographic effect was observed for many pesticides, for example between dimethoate and chlorpyrifos. Highly mobile pesticides such as atrazine and dimethoate were likely to suffer loss at the beginning of the runoff event, while strongly sorbing pesticides such as chlorpyrifos were slightly delayed. This indicates an interaction with the soil matrix, during transport along a sub-surface pathway. The results obtained in the middle of the rainy season in August and September events showed that antecedent rainfall plays an important role in triggering pesticide transport by preferential interflow. In both events the sporadic appearances of strongly sorbing pesticides such as chlorothalonil and chlorpyrifos after peak flow suggest this transport type. For ecotoxicological risk assessment, the highly dynamic nature of pesticide input to surface waters must be considered in the design of representative monitoring schemes. Not only the periods during rain event and peak runoff, but also the following recession phase, during which short and pulsed concentration peaks might show up, must be captured by a representative sampling scheme. Therefore, a high temporal resolution is advisable.

To study the long-term dynamics of seven selected pesticides in the Mae Sa River and to evaluate their environmental impacts to aquatic organisms, the exposure concentrations of the pesticides in water and sediment samples were monitored at three stations (HW, Mae Sa Noi flume (MSN), and OL) in the watershed over a period of one and half year (from July 2007 to November 2008). Aquatic risk assessment concerning the observed pesticide concentrations was performed by using the risk characterization ratio (RCR). Chlorpyrifos was the most frequently detected pesticide in surface water at the HW and OL. Cypermethrin was the most frequently detected pesticide in bed and suspended sediment samples along the Mae Sa Noi tributary and at the HW. Regarding the change of pesticide use in the area (compared with data recored in 2002), the measurements suggest that the use of endosulfan has been reduced in recent years, while the observed concentrations of chlorothalonil and chlorpyrifos were in the same concentration ranges as in 2002. The temporal distribution of pesticides shows that the concentrations are highest during the rainy season. Outstandingly high losses of dichlorvos and atrazine were found at Mae Sa Noi flume. Loads of chlorothalonil and chlorpyrifos in stream water were extremely high in the headwater area. Based on interview data of pesticide

use in the Mae Sa watershed, in both years the losses of single pesticides to surface water ranged from 0.004 % (chlorothalonil) to 4.7 % (dimethoate) of the applied pesticide mass. The loss of atrazine could not be included because the data did not contain information on the application rate of atrazine.

The risk assessment shows that particularly dichlorvos and endosulfan have a high potential to cause adverse effects to the aquatic ecosystem. The RCRs of endosulfan and cypermethrin show that they are the main stressors in the sediment phase. This reveals that aquatic ecosystem of the Mae Sa watershed is facing adverse effects by the contamination of surface water and sediment with pesticides. Hence, measures are urgently needed to reduce the loss of pesticides from soil to surface waters.

9. Zusamenfassung

Transport von Pestiziden in einem Fluss eines tropischen bergigen nordthailändischen Einzugsgebiets

In den Bergregionen Nordthailands haben Bevölkerungswachstum und die Zuwanderung aus dem Tiefland die Landnutzungssysteme drastisch verändert. Die Expansion der Landwirtschaft in immer empfindlichere Regionen, wie z.B. bergige Wassereinzugsgebiete, hat zunehmend negative Auswirkungen auf die Umwelt. Insbesondere die intensive Nutzung von Pestiziden stellt ein Risiko für aquatische Ökosysteme dar. Die vorliegende Arbeit untersucht auf Einzugsgebietsebene und unter üblichen landwirtschaftlichen Praxisbedingungen das Transportverhalten von Pestiziden nach Niederschlagsereignissen. Die untersuchten Pestizide weisen dabei sehr verschiedene physikochemische Eigenschaften auf. Darüber hinaus wurden die Expositionskonzentrationen häufig applizierter Pestizide im Rahmen von Langzeitmessungen in Oberflächenwasser und Sedimentproben im Einzugsgebiete gemessen. Die gewonnenen Daten wurden zur Berechnung der Pestizidfrachten im Mae Sa Wassereinzugsgebiet (Chiang Mai, Thailand) und zur Abschätzung des ökologischen Risikos für das aquatische Ökosystem verwendet.

Vor Beginn der Untersuchung wurden die Methoden zur Extraktion und Analyse der Pestizide in Oberflächenwasser- und Sedimentproben etabliert. Die Pestizide in den Wasserproben wurden mit Hilfe einer Festphasenextraktion an graphitierter Aktivkohle analysiert. Die Wiederfindungsraten der sieben untersuchten Pestizide (Dichlorvos, Atrazin, Dimethoat, Chlorthalonil, Chlorpyrifos, (α, β) Endosulfan, Cypermethrin) variierten zwischen 58 % und 117 % bei einer generell hohen Reproduzierbarkeit (RSD<20%). Eine Ausnahme bildete Chlorthalonil mit einer RSD von 27 %. Für Sedimentproben wurde eine abgewandelte QuEChERS Methode entwickelt. Die Extraktionsbedingungen wie Lösungsmittel, Partitionierung der Pestizide durch Aussalzen, und Aufreinigung mit dispergiertem SPE wurden optimiert. Mit Ausnahme von Dichlorvos (Flussbettproben) sowie Dimethoat (Suspensions- und Flussbettproben) lag die Wiederfindungsrate zwischen 81 % und 116 %. Die Ergebnisse zeigen, dass die QuEChERS Methode eine sehr gute Alternative für die Extraktion von Pestiziden aus Sedimentproben darstellt.

Um die Transportpfade aufzuklären, die zum Transfer von Pestiziden aus dem Boden in den Mae Sa Fluss beitragen, wurden automatische Messstationen im Oberlaufbereich und am Auslass des Einzugsgebietes installiert. An den Stationen wurden Wasserproben für die Pestizidanalytik entnommen und der Abfluss gemessen. Während dreier Abflussereignisse in Mai, August und September 2008 wurden Wasserproben mit einer hohen zeitlichen Auflösung (1 Stunde) genommen. Die potentiellen Transportpfade der Pestizide wurden über eine Zeitreihenanalyse untersucht. Drei unterschiedliche Eintragsmuster wurden beobachtet: (a) maximale Pestizidkonzentrationen während des Anstieges des Abflusses, (b) sporadisch auftretende Konzentrationsspitzen während der Abnahme des Abflusses, und (c) niedrige jedoch annähernd konstante Konzentrationen auf Basisniveau. Bei vielen Pestiziden, z.B. Dimethoat und Chlorpyrifos, wurde ein chromatographischer Effekt beobachtet. Sehr mobile Pestizide wie Atrazin und Dimethoat wurden in der Regel zu Beginn des Niederschlagsereignisses ausgetragen, während stark sorbierende Pestizide wie Chlorpyrifos leicht verzögert ausgetragen wurden. Dieses Verhalten deutet auf eine Interaktion mit der Bodenmatrix während des Transports entlang eines unterirdischen Transportpfads hin. Diese Ergebnisse, die während der Hauptregenzeit im August und September erzielt wurden, zeigen weiterhin, dass die unmittelbare Niederschlagshistorie eine wichtige Rolle bei der Aktivierung des Pestizidtransports über präferentiellen Zwischenabfluss spielt. Das bei Niederschlagsereignissen sporadische Auftreten von stark sorbierenden Pestiziden wie Chlorthalonil und Chlorpyrifos nach dem Scheitelabfluss deuten auf diesen Transportmechanismus hin. In ökotoxikologischen Risikoanalysen muss die hochgradig dynamische Art des Eintrags von Pestiziden in Oberflächengewässer bei dem Design von repräsentativen Beprobungsschemata unbedingt berücksichtigt werden. Nicht nur die Zeit während des Niederschlagsereignisses und der Abflussspitze, sondern auch die anschließende Rezessionsphase, bei der kurze und pulsartige Konzentrationspeaks auftauchen können, müssen in einem repräsentativen Beprobungsschema berücksichtigt werden. Deshalb sind Probenahmeverfahren mit einer hohen zeitlichen Auflösung zweckmäßig.

Um die Langzeitdynamik von sieben ausgewählten Pestiziden im Mae Sa Fluss und ihren Umwelteinfluss auf aquatische Organismen zu untersuchen, wurden die Expositionskonzentrationen der Pestizide in Wasser- und Sedimentproben an drei Stationen über den Zeitraum von anderthalb Jahren (von Juli 2007 bis November 2008) bestimmt. Die Risikobewertung der gefundenen Pestizidkonzentrationen wurde mit Hilfe des Risikoquotienten durchgeführt. Chlorpyrifos war das am häufigsten gefundene Pestizid im

Oberflächenwasser der Oberlauf- und Auslassstation. Cypermethrin war das am häufigsten detektierte Pestizid in den Flussbett- und Suspensionsproben entlang des Mae Sa Noi Nebenflusses und der Oberlaufstation. Verglichen mit Daten von 2002 wurde in den letzten Jahren die Applikation von Endosulfan verringert, während sich die gefundenen Konzentrationen von Chlorthalonil und Chlorpyrifos in der selben Größenordnung befanden haben wie 2002. In der Regenzeit sind die Pestizidkonzentrationen am höchsten. Außerordentlich hohe Austräge von Dichlorvos und Atrazin wurden am Mae Sa Noi Messgerinne beobachtet. Die Frachten von Chlorthalonil und Chlorpyrifos im Flusswasser waren extrem hoch. Basierend auf Befragungsdaten wurde die eingesetzte Pestizidmenge abgeschätzt. In beiden Jahren lag der geschätzte Austrag für einzelne Pestizide ins Oberflächenwasser zwischen 0.004 % (Chlorthalonil) und 4.7 % (Dimethoat) des Eintrags. Der Austrag von Atrazin konnte nicht ermittelt werden, da hierfür keine Befragungsdaten zur applizierten Menge vorlagen.

Die Risikobewertung zeigt, dass insbesondere Dichlorvos und Endosulfan ein hohes Potential besitzen, unerwünschte Auswirkungen auf das aquatische Ökosystem auszulösen. Des Weiteren zeigen die Konzentrationsniveaus von Endosulfan und Cypermethrin, dass diese beiden Pestizide die Hauptstressoren in der Sedimentphase sind. Dies zeigt, dass das aquatische Ökosystem des Mae Sa Einzugsgebietes nachteilige Auswirkungen durch die Kontamination der Oberflächengewässer und des Sediments durch Pestizide erfährt. Daher werden dringend Maßnahmen zur Reduzierung des Austrages von Pestiziden aus dem Boden in Oberflächengewässer benötigt.

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