FATE OF TWO CURRENTLY-USED PESTICIDES IN WATER-SEDIMENT SYSTEMS

PhD Thesis

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ABSTRACT

Experiments were undertaken to understand the fate of selected pesticides in water-sediment systems and to determine whether laboratory experimental data coupled with mathematical modelling is able to represent behaviour in outdoor condition. Two pesticides were selected for study; thiamethoxam has a low sorption coefficient (K_{oc}) and is susceptible to hydrolysis and photolysis, whilst metalaxyl-M has moderate sorption but is stable to hydrolysis and photolysis. A sequence of experiments was carried out starting with investigation of simple, single-phase systems and building additional complexity first in the laboratory and subsequently in the field.

Hydrolysis of thiamethoxam was pH-dependent; the rate was very slow under acidic and neutral conditions and significantly higher at alkaline pH ($p<0.001$). Photolysis of thiamethoxam was also strongly influenced by pH ($p<0.001$) with the rate of photolysis 4.30 and 3.85 times faster at pH 10 than at pH 9 for pure and natural water, respectively. The presence of nitrate anions significantly ($p<0.05$) decreased rate of photolysis of thiamethoxam and this was attributed to a direct competition for absorption of light. Sorption of the two pesticides to a natural sediment (K_{oc} 32.6 and 36.6 L kg^{-1} for thiamethoxam and metalaxyl-M, respectively) suggested that these pesticide are weakly sorbed and likely to be present predominantly in the water phase.

Pesticides in water-sediment systems with plants (*Myriophyllum spicatum*) degraded much faster than in systems without plants under both laboratory and outdoor conditions. Plants had direct effects through sorbing and taking up pesticide, but the dominant influence was indirect due to changing pH to alkaline conditions and thus increasing the rate of photolysis and hydrolysis. Degradation in water broadly translated from the laboratory to outdoor experiment, but sorption behaviour in simplified systems greatly overestimated pesticide sorption in complex systems in outdoor experiments. There was less intense contact between pesticide and sediment in vessels under outdoor conditions and pesticide degraded from water much more quickly, limiting the time available for sorption. A previously unreported tendency

for photolysis of metalaxyl-M in outdoor experiments showed the importance of selecting laboratory conditions able to mimic behaviour of pesticides under outdoor conditions. TOXSWA predictions for fate of the two pesticides in outdoor experiments showed a reasonable match to measured data for the water phase, although residues were overestimated at initial and after a few days of experiment. Model efficiency was -1.81 and 0.944 for thiamethoxam and metalaxyl-M, respectively. The simulations showed a reasonable match with measured data in plants for thiamethoxam, but underestimated concentrations of metalaxyl-M in plants. Concentrations of both pesticides in sediment were overestimated by the model at model efficiencies of -84.0 and -2.14 for thiamethoxam and metalaxyl-M, respectively. Further work could apply alternative models such as EXAMS or develop a new model able to account for all relevant processes acting on pesticides in surface waters. This work considered two pesticides in detail and further research with a wider range of pesticides is needed to develop generalised conclusions.

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AUTHOR'S DECLARATION

I confirm that the work presented in this thesis is my own original research undertaken as a PhD student at the University of York, and within the FESF team of the Food and Environment Reasearch Agency (FERA), York.Where the research draws on the work of others, this is clearly stated in the text. The water-sediment model in ModelMaker that is used in Chapter 5 was developed by Dr Wendy van Beinum, FERA.

Kanyapat Traisup

CHAPTER 1

1. INTRODUCTION

Studies investigating pesticides in Thailand focused on compounds that are now restricted such as the organochlorines (Kruawal et al., 2005; Poolpak et al., 2008; Samoh and Ibrahim, 2008). Some pesticides in Thailand are inappropriately used and managed (Plianbangchang et al., 2009). Those pesticides are potentially assimilated in crops, animals and the environment where the concentration can reach a harmful dose. Water-sediment systems are crucial for pesticide study in Thailand as rice cultivation is a major component of agriculture in Thailand and many reports showed pesticides were left over in crops (Panuwet et al., 2012) and surroundings (Jaipieam et al., 2009; Panuwet et al., 2012). Much recent research has considered routes of pesticide transfer into water and persistence of pesticides in simple systems such as water or soil/sediment alone; much less work has been done on what happens when pesticides enter natural water-sediment systems. Understanding the behaviour of pesticides in water and sediment phases will allow prediction of persistence of pesticides in the environment. More work on current-use unrestricted pesticides and fate of pesticides in water-sediment systems is required to support risk assessment, policy and health and safety.

Pesticides have been widely used in agriculture for a long time for crop protection. Pesticides have not only been used in agriculture, but also are used in households and industries to control pests and diseases transmitted by insects and/or fungi. Most of the pesticides used are potentially harmful contaminants to human health, non-target living organisms, and the environment in general. As a result of being continuously applied, common and/or persistent pesticides are frequently found as hazardous contaminants in soil (Riise et al., 2004), surface water (Kruawal et al., 2005; Samoh and Ibrahim, 2008) , groundwater (Jaipieam et al., 2009), and sediment (Poolpak et al., 2008). From treated fields, pesticides are potentially distributed to non-target areas by different carriers such as water, wind and soil particles. Especially, water can transport pesticides and/or soil particles sorbing pesticides to aquatic-sediment systems. Pesticides in water-sediment

systems have the potential to undergo various processes such as hydrolysis, photolysis, microbial degradation, sorption/desorption in soil/sediment, volatilization, and uptake by plants or animals (Katagi, 2006; vanLoon and Duffy, 2005). Physico-chemical properties of the pesticide itself and characteristics of the environment where the pesticide is present are influences on these processes (Katagi, 2006).

Pesticide fate modelling has been utilised to predict pesticide concentrations for new pesticides (unregistered) and currently-used pesticides in different environmental compartments. Predictions by models were often found to be different from measured data (Beulke et al., 2000). In general, prediction from models needs field data to validate the results as being able to represent the field situation. Dubus et al. (2003) suggested that part of the discrepancy will come from uncertainty in input data including uncertainty of model parameters. For example, fate of pesticides in the environment is a complex process and can vary from pesticide to pesticide and also field to field so half-lives of a pesticide from the pesticide database (PPDB, 2009) or the literature cannot describe all environmental situations.

Bromilow et al. (2006) showed that laboratory experiments were able to emulate fate of some pesticides including isoproturon, chlorotoruron, chlopyrifos, and pendimethalin in water-sediment systems under outdoor conditions but not others such as permethrin and difenoconazole. It is not clear from their work why the extrapolation was successful for some pesticides but not others. This implies that further research is required to examine the extrapolation from simple laboratory experiments to complex field systems. If data obtained from the laboratory could represent realistic conditions without requiring field data, there would be many advantages such as experiments being repeatable, less expensive and less time consuming.

1.1 Aim and objectives

The aim of this research is to understand the fate of selected pesticides in water-sediment systems and to determine whether laboratory experimental data coupled with mathematical modelling is able to represent behaviour in the field

The specific objectives are to:

1. Understand individual factors which influence fate of pesticides after entry into water.

2. Study the fate of pesticides in controlled water-sediment systems.

3. Determine the fate under more realistic conditions.

4. Use experimental data in TOXSWA to predict fate of pesticides in water-sediment systems.

The chapters of this thesis follow the objectives from understanding of the behaviour of metalaxyl-M and thiamethoxam in simple systems (water and sediment alone) through to a complex water-sediment system under field conditions.

Chapter 2 presents a literature review introducing routes of pesticide contamination of water, processes governing fate of pesticide in the environment, environmental models used to predict pesticide fate in water.

Chapter 3 reports the results of individual factors influencing hydrolysis and photolysis of thiamethoxam in water and sorption properties of thiamethoxam and metalaxyl-M in sediment. Hydrolysis and photolysis of thiamethoxam were investigated at varying pH in water (acidic, neutral and alkaline condition) and with different nitrate concentration and water types.

In Chapter 4 sorption studies of thiamethoxam and metalaxyl-M were carried out using a natural sediment that was used in the subsequent studies.

Chapter 5 reports the results of fate of the two pesticides in water-sediment systems under dark conditions excluding photolysis. The results were processed using ModelMaker to simulate dissipation of the two pesticides from water and sediment phases.

Chapter 6 reports the fate of two pesticides in water-sediment systems containing a single species of aquatic plant (*Myriophyllum spicatum*) under controlled conditions. The results demonstrate the role of the plants in dissipation of the two pesticides.

Chapter 7 reports the fate of the two pesticides in water-sediment systems under outdoor conditions (parallel experimental treatments to Chapter 6). Comparison of results from outdoor experiments with those from the laboratory experiment (Chapter 6) determined the effect of fluctuating light conditions (illuminated duration, light intensity) and temperature. The experimental data were used as input to the TOXSWA model to predict pesticide concentrations in water and sediment and to assess the ability of the model to extrapolate laboratory data to represent field behaviours.

Chapter 8 summarises the main conclusions and requirements for further work.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Environmental fate of pesticides

When pesticides are applied to target areas such as crops, some of the pesticide can be diluted by irrigation or rainfall then transported with water via runoff, drainage and leaching to non-target areas such as aquatic systems and groundwater; other fractions of the pesticide may be deposited on crop surface or volatilized and transported by wind currents or deposited from the atmosphere as shown in Figure 2-1 (Gavrilescu, 2005; vanLoon and Duffy, 2005). Pesticide in the atmosphere, water, and soil/sediment can be degraded via photolysis, hydrolysis, microbial degradation and biotic uptake.

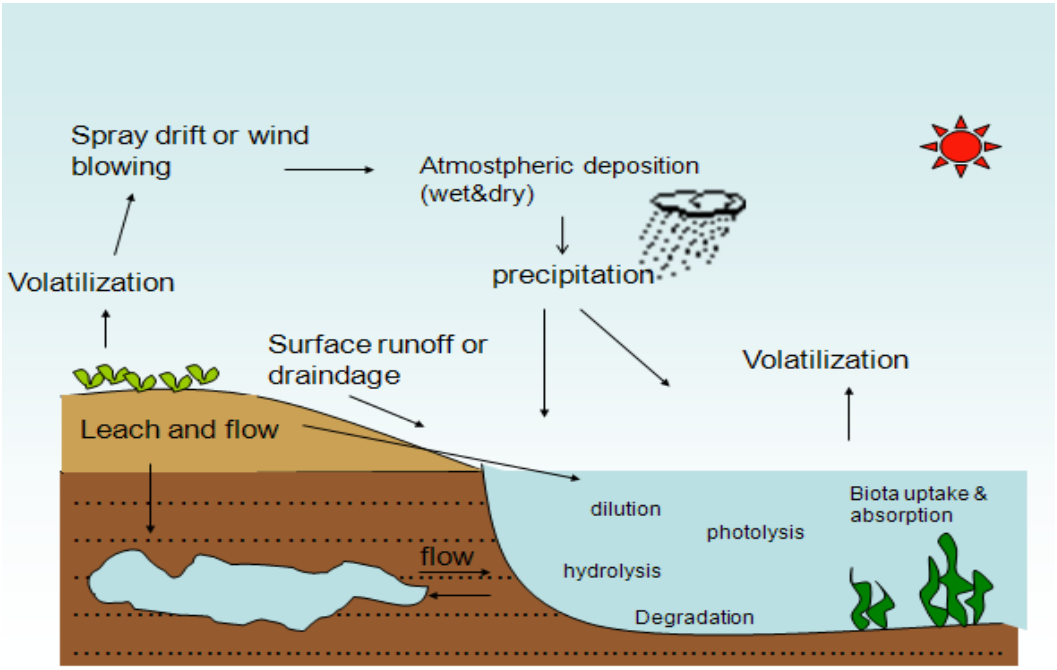

Figure 2-1 Major processes affecting pesticides after application (vanLoon and Duffy, 2005)

2.2 Routes of pesticide entry into water

Routes of pesticide entry into water include directly application to water to control pests/weeds (Carter, 2000). Indirect routes of entry include via deposition (wet and dry) of pesticide from the atmosphere, surface runoff, drainage and leaching (Carter, 2000).

Atmospheric deposition possibly occurs following spray drift or volatilisation of pesticide from crop surfaces, soil or water and/or erosion of fine soil particles able to be held in the atmosphere. Yeo et al. (2004) reported that atmospheric concentrations of organochlorine pesticides (heptachlor, chlordane, DDTs, hexachlorocyclohexanes and endosulfan) showed seasonal variation as the maximum and minimum concentration in a rural area (Ansung) and an urban area (Seoul) in Korea was in summer and winter, respectively. The authors found a correlation between the atmospheric concentration and temperature as the atmospheric concentration increased with increasing temperature suggesting re-volatilization of the pesticide from plant and soil surfaces.

Surface runoff (overland flow) is movement of water across the soil surface when inputs of water from rain/snow melt/irrigation on to the soil surface exceed the amount that can infiltrate into soil. Applied pesticide can move with surface runoff either dissolved in water and/or sorbed to eroded soil particle. Pesticide properties, soil characteristics and environmental conditions, including weather conditions, influence pesticide runoff. Pesticide properties such as aqueous solubility, sorption and persistence determine the amount of pesticide dissolved in surface runoff; pesticides with high aqueous solubility and less sorption to soil are likely to move with water runoff (Matocha et al., 2006). Pesticide persistence influences the amount available to move with runoff. Soil characteristics such as soil texture and soil moisture are important as water surface runoff is likely to occur in soil with saturated soil moisture and soil with a compacted layer as it is difficult for water to move downward through the soil. Rainfall/irrigation, vegetation and slope are environmental condition that affect on pesticide runoff (Patakioutas and Albanis, 2004; Triantafyllidis et al., 2006). Heavy rain/irrigation can cause transportation of

pesticide with surface runoff and soil erosion when rainfall intensity exceeds the infiltration capacity of the soil. Pesticide runoff may be greater in areas with steep slopes because runoff water moves more quickly resulting in less time for pesticide sorption to soil. Vegetation helps to slow surface runoff, and enhance bio-degradation of pesticide (Patakioutas and Albanis, 2004) resulting in reduced concentration of pesticide in water.

Drainage is the movement of excess water from soil through pipes. Riise et al. (2004) found that loss of pesticide via runoff and drainage varied among three fields and was determined by content of organic carbon, aggregate stability and porosity. The authors found that high organic content, large pore-volume and better aggregate structure of soil resulted in reduced concentrations of bentazone and propiconazole in runoff and drainage water due to greater microbial activity, favourable conditions for sorption and the soil being less prone to erosion. Loss of the two pesticides via surface runoff and drainage was <0.5% of that applied to the three agricultural fields (Riise et al., 2004). Loss of a mobile pesticide, (bentazone, K_{oc}~34 L kg^{-1}) was higher compared to a strongly sorbed pesticide, propiconazole (K_{oc}~1800 L kg^{-1}). Brown and van Beinum (2009) reviewed loss of pesticides via drainflow and found that the seasonal loss accounted from not detectable to 10.6% of initial amount based on 97 records in seven countries in Europe. The concentration and loss of pesticide to drains were significantly influenced by strength of pesticide sorption to soil, half-life of pesticide in soil, the interval between application and first drainflow and clay content of soil. The concentration and loss of pesticide decreased with high strength of sorption with a short half-life due to the applied pesticide being degraded and sorbed to soil. Generally, pesticide concentration was found to be highest in the first drainflow after pesticide application because there is a shorter time for sorption and/or degradation (Brown and Van Beinum, 2009).

Leaching is the movement of water downward through soil. Pesticide can contaminate groundwater if it dissolves in water so that it is able to leach. Lysimeter experiments under outdoor condition by Renaud et al. (2004) showed that leaching of three pesticides (isoproturon, chlorotoluron and triasulfuron) was influenced by sorption distribution coefficient resulting in losses in the order triasulfuron (K_{oc} 1.7

to 34 L kg^{-1}) > isoproturon (K_{oc} 66 to 68 L kg^{-1}) > chlorotoluron (K_{oc} 92 to 142 L kg^{-1}). The authors also found that preferential flow was an important transport process as the leached load increased with increasing clay content of soil. The authors suggested five factors that influence leached loads: (i) presence of macropores, (ii) sorption capacity of soils, (iii) degradation of pesticides in soil, (iv) sorption kinetics of pesticides and (v) diffusion of pesticides into soil-aggregates protecting the pesticide from leaching via preferential flow. A lysimeter experiment by Beulke et al. (2004) showed that chlorotoluron and isoproturon concentration in leached water decreased with increasing time from application at incubation temperatures of 5 and 15^{o}C. The authors explained that pesticide degradation in soil, sorption and diffusion of pesticides into intra-aggregate regions where caused less pesticide to be available for leaching. The concentration in leachate at 15^{o}C was smaller than that at 5^{o}C. The authors suggested that an increase in sorption of chlorotoluron and isoproturon at higher temperature resulted in less availability of the two pesticides for leaching.

2.3 Major processes governing fate of pesticide in the environment

Fate of pesticides in the environment will differ among pesticides, field and season as processes governing fate such as volatilization, photolysis, sorption, hydrolysis and biodegradation are influence by physico-chemical properties of the pesticide and environmental conditions.

2.3.1 Volatilization

Volatilization is the process whereby a pesticide changes in form from the solid and/or liquid phase into the gas phase (Racke et al., 1999). Volatilization of pesticide from matrices is influenced by other processes including transportation of pesticides to the surface of the matrix (water, soil, and plants), sorption to the surface of the matrix (Van Wesenbeeck et al., 2008), diffusion through the boundary layer, and transportation by air.

Factors influencing volatilization of pesticides are physico-chemical properties of pesticides (Guth et al., 2004) including vapour pressure, water solubility, Henry's

law constant, adsorption properties, and some environmental factors including soil moisture and soil/air temperature. Guth et al. (2004) reported that vapour pressure, water/air and soil/air coefficient can be used to predict volatilization from crop and soil surfaces based on 80 different chemicals, 123 soils and 71 crops. Direct and indirect measurement of volatile loss showed that chemicals with vapour pressure less than 10^{-3} and 10^{-4} Pa had negligible loss from soil and plants, respectively (Guth et al., 2004).

Incorporation into the matrix (such as soil and plants) results in decreased volatilization (Bedos et al., 2006). Loss of trifluralin via volatilization was very high (1900 ng m^{-2} s^{-1}) after applicationthen after 24 hours of application, loss of the pesticide via volatilization decreased to 100 ng m^{-2} s^{-1} (Bedos et al., 2006). The authors suggested that 99% of the loss of trifluralin occurred before the pesticide was incorporated into the soil. Additionally, different volatilization rates from different matrices were reported (Guth et al., 2004). Most volatilization rates from plant surfaces are higher than those from soil because there is generally less potential for incorporation into the matrix (Guth et al., 2004).

2.3.2 Photolysis

Photolysis occurs when compounds receive enough energy from either visible and/or ultraviolet light to cause breakdown of the molecule. There are two possible photolysis processes in water: direct and indirect photolysis (Hemond and Fechner-Levy, 1999; vanLoon and Duffy, 2005). There are various transformation processes that can occur within a molecule of pesticide receiving light energy including cleavage of a C-C bond generating a key radical, isomerization, ester cleavage, decarboxylation, or decarbonylation at an ester or ketone, dehalogenation at a C-halogen bond (Cl, Br and I), oxidation with O_2 or reactive oxygen species (Katagi, 2004). The reaction rate of direct and indirect photolysis depends on the absorption spectrum of the substance (Hemond and Fechner-Levy, 1999), presence of intermediate compounds inducing indirect photolysis, the emission spectrum of the light source (Katagi, 2006), light intensity, and the matrix (water, soil, plant or etc.) where photolysis occurs (Hemond and Fechner-Levy, 1999; Bhattacharjee and

Dureja, 2002). For instance, the photolysis rate of a sulfonylurea herbicide, tribenuron-methyl on a glass surface (0.0988 $days^{-1}$) was faster than the rate in soils (0.0633 and 0.0417$days^{-1}$ for alluvial, and red soils, respectively) (Bhattcharjeel and Dureja, 2002).

Direct photolysis is the process whereby pesticide directly absorbs light energy causing a chemical reaction within the molecule (Burrows et al., 2002; Hemond and Fechner-Levy, 1999).

Indirect photolysis occurs where light-absorbing molecules or photo-sensitizers absorb energy from sunlight and subsequently either transfer energy to the pesticide or in association with electrons or highly reactive species attack and degrade pesticides (Hemond and Fechner-Levy, 1999). Examples of highly reactive species are singlet oxygen ($^1O_2$) and hydroxyl radicals which can be formed by several processes including photolysis of nitrate ions (Hemond and Fechner-Levy, 1999).

Some chemicals act as sensitizers or radical initiators such as humic substances (Hemond and Fechner-Levy, 1999), riboflavin (Chan and Chu, 2009), phosphate (El Gaini et al., 2010), chlorophyll, nitrate and nitrite (Mack and Bolton, 1999; Nelieu et al., 2004; Shankar et al., 2007; Ukpebor and Halsall, 2012), and titanium dioxide (TiO_2).

Humic acids are naturally present in water; the light absorption wavelength of humic acids covers a wide range so they can compete in absorbing light energy with pesticides if the absorption wavelength overlaps, resulting in a decrease in photolysis rate. The presence of dissolved organic matter or humic acids can either increase or decrease the photodegradation rate of pesticides (Dimou et al., 2005; Pinna and Pusino, 2012; Ramezani et al., 2008; Xu et al., 2007). Xu et al. (2007) reported the effect of humic acids on photolysis of three chloroactanilide herbicides (acetochlor, propisochlor and butachlor); the photolysis rate of propisochlor increased at low concentration of humic acids (1 mg L^{-1}) whilst at higher concentration (5 and 10 mg L^{-1}), the rate decreased. Photolysis of acetochlor and butachlor was only inhibited in the presence of humic acids, namely the higher the concentration of humic acid, the less photolysis degradation. Dimou et al. (2005) reported that the photodegradation

rate of metalachlor increased in the presence of nitrate anions due to formation of hydroxyl radicals involved in photodegradation of metalachlor, the reverse effect was seen in the presence of dissolved organic matter due to competitive absorption of emitted photons from light energy.

2.3.3 Sorption to soil/sediment

Sorption to sediment or soil is a process whereby the pesticide molecule adheres to an active site of sorption (Gavrilescu, 2005; Harrison, 1999). Factors influencing sorption are soil properties, temperature, water content, pesticide properties, and experimental factors, including the role of ionic strength of the aqueous phase (Kah and Brown, 2006).

Many studies reported that properties of soil/sediment including organic matter content (Čadková et al., 2012; Kasozi et al., 2012; Sun et al., 2012), clay minerals (Peng et al., 2009; Polati et al., 2006) and aluminium and iron (hydr)oxides influence sorption (Harrison, 1999; Wang et al., 2008). Pesticides interact mainly with organic matter because hydrophobic pesticides are attracted to the hydrophobic sites of organic matter via hydrophobic sorption (Kah and Brown, 2006). Montmorillonite, kaolinite, and illite show different sorption properties due to Van der Waals forces and/or electrostatic interactions between ionic/polar pesticides and surface charges of the clay minerals (Harrison, 1999).

Environmental conditions including soil pH (Harrison, 1999; Muhamad et al., 2011) and temperature (Broznić and Milin, 2012) also affect sorption of pesticide. Muhamad et al. (2011) reported that sorption of paraquat to clay and clay loam soil was pH dependent, with sorption of paraquat increasing with increasing pH. Sorption of paraquat to the two soils was similar, namely sorption to clay soil was 3.57 and 4.05 µg g^{-1} at pH 2 and 11, respectively and the sorption to clay loam was 3.72 and 4.08 µg g^{-1} at pH 2 and 11, respectively. Sorption decreased with increasing temperature for imidacloprid (Broznic and Milin, 2012) and diuron (Liu et al., 2010) Broznic and Milin (2012) explained that the value of the thermodynamic parameter ΔH^o for imidacloprid was negative and small (-19.79 to -8.89 kJ mol^{-1}) suggesting

weak forces of interaction in accordance with a decrease in K_{oc} with increasing temperature suggesting that greater solubility of imidacloprid resulted in a decrease in sorption.

Sorption of pesticide to soil particles is influenced by properties of the pesticide. Hence ionisable compounds (cations) are likely sorbed to soil colloids due to the isomorphous substitution of a clay mineral substituent and/or the pH dependent charges on oxides of Fe, Al, Mn and Si (Harrison, 1999) whilst non-ionisable compounds are likely sorbed to soil humic material (Harrison, 1999) or colloidal organic matter. Kah and Brown (2007) reported that sorption of acidic ionisable pesticides was weaker than that of basic ionisable pesticides. Adsorption was negatively correlated with soil pH and positively correlated with carbon content. The authors suggested that prediction of sorption of acidic pesticide can be based on log D (K_{ow} corrected for soil pH), the soil organic carbon content, and a pesticide descriptor related to the Van der waals volume; sorption of basic pesticides was more complex and found to be specific to each compound.

Sorption is a dynamic process in which sorbed molecules can exchange between the solid and liquid phases. Many studies on sorption of pesticides reported sorption mechanisms related to one or more force interactions (Kah and Brown, 2006), including hydrophobic sorption, Van der Waals interaction, H-bonding, ionic exchange, charge transfer, ligand exchange, and cation (or water) bridging.

2.3.4 Hydrolysis

Hydrolysis is a chemical process where molecules react with water causing replacement by the hydroxyl group of water (OH^-) in an interacting molecule. Hydrolysis reactions can occur either by purely chemical or microbiological mechanisms (Connell, 2005; vanLoon and Duffy, 2005). The hydrolysis process can be represented as a simple equation:

$$R - X + H_2O \rightarrow R - OH + HX$$

where “R” represents a hydrocarbon group and “X” represents a halogen atom or ester group or analogue of an ester group (amide, thioester).

The pH of the water affects the hydrolysis rate of some pesticides. For example, degradation of phoxim over 24 hours ranged from 41% (pH 4) to 85% (pH 9) indicating that an increase in pH of water resulted in faster hydrolysis (Gatidou and Iatrou, 2011). Two sulfonylurea herbicides (pyrazosulfuronethyl and halosulfuron methyl) were hydrolyzed faster under acidic and basic conditions than neutral conditions (Zheng et al., 2008). The authors found that there were two hydrolysis pathways for the two herbicides, namely cleavage and contraction at the sulfonylurea bridge. Under acid conditions, cleavage and contraction occurred at similar rates whilst under alkaline conditions, chlorine substitution on halosulfuron methyl’s pyrazole ring made the herbicide more susceptible to sulfonylurea bridge contraction than pyrozosulfuronethyl under alkaline conditions. Additionally, the hydrolysis rate of the two sulfonylurea herbicides also depended on temperature (Zheng et al., 2008); when the temperature increased by 10^{o}C, the hydrolysis rate increased about 2.4 and 4.5 times for pyrazosulfuronethyl at pH 3 and 9, respectively and the hydrolysis rate increased about 2.9 and 3.2 times for halosulfuron methyl at pH 3 and 9, respectively. Other pesticides where hydrolysis is known to be temperature-dependent include mefenpyrdiethyl (Chnirheb et al., 2010), sulfonylurea herbicides (Zhen et al., 2008) and the fungicide cymoxanil (Morrica et al., 2004). The relationship between temperature and hydrolysis rate can be expressed by the Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

where k is hydrolysis rate (days^{-1}), E_a is activation energy (kJ mol^{-1}), R is gas constant = 8.314x10^{-3} kJ mol^{-1} K^{-1}, T is temperature in Kelvin (K) and A is a frequency factor describing the number of time two molecules will collide (days^{-1}).

2.3.5 Biodegradation

Biodegradation is a transformation process mediated by living organisms such as plants, algae, bacteria or fungi. Complex carbon compounds (including some toxic and synthetic substances) may be used as an energy source or nutrient substrate required for growth (Katagi, 2006; Navarro et al., 2000), or the compounds can be degraded without providing energy or nutrients (co-metabolism). Usually, co-metabolism occurs when enzymes of low specificity are produced to alter or degrade substrates; some compounds that are similar in structure to the target compounds may be transformed or degraded by the enzymes as well (Connell, 2005).

Structural variabiliy of compounds and bacteria with enzymes able to degrade compounds determine extent of biodegradation (Hussain et al., 2009; Murthy and Manonmani, 2007). Murthy and Manonmany (2007) reported that there were differences in biodegradation of hexaclorocyclohexane (HCH) isomers. The degradation of HCH-isomers by microbial communities was in the order of $\gamma > \alpha > \beta > \delta$ at 10 mg L^{-1} under conditions of an inoculum level of 100 μg protein mL^{-1}, pH 7.5, and at ambient temperature (26–28^{o}C) (Murthy and Manonmani, 2007). Environmental conditions including temperature and pH also affect biodegradation rate as described below.

- *Microbial degradation*

Most pesticides have been reported to be degraded by bacteria and fungi including DDT (Lin et al., 2012), cypermethrin (Rani and Juwarkar, 2012), and chlopyrifos (Briceño et al., 2012). Factors influencing microbial degradation include presence of plants/some animals (such as earthworms), soil moisture (El Sebai et al., 2010), temperature (Benoit et al., 2007), pH, carbon source concentration, soil organic matter and pesticide concentration (Caceres et al., 2008; Chiu et al., 2005; Druzina and Stegu, 2007; Lin et al., 2012; Rani and Juwarkar, 2012; Xie et al., 2011). In general, highest microbial activity is found for warm temperature, neutral pH and moist soil (Gavrilescu, 2005)

Xie et al. (2011) found pH, temperature, concentration of DDT and the presence of an additional carbon source affected degradation of DDT by the bacteria *Alcaligenes* strain KK. The degradation of DDT was maximal following addition of a carbon source (glucose) at a concentration of 0.5% and the degradation reduced at a carbon concentration of 1.5%. Fastest degradation was at 30^{o}C, whilst extreme temperature (10 and 50^{o}C) resulted in lowest degradation. The degradation increased with increasing pH of the medium (pH ranged from pH 4-10) where the degradation at pH 4 was lower than at other pH and the fastest degradation was at pH 6. The peak degradation of DDT was found at an application concentration of 10 mg L^{-1} and degradation rate decreased at a concentration of 20 mg L^{-1}.

The presence of other living organisms, including earthworms (Lin et al., 2012) and plants (Rani and Juwarkar, 2012), affects pesticide degradation via microorganisms. Lin et al. (2012) found that the earthworm *Eisenia foetida* enhanced microbial degradation of DDT in soil due to an increase in microbial biomass, carbon and nitrogen relative to the control whilst *A. robustus* E. Perrier enhanced DDT degradation via DDT bioavailability, soil aeration and intestinal digestion. DDT was degraded 50.0-64.2% and 48.2-70.8% for *Eisenia foetida* and *Amythas robustus* E. Perrier treatments, respectively after 360 days whilst DDT in the control was degraded 23.7%. Rani and Juwarkar (2012) showed that bacterial degradation of phorate (64$\pm$5% over 30 days) in the presence of the plants *Brassica juncea* was higher in comparison with the degradation (55$\pm$4% at concentrations of phorate of 10 and 20 µg ml^{-1}) in the treatments with bacteria alone in soil and the degradation (38$\pm$4%) in the treatment with the plants alone. Chen et al. (2012) showed that a co-culture of *Bacillus cereus* ZH-3 and *Streptomyces aureus* HP-S-01 was more effective in cypermethrin degradation in comparison with mono-culture; cypemethrin (50 mg L^{-1}) was metabolized 73.1%, 37.5% and 23.0% after 24 hours in co-culture, ZH-3 and HP-S-01 treatments, respectively.

- *Phytoremediation*

Plants are able to remove pesticides from the environment via a number of processes including direct uptake. Root exudates enhance bacterial degradation by providing

an additional carbon source and plant roots aggregate soil/sediment allowing more oxygen to reach the root zone (Gerhardt et al., 2009; Susarla et al., 2002). Physico-chemical properties of the pesticide (such as K_{ow}, solubility and volatility), mode of application, environmental characteristics (soil type, soil pH, organic matter, and temperature), plant species and climate factors will all affect pesticide uptake by plants (Gavrilescu, 2005).

Bouldin et al. (2005) found that uptake of atrazine and lambda-cyhalothrin from microcosms was different for two different plants (*Ludwigia peploides* and *Juncus effuses*). The highest pesticide concentration in *L. peploides* was 426.2 and 86.50 µg kg^{-1} at 24 hours for atrazine and lambda-cyhalothrin, respectively. In the same microcosm, the peak pesticide concentration in *J. effuses* was 343.4 µg kg^{-1} at day 14 for atrazine and 19.82 µg kg^{-1} at day 7 for lambda-cyholothrin. Bicalho and Langenbach (2012) also found that bioaccumulation of atrazine varied between two plants, *Cecropia hololeuca* Miq. and *Trema micranta* (L.) Blum. growing in a microcosm. The bottom of the microcosm was treated with atrazine at one-tenth of the field-recommended dose to investigate movement of contaminated groundwater to the upper soil layers and into plants. The authors found that the degradation of atrazine increased from 1.2% (control without plants) to 10.2-10.9% (microcosm with plants) of the applied amount after 25 to 30 days. The applied atrazine was taken up about 45$\pm$14% (with 64 g plant weight) and 35$\pm$16% (with 28 g plant weight) by *C. hololeuca* and *T. micrantha*, respectively and atrazine was mainly accumulated in roots and leaves. De Calvaho et al. (2007a) reported that uptake of non-ionised pesticides by roots of the submerged aquatic plant *Lagarosiphon major* was dominant for pesticide with log K_{ow} >1 and by roots of floating plant, *Lemna minor* with log K_{ow}>1.8. The uptake process of non-ionised pesticide was controlled by diffusion of pesticide into the plant followed by equilibration in the aqueous phase in the plant cells together with partitioning onto plant solids. Uptake of non-ionised pesticide had a positive correlation with log K_{ow} as pesticides with high lipophilicity were more likely to be taken up (De Carvalho et al., 2007a; de Carvalho et al., 2007b).

Peter et al. (2007) reported different uptake of p, p'-DDE from soil and compost by two plant species, *Cucurbita pepo* and *Cucurbita maxima*. Uptake of the pesticide by plants was seven to eight times higher from soil (1.4% organic carbon) than from compost (37.0% organic carbon). The authors suggested that organic carbon affected availability of DDE as demonstrated by rate of desorption of DDE from soil (16.3%) and compost (7.12%) and uptake by the plants.

A number of studies (Ahmad et al., 2012; Dams et al., 2007) reported that the action of plants and microorganisms in combination enhances pesticide degradation. For example, Dam et al. (2007) reported that a combination of presence of plants and microorganisms was efficient for pentachlorophenol degradation. The fastest degradation of pentachlorophenol was found in treatments with plants (*Triticum aestivum*) and microorganisms, *Sphingobium chlorophenolicum* (about 80% loss from initial concentration after 6 days) in comparison with other treatments; loss of the pesticide in control treatments (a loamy sandy soil with the pesticide), treatments with plants, and treatments with inoculum microorganisms was similar at about 10-15% at day 6. The presence of microorganisms reduced toxicity of pentachlorophenol to winter wheat (*Triticum aestivum*) as average plant weight in the presence of the pesticide (0.3 g) was significantly smaller than that in the presence of microorganisms (0.6 g) and plants alone without the pesticide (0.6 g). The authors also found that an increase in the population number of *S. Chlorophenolicum* in treatments with plants resulted in an increase in degradation of the pesticide and reduced toxicity to the plants. A similar finding was found by Ahmed et al. (2012) that there was enhanced degradation of chlopyrifos in contaminated soil in the presence of bacteria strain *Bacillus pumilus* C2A1 together with ryegrass, *Lolium multiflorum*. Degradation of chlopyrifos (at applied concentration of 50 mg kg^{-1}) was 11, 89, 76 and 98% for control (no inoculation and no plants), treatment with the bacteria, treatment with plants, and treatment with a combination of bacteria and plants, respectively.

2.4 Mathematical models to describe the fate of pesticides in surface water

Mathematical models have been developed and used as a tool to simulate and predict fate of pesticide in space and time because input parameters within the models can be adjusted resulting in an illustration under simulated scenarios (Wainwright and Mulligan, 2004). There are a number of models that can describe fate of pesticide in pesticides in surface water including ABIWAS, BASINS, SWAT, MIKE-SHE, HSPF, CHEMCAN, GIBSI, SLOOT.BOX, WASP, TOXSWA and EXAMS (Holvoet et al., 2007; Quilbe et al., 2006). Adriaanse et al. (1997) summarized the features of the main surface water models as given in Table 2-1.

A set of models comprising SWASH, MACRO, PRZM and TOXSWA has been used to estimate predicted environmental concentrations of applied pesticides supporting the pesticide registration procedure in the Netherlands and the EU (Adriaanse et al., 2002; Beltman and Adriaanse, 1999). Padovani and Capri (2005) reported that the model over estimated predicted pesticide concentrations in water by a factor of eight under Mediterranean climatic conditions base on two scenarios A and B. Knabel et al. (2012) reported that FOCUS_TOXSWA tended to overestimate pesticide concentration (five organophosphorus, endosulfan and ten pyrethroid) in water (overestimate ranged from 57 to 96%) and sediment (overestimate ranged from 51 to 100%) based on 122 measured field concentrations from 22 field studies in the EU.

McCarthy et al. (2007) modified a steady-state EXAMS model to simulate pesticide concentrations in a tidally-influenced ecosystem. The steady-state EXAMS model does not allow simulation of fate of pesticide under temporal change in flow and water volume so the authors created a time variant tidally-driven model. The authors found that when important environmental parameters (such as how pesticide concentration change by volume and area fluctuated with the tide) were included in model simulation, it improved accuracy of predictions for metolachlor (comparison with prediction by the steady-state EXAMS).

A review by Quilbe et al. (2006) based on 36 models of pesticide fate showed how variability in processing and data requirement for each model contributes to different strengths and weaknesses. Most of the models require data about weather (temperature, rainfall), soil properties (organic matter) and pesticides properties (sorption, degradation). In general, the models also need field data (such as pesticide concentration) to validate output of the model as discrepancy between model results and observed data is likely to occur. Beulke et al. (2000) found that the persistence of pesticides in soil obtained from a model overestimated field behaviour by more than a factor of 1.25 for 43.8% of 178 studies whilst underestimated persistence occurred in 16.9% of cases. There were a number of possibilities that contributed to the discrepancy including difference in temperature and soil moisture conditions between laboratory and field (generally, static conditions in the laboratory and fluctuating conditions in the field), biological, chemical and physical properties of prepared soil may be different from soil in the field, difference in laboratory experimental conditions (applied concentration of pesticide, temperature) used to obtain half-life in the pesticide, and variation in persistence of pesticide in different seasons and fields (Beulke et al., 2000).

As there are several alternative models for fate of pesticide in surface water, the model selected by the user will depend on characteristics including availability of required data, fit with the purpose of the study, model availability (some models are free for download whilst others have to be purchased) and ease of use (Quilbe et al., 2006).

Table 2-1 Main features of models for pesticide fate in surface (Adriaanse et al., 1997)

Model	Layout water network	Hydrology	Entry routes	Pesticide processes	
				Water column	Sediment
ABIWAS	One segment	Steady state	Initial concentration	- Only abiotic degradations are separated in input data - Sorption to suspended solids is considered	- Sediment layer does not included
SLOOT.BOX	One segment	Steady state	Pulse type input	- Degradation consider as a whole degradation (it does not differentiated as hydrolysis, photolysis and biodegradation) - Sorption to suspended solids is considered	- Sedimentation is described but do not calculate predicted environmental concentration in sediment
EXAMS	Many segment (include branches)	Steady state	Pulse or continuous type input	- Degradation is distinguish between hydrolysis, photolysis, redox reaction and biolysis - Sorption to suspended solids and plankton included	- Calculate pesticide concentration in sediment - Sorption to solid phase, sediment, benthos is described but sedimentation and water flow do not included
WASP	Many segment (include branches)	Dynamic	Pulse or continuous type input	- Degradation is differentiated to hydrolysis, photolysis, redox reaction and biolysis - Sorption to suspended solids, plankton included	- Calculate pesticide concentration in sediment, - Sedimentation, sorption to solid phase, sediment and water flow including benthos included
TOXSWA	Different segment (no branches)	Steady state	Pulse or continuous type input	- Degradation consider as a whole degradation - Suspended solids, macrophyte are considered	- Calculate pesticide concentration in sediment - Not concern sedimentation - Sorption to solid phase and sediment, water flow included

2.5 Conclusions

A number of studies reported pesticide contamination in water in Thailand and most reports concern banned/restricted pesticides (Samoh and Ibrahim, 2008; Poolpak et al., 2008; Kruawal et al., 2005; Boonyatummanond et al., 1997). There is limited study of currently-used pesticides and this needs more research because it is possible that currently-used pesticides can contaminate the environment including being assimilated at harmful doses into biota. Knowledge on currently-used pesticides will help to guide policy planning and management.

Models have been widely used to predict fate of pesticides in the environment. However the predictions are often found to deviate from measured data (Knabel et al., 2012 and Beulke et al., 2000) as fate of a pesticide is determined by multiple processes and will differ amongst pesticides and under different environmental conditions (pH, light intensity and temperature). Experimental studies can performed to determine influence of each factor on fate of pesticides and so to reduce uncertainty in input data to the models. Further studies are needed to determine whether experimental data coupled to models provide a reasonable prediction for fate of pesticides under field conditions.

CHAPTER 3

3. EFFECT OF WATER TYPE, PH AND NITRATE CONCENTRATION ON PHOTO-TRANSFORMATION OF THIAMETHOXAM

3.1. Introduction

Photo-transformation can be classified as direct or indirect photolysis. Direct photolysis occurs when a molecule absorbs energy from light which results in the molecule becoming unstable and degrading by itself (Hemond and Fechner-Levy, 1999). Indirect photolysis occurs when reactive molecules absorb energy and then react with pesticides, resulting in breaking down the pesticide molecule (Hemond and Fechner-Levy, 1999). There are several potential active molecules such as humic acids (Xu et al., 2007), nitrate and nitrite anions that induce an indirect photolysis reaction (Mack and Bolton, 1999; Nelieu et al., 2004; Shankar et al., 2007).

Nitrate anions absorb light energy between 290 and 400 nm with λ_{max} 302 nm whilst nitrite anions have λ_{max} of 352 nm . Irradiation of nitrate anions causes a formation of hydroxyl radicals and nitrite radicals (Nelieu et al., 2004; Shankar et al., 2007; Nelieu et al., 2008):

$$NO_3^- + h\nu \rightarrow NO_2^o + O^{o-}$$

$$O^{o-} + H^+ \leftrightarrow OH^o$$

$$NO_3^- + h\nu \rightarrow NO_2^- + O\,(^3P)$$

$$NO_2^o + NO_2^o \rightarrow N_2O_4$$

Irradiation of nitrite anions induces a number of pathways (Nelieu et al., 2004; Shankar et al., 2007 and Nelieu et al., 2008) giving OH^o, NO^o and NO^o_2 radicals:

$$NO_2^- + hv \rightarrow NO^o + O^{o-}$$

$$NO_2^- + hv \rightarrow NO_2^o + e_{aq}^-$$

$$e_{aq}^- + O_2 \rightarrow O_2^{o-}$$

$$O_2^{o-} + NO_2^- + 2H^+ \rightarrow H_2O_2 + NO_2^0$$

Transformation products of photolysis vary depending on how the photo-radical reacts with the parent compound. The reaction could be hydroxylation of a phenyl ring, N-terminus substitution or Cl/OH substitution (Nelieu et al., 2004). Nitrate and nitrite anions occur naturally, and nitrate can also be added in agricultural areas by farmers, resulting in contamination of water resources. Hence it is interesting to investigate whether nitrate has an influence on pesticide degradation by photolysis.

In water systems, there may be concurrent hydrolysis of the pesticide during photolysis of pesticides. Hence a measured rate constant of reaction is based on the rate constant of photolysis and the rate constant of hydrolysis. In order to get a rate constant solely for photolysis, it is necessary to carry out a parallel experiment in the dark to determine a rate constant of hydrolysis.

Two currently-used pesticides; metalaxyl-M and thiamethoxam, were selected to study the fate of pesticides in water-sediment systems. Metalaxyl-M is moderately sorbed in soil/sediment whilst thiamethoxam is less strongly sorbed. Metalaxyl-M is a fungicide used to control various diseases such as downy mildews, late blight, damping off and root, stem and fruit rots in sugarcane, mustard, rapeseed, sunflower, maize, tobacco, tomato and various other crops (Timlin, 1997; Sukul and Spiteller, 2000). It is a systemic fungicide with curative and protective action, absorbed through the leaves, stems and roots. In fungi, metalaxyl-M inhibits protein synthesis by interference with the synthesis of ribosomal RNA. Metalaxyl-M is highly water soluble (Table 3-1). The compound is resistant to photolysis and hydrolysis but it can

be degraded in soil moderately quickly under aerobic conditions. Metalaxyl-M is moderately persistent in water-sediment systems (half-life 56 days; PPDB, 2008). Toxicity of this pesticide is classified as moderate to birds (Colinus virginianus), fish (Oncorhynchus mykiss) and aquatic invertebrates (Dapnia magna) whereas toxicity is low to Lemna gibba and arthropods (Tomlin, 1997).

Thiamethoxam is a neonicotinoid insecticide used to control a wide range of pests such as hopper species, aphids, whiteflies, thrips, mealybugs, wireworms and ground beetles (Tomlin, 1997). The action of thiamethoxam is broad spectrum and systemic with contact and stomach action as a nicotinic acetylcholine receptor (nAChR) agonist. In plants, thiamethoxam can be either taken up via the roots being distributed via xylem to protect new growing shoots and/or penetrate into the leaf lamina to control pests on the lower side of the leaf as a result of the good translaminar activity. Thiamethoxam is highly water soluble (Table 3-1), and sorption to organic carbon is relatively weak (Table 3-1). Thiamethoxam is not dissociated and is non-volatile (Table 3-1). Thiamethoxam is resistant to hydrolysis except under alkaline conditions (above pH 8). The compound is rapidly degraded via photolysis but it is persistent in soil. Thiamethoxam is degraded moderately quickly in water-sediment systems. Toxicity of this pesticide is classified as moderate to birds (Anas platyrhynchos), mammals and aquatic invertebrates (Daphnia magna) whereas it has low toxicity to Lemna gibba and fish (Oncorhynchus mykiss) (Tomlin, 1997).

The aim of these experiments was to investigate the influence of pH and water type on photo-degradation of thiamethoxam in water and the influence of nitrate and water type on photo-degradation of thiamethoxam in water. Two separate experiments were undertaken to investigate the effects of pH and nitrate. Both experiments also compared photolysis in natural water with that in pure water.

3.2. Material and methods

There is a range in the susceptibility of pesticides to photolysis. There were two pesticides of interest for this project (thiamethoxam and metalaxyl-M) and Table 3-1 gave their most important properties. Only thiamethoxam is subject to significant

photolysis (Table 3--1) so this was the only compound used in the photolysis experiments.

Table 3-1 Major properties of metalaxyl-M and thiamethoxam (PPDB, 2009)

	Metalaxyl-M	Thiamethoxam
Pesticide type	Fungicide	Insecticide
Chemical group	Phenylamide	Neonicotinoid
Chemical Formula	$C_{15}H_{21}NO_4$	$C_8H_{10}ClN_5O_3S$
Molecular Mass(g $mole^{-1}$)	279.33	291.71
Solubility in water at 20°C (mg L^{-1})	7100	4100
Solubility in organic solvents at 20°C (mg L^{-1})	550000 in Benzene 9100 in Hexane 650000 in Methanol 750000 in Dichloromethane	48000 in acetone 7000 in ethyl acetate 1 in hexane 680 in toluene
Vapour pressure at 25°C (mPa)	0.75	$6.60x10^{-06}$
Henry's Law constant at 25°C (Pa m^3 mol^{-1})	$1.60 x10^{-05}$	$4.70x10^{-10}$
Octanol-water partition coefficient at pH7, 20°C	P: 44.67 Log P: 1.65, low	P: -0.13
Dissociation constant at 25°C (pKa)	0	Not applicable Note: no dissociation
Aqueous hydrolysis DT50 at pH 7, 20°C (days)	106	pH sensitive: stable pH 1 to pH 7, DT50 11.5 days at pH 9, all at 20°C
Water-sediment DT50 (days)	56	40
Water phase only DT50 (days)	56	30.6
Aqueous photolysis DT50 at pH 7 (days)	Stable	2.7

Thiamethoxam (99.7% purity) was purchased from Sigma-Aldrich Ltd. Methanol and pure water (HPLC Fluorescence grade) were purchased from Fisher Scientific Ltd. $NaNO_3$ (98.0% purity) was purchased from Alfa Aesar Company.

3.2.1. Nitrate experiment

Natural water from an artificial lake at the Food and Environment Research Agency (FERA) (54^o 0' 56"N; 0^o 58' 10"E) was collected in July 2009 containing nitrate at 0.447 mg L^{-1}. A report by WHO (2011) reported that nitrate concentration in surface water ranged from 0 to 18 mg L^{-1} (WHO, 2011) and the concentration can be increase by agricultural runoff and human/animal waste. Nitrate concentrations at 25 and 100 mg L^{-1} were selected to represent medium and high concentration in water, respectively. Nitrate solution was prepared by using $NaNO_3$ dissolved in pure water and in natural water to give concentrations of 25 and 100 mg NO_3^- L^{-1}. Subsequently, solutions were used to make up thiamethoxam solutions at a concentration of 2 mg thiamethoxam L^{-1}. Aliquots of 20 mL of the solutions were placed into quartz tubes to give two sets (light set and dark set) of three replicates of each nitrate concentration and water type. There was no blank employed in this experiment.

The experiment was carried out in a "Suntest" apparatus (Heraeus, Hanau, Germany) with an emission range of 300-1500 nm at a light intensity of 1.27 kW m^{-2}. The temperature of the "Suntest" apparatus in operation was 31 ± 2^oC. The tubes for the dark experiment were wrapped in aluminum foil and then incubated under the same conditions as the light experiment. Aliquots of 1 mL were removed simultaneously from the light sets after 0, 0.5, 1, 2, 4 and 6 hrs. Aliquots from the dark set were collected only after 0 and 6 hrs. All samples were analyzed by HPLC.

3.2.2. pH experiment

Natural water from the lake at FERA was collected in August 2009. Natural water and pure water were adjusted to pH 5, 6, 7, 8, 9 and 10 using buffers recommended within

OECD Guideline 316 for direct photo-transformation of chemicals in water (Organisation for Economic Co-operation and Development, 2008).

0.05M NaH_2PO_4, KH_2PO_4, and H_3BO_3 were made up and then the base/acid solution was added dropwise until reaching the desired pH. A NaH_2PO_4/HCl solution was used to adjust pH in the range of 3 to 6, whilst a KH_2PO_4/NaOH solution was used to adjust pH in the range of 6 to 8, and water pH in the range of 8 to 10 was adjusted using a H_3BO_3/NaOH solution. Thiamethoxam was dissolved into the buffered solutions to give a final concentration of 2 mg thiamethoxam L^{-1}. Aliquots of 20 mL of thiamethoxam in buffer were placed into quartz tubes to give two sets of three replicates of each pH and water type. There was no blank employed in this experiment.

The experiment was again carried out in the "Suntest" apparatus. Aliquots of 1 mL were removed simultaneously from the light set after 0, 0.5, 1, 2, 4 and 7 hrs. Aliquots from the dark set were collected only after 0 and 7 hrs. All samples were analyzed by HPLC.

3.2.3. HPLC analysis

Pesticide concentrations were determined by HPLC-UV using an Agilent 1100 Series apparatus equipped with two pumps, an auto sampler, a photodiode array detector (model Agilent 1100 Series, G1365B MWD) and a C_{18} reversed-phase column (Supelco Discovery C18, 150 x 4.6 mm, 5 μm). Mobile phases were mixtures of water acidified with 0.1% phosphoric acid and methanol at a constant flow rate of 1 mL min^{-1}. The absorbance was measured at 252 nm. The limit of detection for thiamethoxam ($\pm$standard deviation) in water was 0.01$\pm$0.003 mg L^{-1}. The retention time of thiamethoxam was 4.8$\pm$0.2 mins.

3.2.4. Processing of results and statistics

It was assumed that three degradation processes (photolysis, hydrolysis and biodegradation) were operating concurrently in irradiated samples. The dark samples

were subject to hydrolysis and biodegradation. The photolysis rate constant was calculated as the difference between the overall rate constant and the hydrolysis rate constant:

$$k_{photolysis} = k_{overall} - k_{hydrolysis+biodegradation}$$

where $k_{photolysis}$ is photolysis rate constant (day^{-1})

$k_{overall}$ is overall (hydrolysis + photolysis+biodegradation) rate constant (day^{-1})

$k_{hydrolysis+biodegradation}$ is hydrolysis rate constant plus biodegradation rate constant (day^{-1})

Photolysis and hydrolysis were assumed to be governed by first-order degradation kinetics. This was checked by fitting a first-order equation to the data using an Excel spreadsheet (created by Dr Sabine Beulke, Food and Environment Research Agency) and examining the residuals. The equation for calculation of a first-order rate constant is:

$$C_t = C_0 e^{-kt}$$

where C_t is test chemical concentration at time t ($mg\ L^{-1}$)

C_0 is initial test chemical concentration at time t=0 ($mg\ L^{-1}$)

k is the first-order rate constant ($days^{-1}$)

t is time (days)

The half-life can be calculated by substituting the first-order rate constant into the following equation:

$$t_{\frac{1}{2}} = \frac{ln2}{k}$$

where $t_{\frac{1}{2}}$ is the half-life (days)

Statistical analyses were carried out using GenStat Release 12.1. Two-way ANOVA was used to investigate any treatment-related differences.

3.2.5. Sample absorbance

Solutions used in the photo-transformation experiment were investigated for any shift in absorbance spectra profile that would indicate a change in the chemical properties of the systems using a UV-visible recording spectrophotometer, UV-160A Shimadzu. Measurement was made against a matrix-matched solution (without thiamethoxam). Samples in pure and natural water were scanned for absorbance including (i) nitrate 25 and 100 mg L^{-1} (ii) pure water with pH of 5.01, 5.94, 7.08, 8.10, 9.19, 10.11 and natural water with pH of 4.99, 6.09, 7.05, 8.25, 9.09, 10.08 (iii) humic acids (10 mg L^{-1}). Humic acids were included in the sample absorbance measurement because humic acids are commonly found in natural water (Connell, 2005).

3.3 Results

3.3.1. Fitting test to first-order kinetics

Thiamethoxam concentration was plotted against time to check whether the data fitted to first-order kinetics. An example of thiamethoxam in pure water adjusted to pH 9.03 is given in Figure 3-1 and the residual plot is shown in Figure 3-2. The calculation for single first-order kinetics was close to measured data indicating that the measured data were a good fit with the first-order degradation kinetics and this was supported by the random dispersal of residuals and a Chi^2 statistic test. In the example shown in

Figure 3-1, Chi^2 was 1.35 and was smaller than the acceptance criteria at $P<0.05$ of 9.488. All the fitting parameters and statistical results are given in Appendices A-2 and A-3 for pure and natural water, respectively.

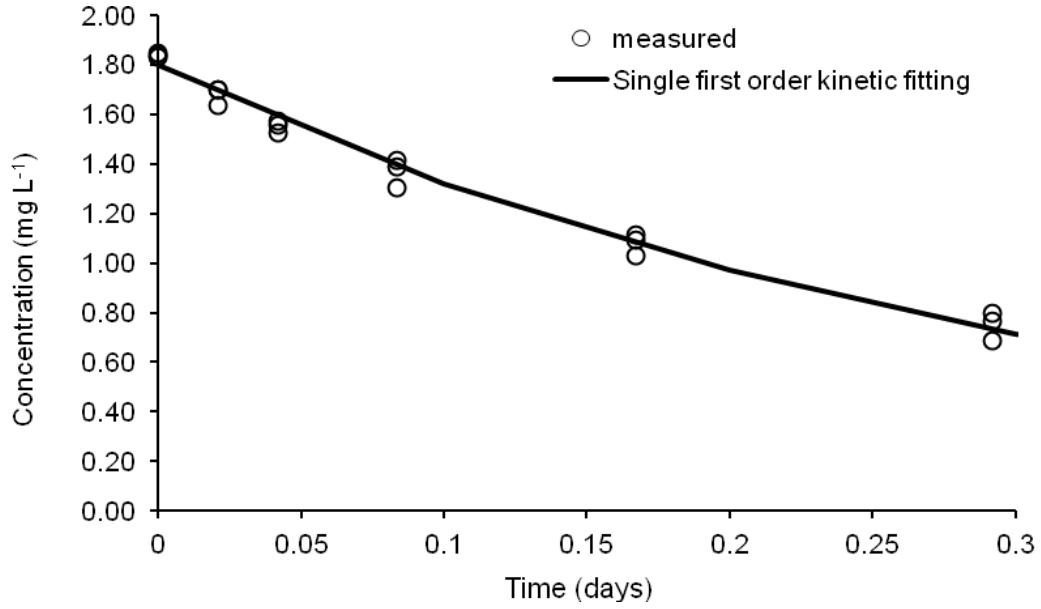

Figure 3-1 Fitting of first-order kinetics to the change in thiamethoxam concentration with time in pure water adjusted to pH 9.03 under radiation conditions.

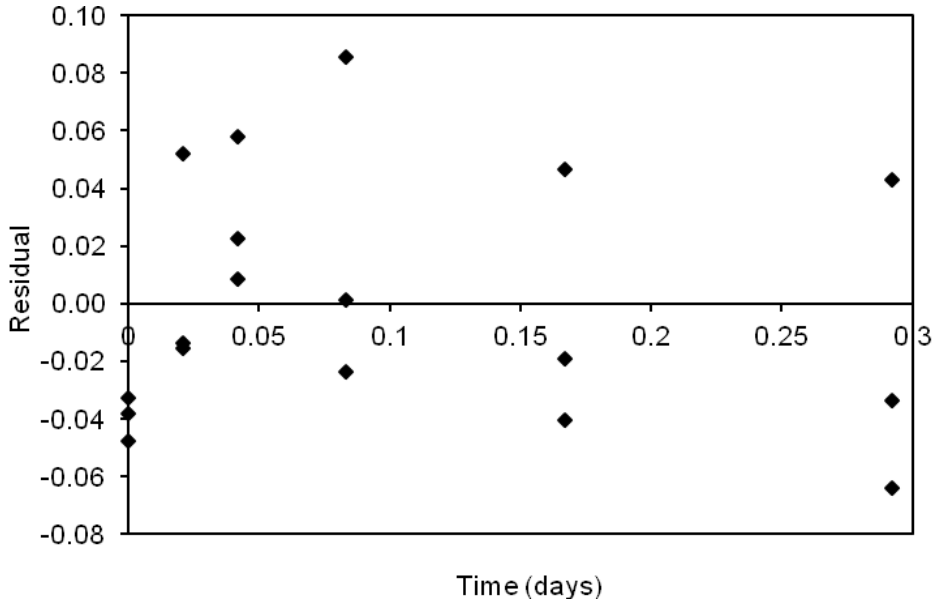

Figure 3-2 Plot of residuals calculated as the difference between measured and simulated thiamethoxam concentration shown in Figure 3-1

3.3.2. Nitrate experiment

There was negligible loss of thiamethoxam under dark conditions. The percentage of thiamethoxam remaining after 6 hours in pure water was 99.6±0.3, 99.8±0.3, and 99.6±0.2% at 0, 25 and 100 mg NO^-_3 L^{-1}, respectively. In natural water, the percentage of remaining thiamethoxam showed similar values at 97.9±2.3, 99.4±3.1, and 99.7±1.1% at 0, 25 and 100 mg NO^-_3 L^{-1}, respectively. It was assumed that the rate constant for hydrolysis and biodegradation of thiamethoxam was zero for the conditions studied.

Photolysis rate constants for thiamethoxam at different nitrate concentrations (very low, moderate and very high) were 3.01±0.3, 2.62±0.2 and 2.39±0.2 day^{-1}, respectively in pure water and 2.09±0.2, 2.01±0.2 and 2.02±0.05 day^{-1}, respectively in natural water. Figure 3-3 suggests no effect of nitrate concentration on photolysis in natural water but there was a negative relationship between photolysis and nitrate concentration in pure water.

Two-way ANOVA (Table 3-2) suggested that nitrate concentration ($p<0.01$), type of water ($p<0.001$) and nitrate concentration coupled with type of water ($p<0.05$) were significant influences on the rate of photolysis of thiamethoxam.

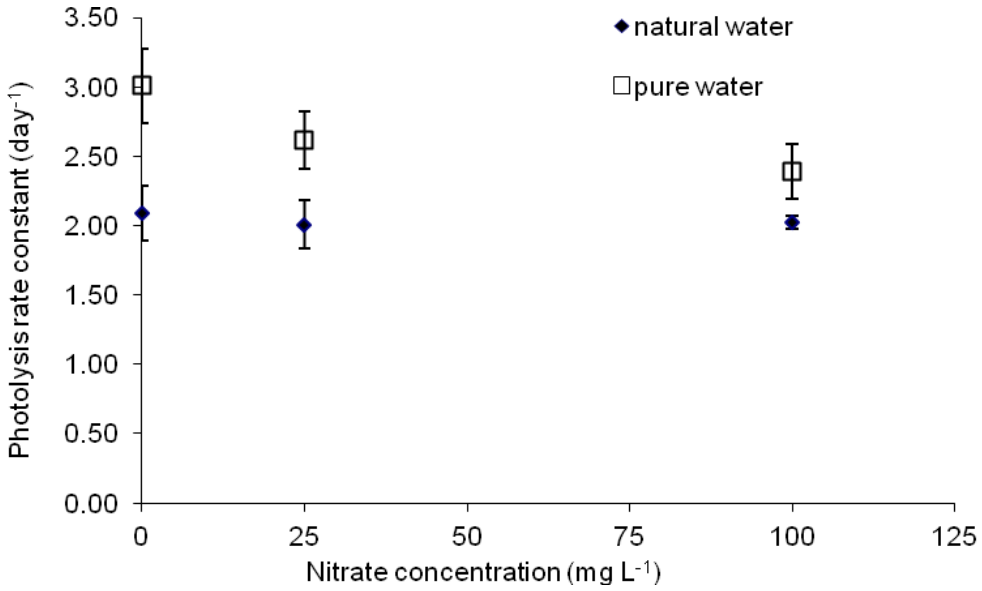

Figure 3-3 Photolysis rate constant of thiamethoxam in pure and natural water as a function of nitrate concentration

Table 3-2 Analysis of variance of influence of nitrate concentration on photolysis rate constant of thiamethoxam on water type.

Source of variation	Degrees of freedom	Sum of squares	Mean squares	Variance ratios	F-probability
Replicate stratum	2	0.254	0.127	6.61	
Replicate.*Units*stratum					
Nitrate concentration	2	0.370	0.185	9.62	0.005
type of water	1	1.80	1.80	93.75	<0.001
Nitrate concentration*type of water	2	0.229	0.115	5.96	0.020
Residual	10	0.192			
Total	17	2.85	0.0192		

3.3.3. pH experiment

The hydrolysis study under dark conditions (control set) showed a small loss of thiamethoxam over the study period at pH 5, 7 and 8. The hydrolysis rate increased dramatically when pH was increased to pH 9 and above as shown in Figure 3-4. Hydrolysis rate constants in pure water at pH 5, 7, 8, 9 and 10 were 0.0222±0.0573, 0.0438±0.0810, 0.0254±0.0139, 0.547±0.082 and 3.06±0.184 day^{-1}, respectively (Appendix A-2). The hydrolysis rate constant in natural water at pH 5, 7, 8, 9 and 10 were 0.0121±0.0076, 0.0075±0.0066, 0.0196±0.0093, 0.343±0.018, and 3.08±0.416 day^{-1}, respectively (Figure 3-4; Appendix A-3). The two-way ANOVA (Table 3-3) showed that only pH of water had a significantly effect on the hydrolysis of thiamethoxam ($p<0.001$).

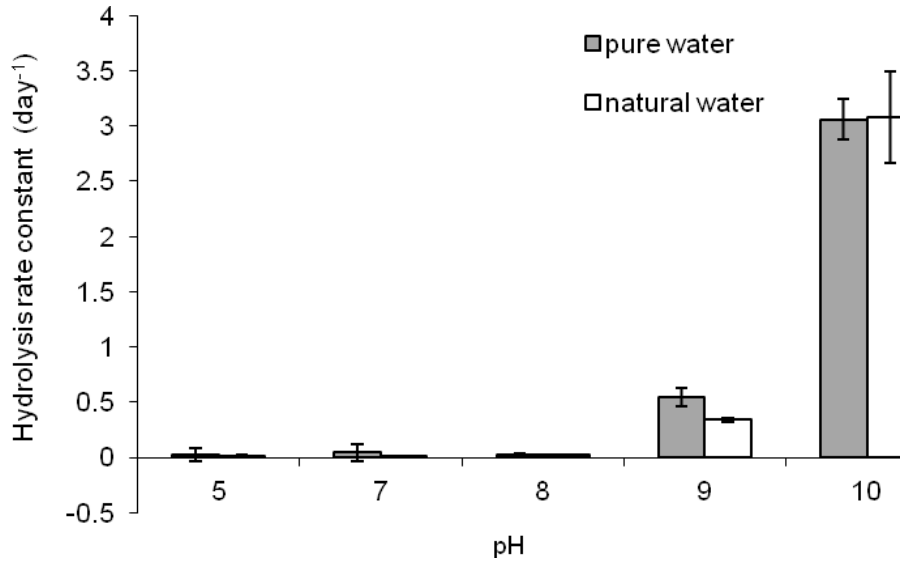

Figure 3-4 Hydrolysis rate constant of thiamethoxam as a function of pH in pure and natural water.

Table 3-3 Analysis of variance of hydrolysis rate constant of thiamethoxam with varying type of water and pH.

Source of variation	Degree of freedom	Sum of squares	Mean squares	Variance ratios	F-probability
Replicate stratum	2	0.0850	0.0425	2.11	
Replicate.*Units*stratum					
pH	4	38.9	9.73	482	<0.001
Type of water	1	0.0815	0.0815	4.04	0.060
pH*type of water	4	0.0620	0.0155	0.77	0.560
Residual	18	0.363	0.0201		
Total	29	39.5			

The photolysis rate constants of thiamethoxam at pH 5, 7, 8, 9 and 10 in pure water were 2.14±0.27, 1.64±0.07, 1.97±0.03, 2.46±0.34 and 11.6±2.42 day^{-1} (Appendix A-2), respectively. The photolysis rate constant of thiamethoxam in natural water was 1.90±0.17, 2.01±0.08, 1.74±0.27, 2.64±0.35, and 11.32±0.56 day^{-1}, at pH 5, 7, 8, 9 and 10, respectively (Appendix A-3). The largest photolysis rate constant in pure and natural water was at pH 10 as shown in Figure 3-5. The ANOVA showed a highly significantly positive effect of pH on photolysis under alkaline conditions ($p<0.001$, Table 3-4). In this case, the statistics showed no significant effect of type of water because there was no consistent trend in photolysis rates in pure water and natural water with varying pH; the photolysis rate of thiamethoxam in pure water was less than that in natural water at pH 7 and 10, but the rate in pure water was higher than that in natural water at pH 5, 6 and 8.

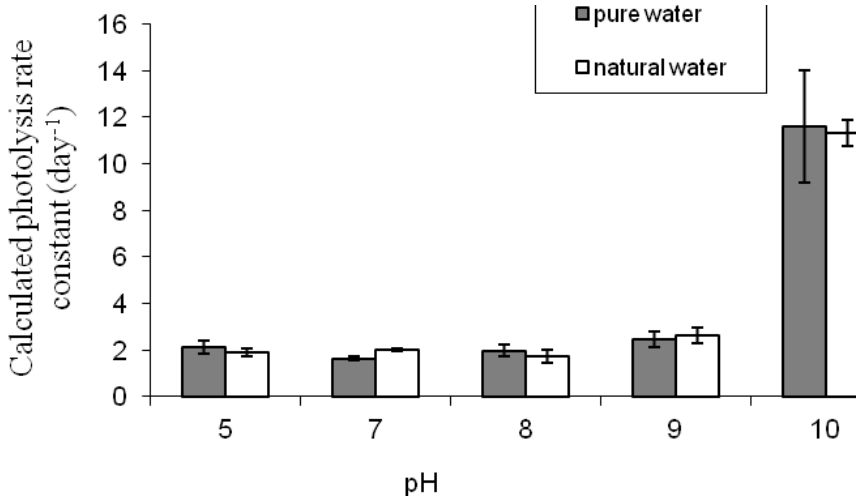

Figure 3-5 Photolysis rate constant of thiamethoxam in pure and natural water as a function of pH

Table 3-4 Analysis of variance of photolysis rate constant of thiamethoxam with varying type of water and pH.

Source of variation	Degree of freedom	Sum of squares	Mean squares	Variance ratios	F-probability
Replicate stratum	2	5.41	2.70	1.55	
Replicate.*Units*stratum					
pH	5	418	83.6	48.1	<0.001
Type of water	1	2.35	2.35	1.35	0.258
pH*type of water	5	10.4	2.09	1.20	0.343
Residual	22	38.3	1.74		
Total	35	475			

3.3.4. Sample absorbance

The absorption profiles shown in Figure 3.6-3.9 were from matrix-matched systems, so indicate absorption of light by thiamethoxam under a range of different conditions. This allows evaluation of whether there were chemical transformations under different conditions that may have changed the route of photoloysis. There was no significant absorption of light at wavelengths over 300 nm in either pure or natural

water. This result is in accordance with the literature (Milz et al., 2012). Light absorption profiles showed no shift with varying pH (Figure 3-6 and 3-8) or in the presence of humic acids in the two waters (Figure 3-7 and 3-9). This suggests that there was no interaction between the thiamethoxam molecules and humic acids or change in the structure of thiamethoxam with pH.

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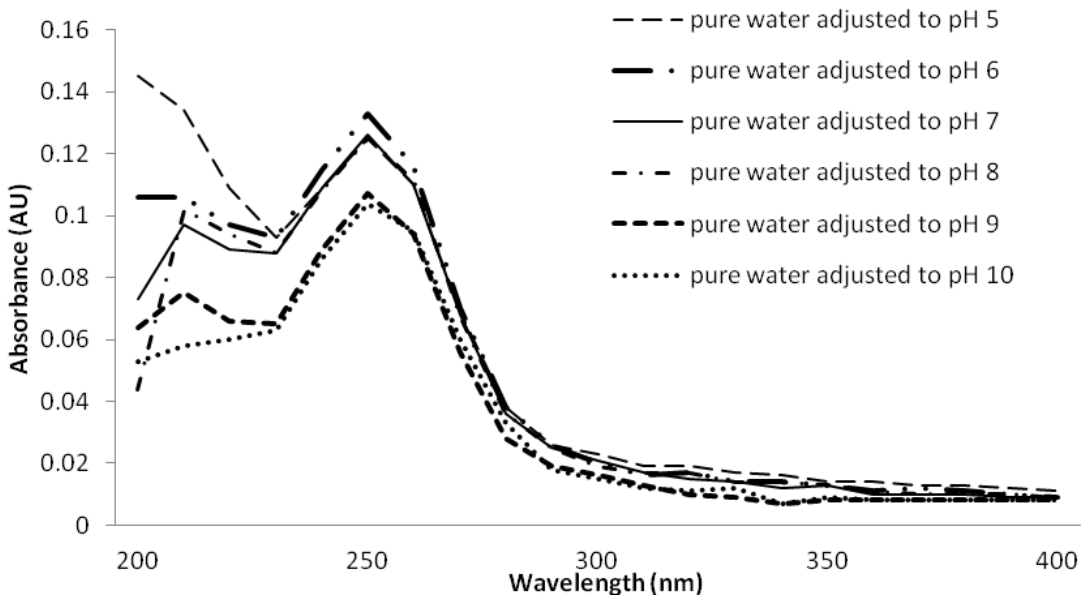

Figure 3-6 UV light absorption profiles of 2 µg thiamethoxam mL^{-1} in pure water varying in pH from 5 to 10.

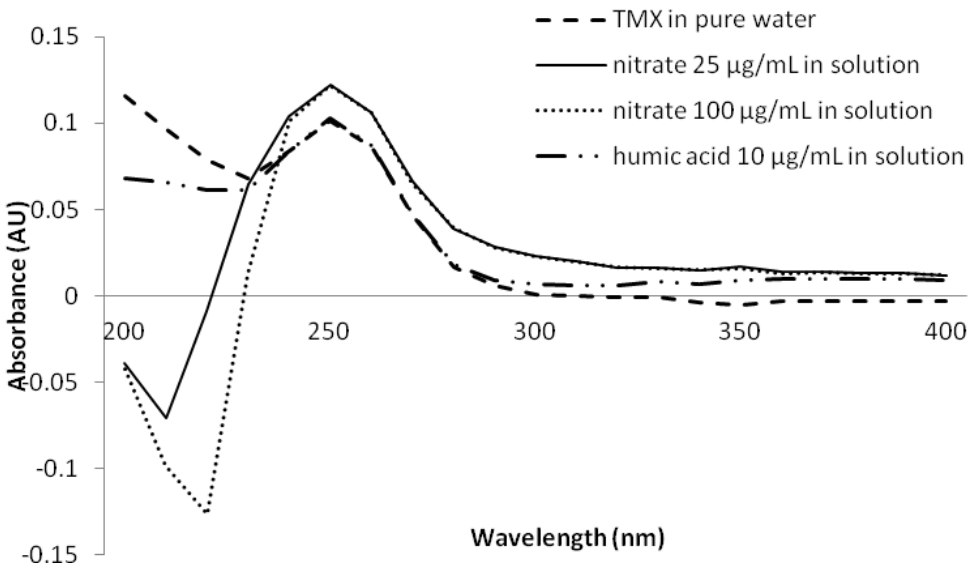

Figure 3-7 Compares light adsorption profiles of 2 µg thiamethoxam mL^{-1} (i) in pure water contain 25 and 100 µg nitrate mL^{-1}, and (ii) in pure water contain 10 µg humic acids mL^{-1}.

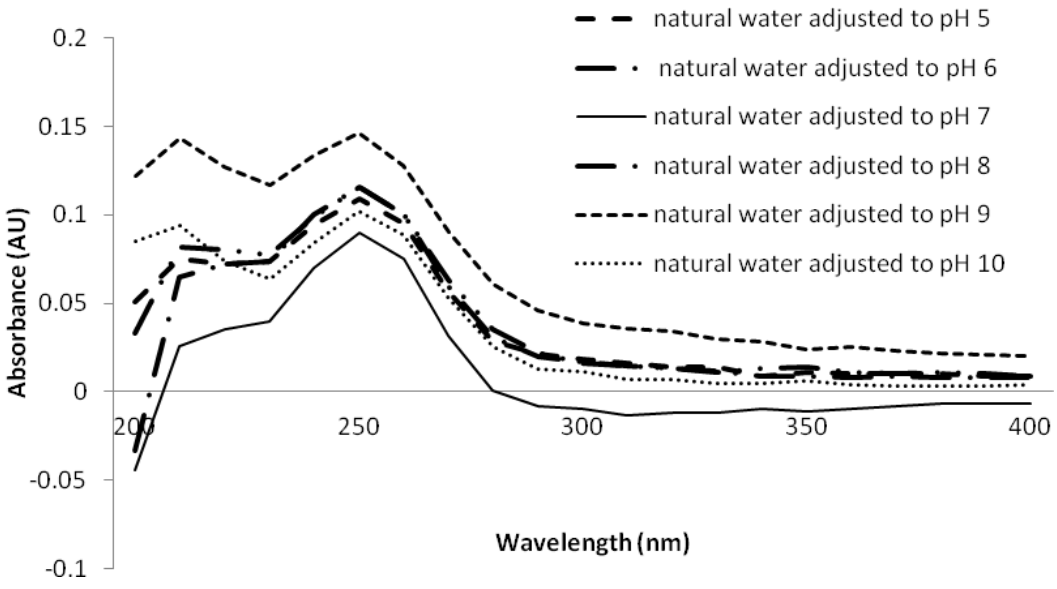

Figure 3-8 Compares light adsorption profiles of 2 µg thiamethoxam mL^{-1} in natural water varying in pH from 5 to 10.

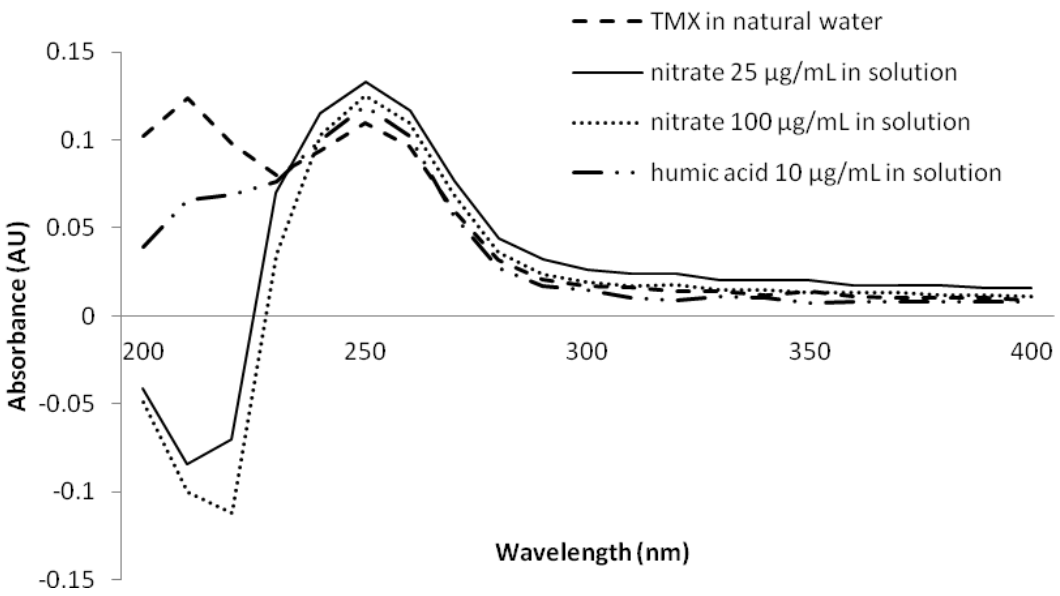

Figure 3-9 UV light absorption profiles of 2 µg thiamethoxam mL^{-1} (i) in natural water containing 25 and 100 µg nitrate mL^{-1}, and (ii) in natural water contain 10 µg humic acids mL^{-1}.

As absorbance of the solution containing nitrate showed negative values in both pure and natural water at wavelength below about 240 nm (Figure 3-7 and 3-9), a further measurement was carried out to measure absorbance of a solution containing nitrate only (without thiamethoxam). The absorption profile of nitrate is shown in Figure 3-10 and 3-11 for pure and natural water, respectively. According to the large absorption for nitrate alone in water solutions (Figure 3-10 and 3-11), it is possible that the negative absorbance values for pesticide solution containing nitrate came from the error in the spectrophotometer subtracting the much greater absorbance of nitrate from that of thiamethoxam

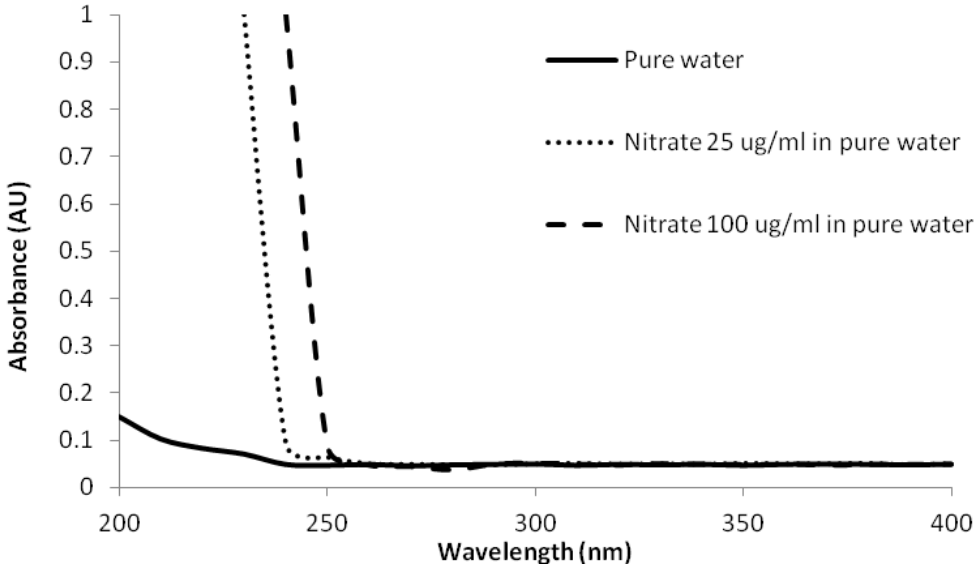

Figure 3-10 UV light absorption profiles of (i) pure water alone and (ii) in pure water containing 25 and 100 µg nitrate mL^{-1}.

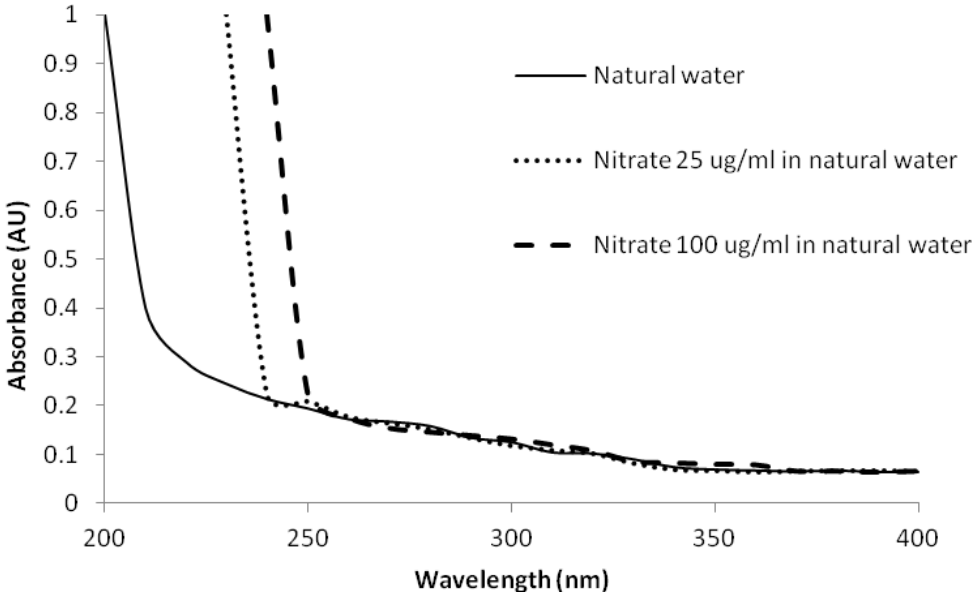

Figure 3-11 UV light absorption profiles of (i) natural water alone and (ii) in natural water containing 25 and 100 µg nitrate mL^{-1}.

3.4 Discussion

3.4.1. Photolysis of thiamethoxam

The photolysis rate constant in pure water decreased with increasing nitrate concentration (Figure 3-3). This may result from competition in light adsorption between nitrate and thiamethoxam because there was overlap in the light absorption wavelength of thiamethoxam and nitrate at some range as thiamethoxam absorbed light energy maximally at wavelength of about 255 nm (Figure 3-6 and 3-7, Pena et al., 2012) whilst nitrate absorbed light energy at wavelengths in the range <200 to 250 nm (Figure 3-8 and 3-9).

Table 3-3 shows that pH significantly influences photolysis of thiamethoxam and that photolysis rate increased at very alkaline conditions (pH 10). Pena et al. (2011) showed that half-lives of thiamethoxam were 0.779, 0.783 and 0.687 days in milli-Q water in solutions containing dissolved organic carbon concentration of 0, 3 and 9 mg L^{-1} (pH 7.5 to 7.7), respectively. The half-lives obtained in the study by Pena et al. (2011) were longer than the half-lives of thiamethoxam obtained in the current experiment (0.408 and 0.348 days for pure (pH 7.02) and natural water (pH 7.02), respectively). An important influence is that the higher light intensity contributed to faster photolysis as the solar radiation from sunlight (Pena et al.'s study) in Spain was lower (average 0.225 kW m^{-2}) than that from the xenon lamp (1.27 kW m^{-2}). Another possibility is that concentration of dissolved organic carbon derived from sewage sludge in Pena et al.'s study is higher than that in this study (>10 mg L^{-1}). This would contribute to a decrease of light intensity reaching the thiamethoxam molecules and would likely result in slower photoloysis. De Urzedo et al. (2007) suggested photolysis pathways of thiamethoxam as shown in Figure 3-12.

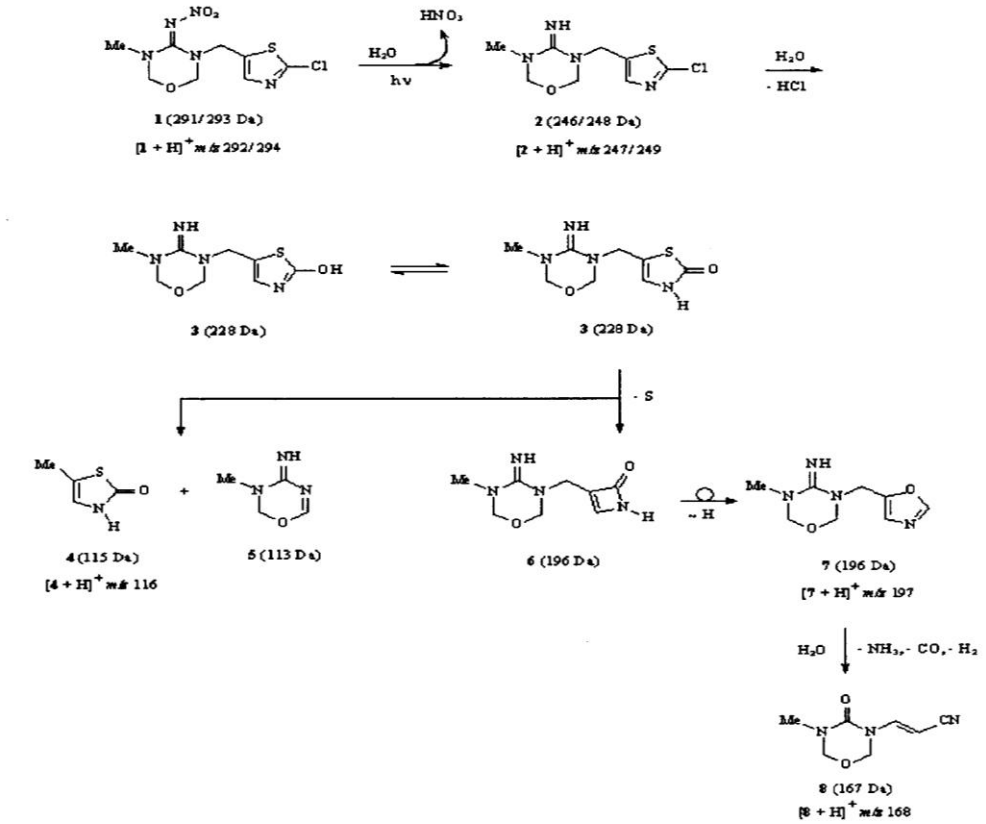

Figure 3-12 Photolysis pathway of thiamethoxam. 1 and 2-8 equate to thiamethoxam and its metabolites, respectively (De Urzedo et al., 2007).

3.4.2. Hydrolysis of thiamethoxam

pH in water influenced hydrolysis of thiamethoxam (present study, Liqing et al., 2006, Guzsvany et al., 2006) with the hydrolysis rate greatly accelerated under alkaline conditions. It was assumed that the more hydroxyl ion (OH^-) in the medium, the more hydrolysis of thiamethoxam because the strong electron of the NO_2 group causing a positive charge at the carbon of the C=N group of the thiamethoxam ring results in it being readily attacked by a hydroxyl ion (Guzsvany et al., 2006; Liqing et al., 2006). A similar hydrolysis cleavage for imidacloprid containing a nitroguanidine functional group has also been reported (Guzsvany et al., 2006; Zheng and Liu, 1999). Karmakar et al. (2009b) reported that hydrolysis rates at 28 ± 2^oC were 0.0216, 0.0103 and 0.145 day^{-1} for pH 4, 7 and 9.2, respectively. Comparison of hydrolysis rates

obtained from this study with those obtained by Karmakar et al. (2009b) showed that the latter were smaller. The higher hydrolysis rate could be due to higher temperature ($31\pm2^{o}C$).

Karmakar et al. (2009b) proposed alkaline hydrolysis mechanisms for thiamethoxam under heating and microwave conditions as shown in Figure 3-13 and a summary of hydrolysis products of thiamethoxam is given in Table 3-4. Under alkaline conditions (pH 9.2, $28\pm2^{o}C$), only the amino methyl compound (2), oxo-compound (4) and 6-hydroxy thiamethoxam compound (5) were found. Figure 3-14 shows acidic hydrolysis mechanisms of thiamethoxam under heating condition (Karmakar et al., 2009b) and a summary of hydrolysis products of thiamethoxam is given in Table 3-4. The major hydrolysis products under neutral (pH 7.0) and acidic (pH 4.0) conditions were the amino methyl compound (2) and guanidine derivative compound (3).

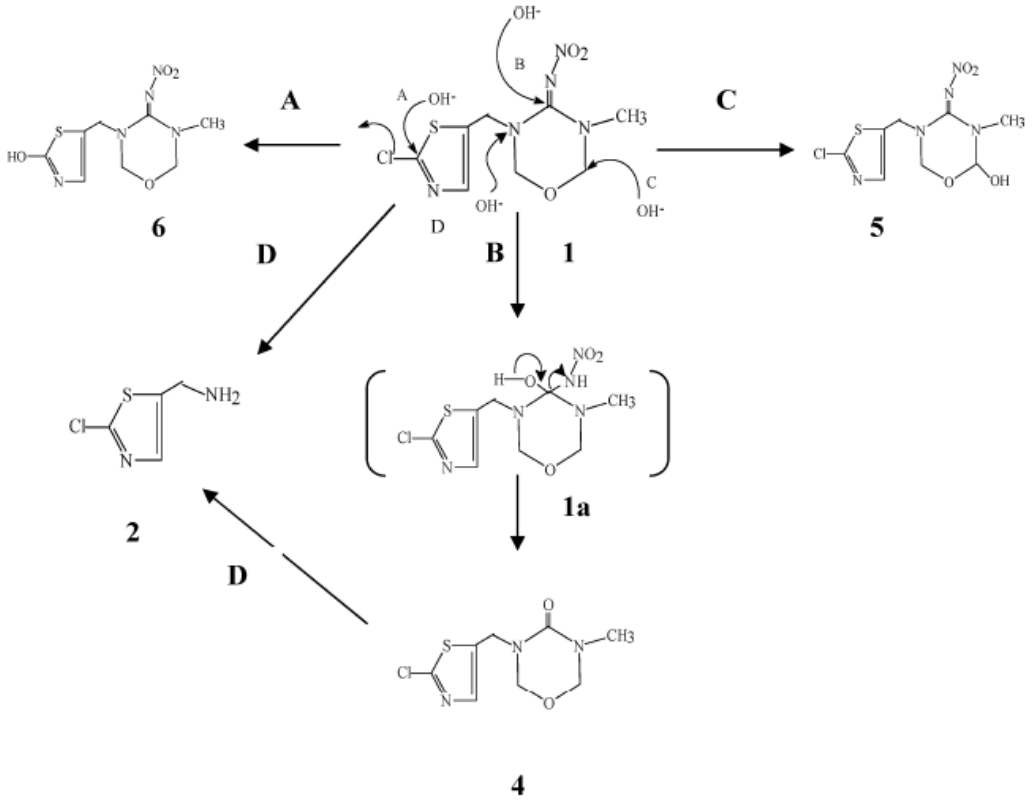

Figure 3-13 Postulated pathway of alkaline hydrolysis of thiamethoxam. (1) and 1a, 2, 4, 5, 6 equate to hydrolysed compound. A, B, C and D are the mechanistic pathways shown by the arrows (Karmakar et al., 2009b).

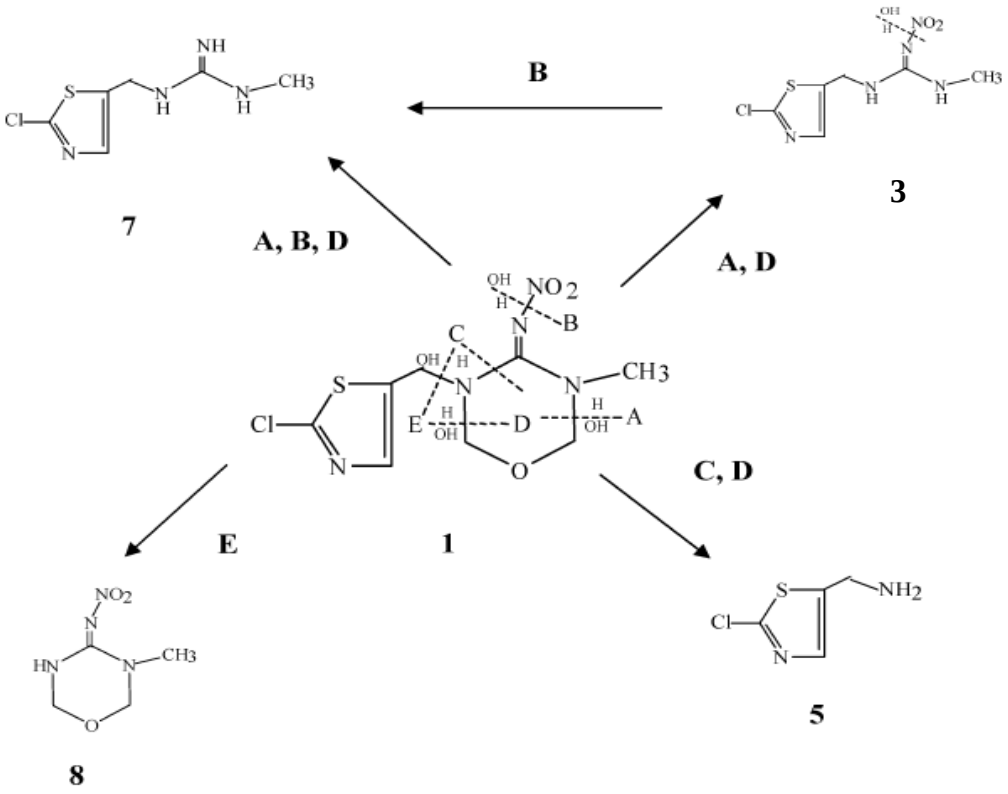

Figure 3-14 Postulated mechanisms of acid hydrolysis of thiamethoxam. 1, 3, 5, 7 and 8 equate to thiamaethoxam (1) and hydrolysed compounds (3, 5, 7, 8); A, B, C, D and E are the cleavage point of bonds as depicted in the present compound thiamethoxam (1) (Karmakar et al., 2009b).

3.4.3. Conclusion

The result shows that the presence of nitrate ions and pH had a significant effect on photo-degradation of thiamethoxam. Influence of the presence of nitrate ions possibly occurred via a competition between nitrate anions in solution (by addition in pure water or natural presence in natural water) and thiamethoxam for light adsorption resulting in decreasing direct photolysis of thiamethoxam. Photolysis of thiamethoxam was greatly enhanced in very alkaline environments (pH 10). Type of water had a significant influence on photolysis at neutral pH (pH~7) whilst at varying pH, there was no significant effect on photolysis and no effect of pH and type of water combined.

Hydrolysis of thiamethoxam was pH-dependent. The hydrolysis rate significantly increased at pH 9 and 10 in agreement with the literature (Liqing et al., 2006; Karmakar et al., 2009b). This experiment only used two types of water so it was not a strong experiment from this respect. Hence type of water did not significantly affect hydrolysis. Inclusion of more types of water would give a more definitive result.

The results will be used in subsequent chapters to aid interpretation of hydrolysis and photolysis behaviour of thiamethoxam in more complex systems.

CHAPTER 4

4. SORPTION OF THE TWO STUDIED PESTICIDES IN SEDIMENT FROM NATURAL STREAM IN SAND HUTTON

4.1 Introduction

When chemical molecules interact with soil or sediment, binding can occur between the two. This process is generally known as "sorption". Sorption is an important factor for pesticide behaviour in the environment because it influences persistence of pesticides in soil, transport of pesticide and potential to pollute groundwater. Influences on pesticide sorption include pesticide properties such as water solubility, octanol-water partition coefficient, and acid-base ionization constant for ionizable pesticides and soil properties including organic matter content, mineral composition and pH of soil (Katagi, 2006; Hiller et al., 2009; Peng et al., 2009). For example, Hiller et al. (2009) reported a significant positive correlation between K_d of acetochlor and organic carbon content at initial concentration 1.0 and 10 mg L^{-1} among 8 soil and 5 sediment samples. The authors showed through analysis of the humus fraction of organic carbon, that humic acid carbon was more strongly correlated to sorption of acetochlor than fulvic acid carbon. Peng et al. (2009) reported linear sorption isotherm of endrin to montmorillonite and kaolinite whereby the sorption increased with increasing ionic strength due to compression of the diffuse double layer supporting the interaction between clay surface and the endrin molecule. The authors also found that pH affected the sorption mechanism, with a charge-dipolar interaction of endrin to montmorillonite and kaolinite as the clay edges of silica-alumina units had variable charge due to the proton shift reaction of the units. Increase in pH contributed neutralized the edges of the units causing a decrease in positive charge of the units and reducing the charge-dipolar interaction. Conversely, the edge of the units was possibly ionized by an increase in pH contributing to an increase in negative charge of the edges that enhanced the charge-dipolar interaction and resulted in increased sorption of endrin (Peng et al., 2009)

In a sorption study, the soil sorption coefficient (K_d) and the soil organic carbon sorption coefficient (K_{oc}) of pesticides are measured parameters. K_d is calculated as a ratio of pesticide concentration in the solid phase to pesticide concentration in the solution phase (Organisation for Economic Co-operation and Development, 2000; Wauchope et al., 2002). Previous work (Banerjee et al., 2008; Wauchope et al., 2002) has shown that the K_d value is often related to organic matter content in soil as soil organic matter serves as a non-polar phase to which non-polar pesticides can be sorbed (Wauchope et al., 2002). Soil organic matter is often measured and expressed as the amount of organic carbon (Wauchope et al., 2002). The soil organic carbon sorption coefficient (K_{oc}) is calculated by dividing a measured K_d in a specific soil by the organic carbon content of the soil (Organisation for Economic Co-operation and Development, 2000; Wauchope et al., 2002).

Gavrilescu (2005) and vanLoon and Duffy (2005) suggested a mobility classification based on the partition coefficient as shown in Table 4-1. A K_{oc} value of greater than 1000 mL g^{-1} indicates that there is very strong sorption of a pesticide to soil and thus it is less likely to move unless soil erosion occurs where a pesticide can be transported sorbed to soil particles. A K_{oc} value less than 50 mL g^{-1} indicates a pesticide that is likely to travel with water either via leaching or surface runoff because of its weak sorption.

Table 4-1 Mobility classification based on soil distribution coefficients of pesticide (vanLoon and Duffy, 2005)

K_{oc} (mL g^{-1})	K_d (mL g^{-1})	Mobility	Class (typical)
0-50	0-0.5	Very high	Aliphatic acids
50-150	0.5-1.5	High	Carbamates
150-500	1.5-5.0	Medium	Benzoic acids
500-2000	5.0-20	Low	Triazines
2000-5000	20-50	Slight	Organophosphates
>5000	>50	Immobile	Organochlorines

This study investigated sorption of metalaxyl-M and thiamethoxam to a natural stream sediment from Sand Hutton, North Yorkshire, UK.

4.2 Material and methods

Metalaxyl-M (99.0% purity) was purchased from Sigma-Aldrich Ltd., $CaCl_2$ was purchased from Fisher Scientific Ltd. and thiamethoxam (99.7% purity) was used as described in section 3.2.

Sediment was collected from a small natural stream in Sand Hutton (54^o 1' 1"N; 0^o 56' 38"E) in December 2009. The sediment was sieved to a particle size ≤2 mm at the stream. The natural sediment before being sieved contained dead leaves, dried stems, dried nuts and small stones (about 50% of original sediment collected from stream) and the fraction that had a particle size ≤2 mm accounted for about 50%.The moisture content of the sediment was analyzed in triplicate (Avery, 1982). For all calculations that relate to the weight of sediment, values were corrected to oven dry mass. The organic carbon content in sediment was 5.0±0.1%. The C/N ratio was 18.2±0.3. The sediment texture of particle size ≤2 mm was sandy clay loam containing sand 48.7±5.5%, silt 19.4±0.8%, and clay 32.0±6.1%.

This sorption experiment was carried out in three stages according to OECD Guideline 106 (Organisation for Economic Co-operation and Development, 2000). First, a screening test was carried out to determine the best ratio between sediment and water. A kinetic test investigated time to sorption equilibrium for the two pesticides studied. Finally, the appropriate soil-to-water ratios and equilibration times were deployed to conduct the sorption experiments.

In order to give a better centrifugation and minimize cation exchange, the sediment was pre-equilibrated with a 0.01M $CaCl_2$ solution for 12 hours before the addition of pesticides. All experiments were carried out in teflon centrifuge tubes at room temperature (20±2^{o}C).

4.2.1. Selection of optimum sediment-to-solution ratio

The sediment-to-solution ratios tested were 1:10, 1:5, 1:4 and 1:2 based on 2, 4, 5 and 10 g sediment (dry weight basis) with 20 mL 0.01M $CaCl_2$. It is desirable that the percentage sorption is more than 20% or preferably >50% so that the change in test substance concentration in the liquid phase is large enough to be measured accurately (Organisation for Economic Co-operation and Development, 2000).

After pre-equilibration, stock solutions of the two pesticides were added to the respective amounts of sediment in order to make final concentrations of metalaxyl-M and thiamethoxam of 1 mg L^{-1}. Control samples were prepared at 1 mg pesticide L^{-1} in 0.01M $CaCl_2$ but without sediment to check pesticide stability in 0.01M $CaCl_2$ solution and possible sorption to the test vessels. Blanks with sediment-to-solution ratios 1:10, 1:5, 1:4 and 1:2 were prepared and subjected to the same test procedure. All test vessels were shaken on a side-to-side shaker at 150 oscillations per minute for 72 hours and then centrifuged at 2500 rpm for 15 minutes. The supernatants were collected and analyzed by HPLC.

4.2.2. Selection of optimum equilibration times

The optimum soil-to-solution ratio from the first test was employed for investigation of equilibration time for the two pesticides studied. After pre-equilibration, stock solutions of the two studied pesticides were added making the final concentrations of metalaxyl-M and thiamethoxam of 1 mg L^{-1}. Control samples were made without sediment whilst blanks with sediment but no pesticide were prepared and subjected to the same test procedure. The test vessels were shaken on a side-to-side shaker at 150 oscillations per minute then were centrifuged at 2500 rpm for 15 minutes to sample after 0.5, 6, 24, 48, 72, and 96 hours. The supernatants were collected and analyzed by HPLC.

4.2.3. Freundlich sorption study

After pre-equilibration with 0.01M $CaCl_2$, different initial concentrations of the two studied pesticide solutions were prepared at 0.2, 0.5, 1, 1.5 and 2 mg thiamethoxam or metalaxyl-M L^{-1} and at a sediment-to-water ratio of 1:2. Each pesticide concentration was studied in triplicate in teflon centrifuge tubes. The suspension was shaken on a side-to-side shaker at 150 oscillations per minute at 20±2°C for 96 hours. The concentration in initial and final solutions was sampled and analyzed by HPLC.

4.2.4. HPLC analysis

Pesticide concentration was monitored by HPLC-UV using the same machine and measurement conditions as described in Section 3.2.3. The absorbance for the two pesticides was measured at 215 nm. The retention time of metalaxyl-M and thiamethoxam was 8.9±0.5 and 4.8±0.2 minutes, respectively.

The limits of detection (LOD) for metalaxyl-M and thiamethoxam in water were 0.017±0.004 and 0.010±0.003 mg L^{-1}, respectively.

4.2.5. Calculation of absorption coefficients

The distribution coefficient; K_d (L kg^{-1}) is the ratio between the concentration of pesticide sorbed in the soil/sediment phase (C_s) and the concentration of pesticide in the solution (C_e) when adsorption equilibration is reached (Organisation for Economic Co-operation and Development, 2000). The equation for calculation of C_s is

$$C_s = \frac{V(C_i - C_e)}{m_s}$$

where C_s is calculated substance concentration sorbed to soil/sediment (mg kg^{-1})

C_i is initial concentration in the liquid phase (mg L^{-1})

C_e is concentration in the liquid phase after equilibration time (mg L^{-1})

V is initial volume of solution (L)

m_s is dry mass of soil/sediment (kg)

The sorption coefficient can be calculated using either the linear or Freundlich model. The linear model is given by:

$$C_s = K_d . C_e$$

The Freundlich sorption isotherm (Carbo et al., 2007; Organisation for Economic Co-operation and Development, 2000), K_f (kg $L^{-n}{}_f$) is calculated as:

$$C_s = K_f . C_e^{n_f}$$

where n_f is the Freundlich exponent (dimensionless).

The organic carbon normalized adsorption coefficient (Organisation for Economic Co-operation and Development, 2000), K_{oc} (L kg^{-1}) relates the linear distribution coefficient K_d to the amount of organic carbon in the soil/sediment sample. K_{oc} is calculated as:

$$K_{oc} = \frac{K_d}{\%OC} . 100$$

where OC is organic carbon in soil

4.3 Results

4.3.1. Optimum sediment-to-solution ratio

Percentage sorption of metalaxyl-M at sediment-to-solution ratios of 1:2, 1:4, 1:5 and 1:10 were 69.4±2.2%, 58.7±3.4%, 51.7±1.0% and 42.1±6.5%, respectively, indicating that the optimum sediment-to-solution ratio was 1:2.

Percentage sorption of thiamethoxam at sediment-to-solution ratios of 1:2, 1:4, 1:5 and 1:10 were 63.5±1.8%, 52.6±0.9%, 51.3±0.7% and 40.5±2.7% respectively. The optimum sediment-to-solution ratio was again 1:2.

4.3.2. Equilibration times

Sorption of thiamethoxam and metalaxyl-M reached a steady state (equilibrium) after 72 hours as shown in Figure 4-1. Subsequent sorption studies were carried out over 96 hours to ensure that sorption of thiamethoxam and metalaxyl-M achieved equilibrium.

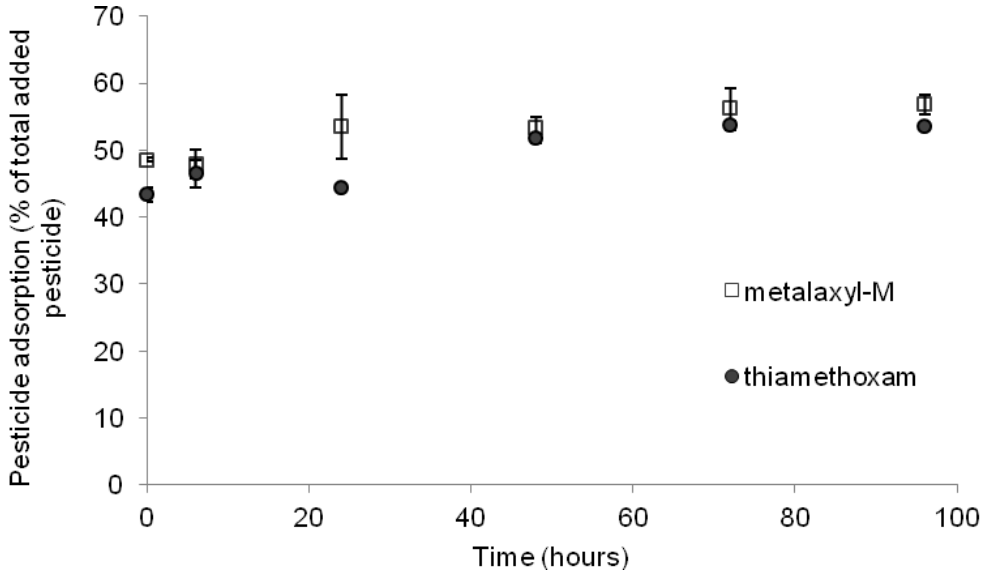

Figure 4-1 Change in sorption of metalaxyl-M and thiamethoxam (from the solution phase) on natural sediment with varying incubation time. Error bar is the standard deviation, n=3.

4.3.3. Sorption study

The pesticide concentration in solution (C_e) was plotted against the pesticide concentration sorbed in sediment (C_s). K_d values were obtained from the slope of the linear regression of pesticide concentration sorbed in sediment against pesticide concentration in liquid at equilibrium as shown in Figure 4-2. K_d values were 1.83 and 1.63 L kg^{-1} for metalaxyl-M and thiamethoxam, respectively. The linear isotherm line

for metalaxyl-M (Figure 4-2) did not fit with most of the observed points as sorption of metalaxyl-M was strongly non-linear. Hence metalaxyl-M was evaluated against fit to a Freundlich isotherm for non-linear sorption as recommended in OECD guildline 106 (Organisation for Economic Co-operation and Development, 2000).

The organic carbon normalized sorption coefficient (K_{oc}) values were 36.6, and 32.6 L kg^{-1} for metalaxyl-M and thiamethoxam, respectively. The K_{oc} values suggest that both compounds were weakly sorbed (vanLoon and Duffy, 2005; Table 4-1) by the sediment and hence that these pesticides are likely to be relatively mobile in the environment with a significant fraction staying in the solution of water-sediment systems.

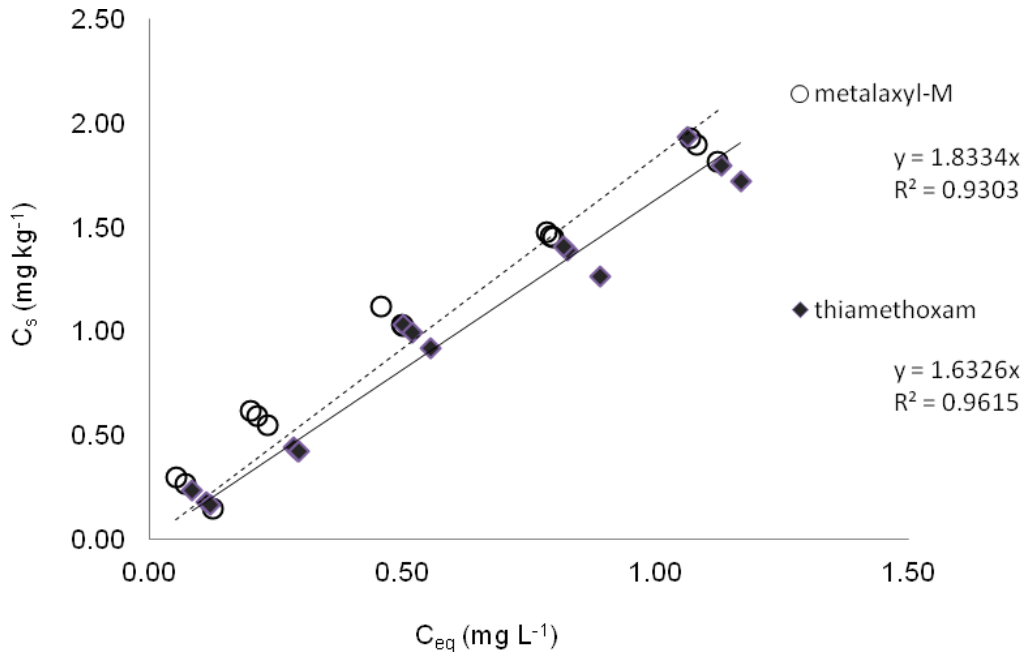

Figure 4-2 Fitting of linear sorption isotherms for metalaxyl-M and thiamethoxam in the natural sediment. Dash line (- - -) is a prediction line for metalaxyl-M and a solid line (-) is a prediction line for thiamethoxam

The pesticide concentration in the solution at equilibrium (C_e) was plotted against the pesticide concentration sorbed to the sediment (C_s) as shown in Figure 4-3 for thiamethoxam and Figure 4-4 for metalaxyl-M. The least squares method with Microsoft Excel Solver was used to determine optimized values of K_f and n_f. The K_f value calculated from the Freundlich sorption isotherm of thiamethoxam was 1.62 kg

L^{-1} and n_f was 0.93. The chi^2 value for the fit was 4.80 indicating an acceptable fit when compared to the critical value at $p<0.05$ of 7.82. The K_f value of metalaxyl-M was 1.76 kg L^{-1} and n_f was 0.74. The fit was again acceptable (chi^2 was 1.80).

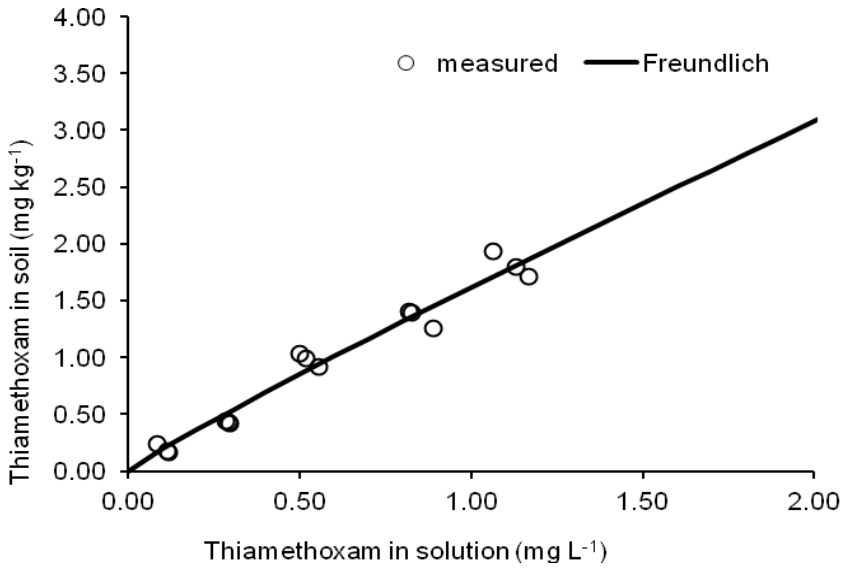

Figure 4-3 Fitting of a Freundlich isotherms to sorption of thiamethoxam to a natural stream sediment

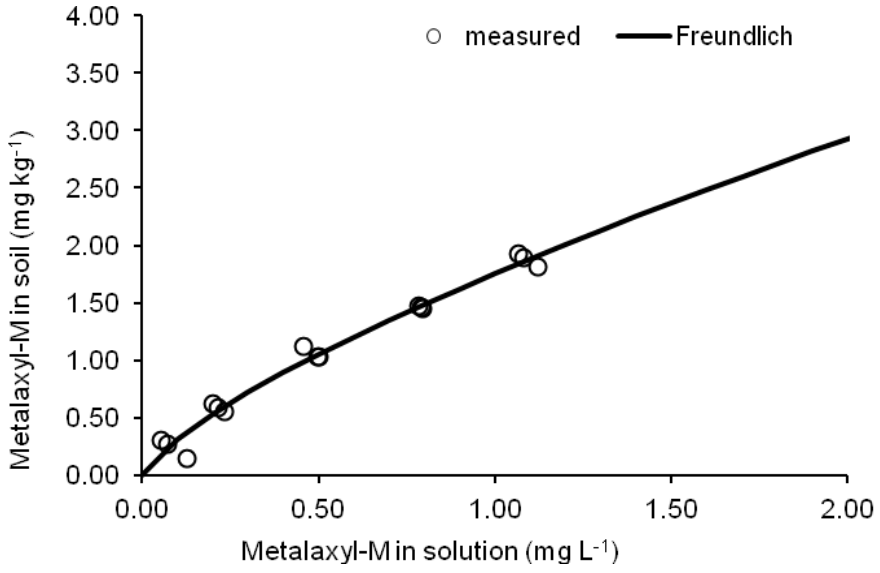

Figure 4-4 Fitting of a Freundlich isotherm to sorption of metalaxyl-M to a natural stream sediment

4.4 Discussion

4.4.1. Sorption of thiamethoxam

The K_{oc} value of the present study was 32.6 L kg^{-1} showing that thiamethoxam was weakly sorbed to the sediment (vanLoon and Duffy, 2005; Table 4-1). The K_{oc} value obtained was lower than some previous studies (Carbo et al., 2007, Banerjee et al., 2008). The reported K_{oc} value of thiamethoxam from previous studies showed a large variation from 0.23 to 2877 L kg^{-1} based on seven soils in three studies (Banerjee et al., 2008; Campbell et al., 2005; Carbo et al., 2007). The K_{oc} is very variable suggesting that sorption of thiamethoxam cannot be explained by %organic carbon alone. The different sorption may result either from composition of the organic carbon and/or composition of clay.

The humic matter in soil is composed of humic and fulvic acids (Tan, 1994). It may be different in soil and stream sediment because of decomposing softwood, hardwood and grass humic matter. Humic matter in stream sediment is composed mainly of fulvic acid (Tan, 1994) which comes from soil humic matter (allochthonous) or aquatic plant material (autochthonous). Soil humic matter mainly consists of a ligno-protein complex whereas aquatic humic matter is mainly carbohydrate-protein complexes (Tan, 1994). Hiller et al. (2009) reported a significant correlation between organic carbon content and K_d of acetochlor and also a significant correlation between humus components and K_d of acetochlor. The authors found that differences in humus components contributed to variation of K_d among soils and sediments where sorption of acetochlor was closely related to humic acid carbon and less related to fulvic acid carbon. The authors suggested that humic acid carbon content was a better predictor of sorption of acetochlor than organic carbon content.

The previous sorption studies on thiamethoxam showed that not only organic carbon and clay content influence sorption processes but also their composition. A sorption study (Banerjee et al., 2008) in three Indian soils from a grapevine growing area showed that organic carbon and clay content in soils gave positive correlations to sorption of thiamethoxam and that the ordering of K_{oc} values of the soils suggested that organic carbon played a dominant role in sorption process rather than the clay

content. A study by Carbo et al. (2007) in two Brazilian soils suggested no significant correlation of thiamethoxam with organic carbon content so mineral constituents in the soils may also play an important role in sorption processes under some circumstances. Previous studies (Čadková et al., 2012; Chen et al., 2009) on other pesticides showed different sorption to different clay constituents. Cadkova et al. (2012) studied tebuconazole sorption onto some soil minerals (birnessite, ferrihydrite, goethite, calcite and illite) and humic acid. The authors found no detectable sorption of tebuconazole to calcite whilst the highest sorption of analytical tebuconazole was found in order humic acid > ferrihydrite > illite > birnessite and goethite (negligible sorption). Chen et al. (2009) reported different adsorption capacity of carbaryl to three minerals, montmorilonite, kaolinite and goethite. The study showed higher adsorption capacity for carbaryl on montmorilonite than that on kaolinite or goethite.

4.4.2. Sorption of metalaxyl-M

The Kf_{oc} value of metalaxyl-M in the present study was 36.6 L kg^{-1} within the range reported by previous studies. The Kf_{oc} value of metalaxyl-M was in the range 20 to 2536 L kg^{-1} based on 36 soils from five studies and a pesticides database (Andrades et al., 2001; Fernandes et al., 2003; Monkiedje and Spiteller, 2002; PPDB, 2009; Sharma and Awasthi, 1997). Organic matter (Andrades et al., 2001; Fernandes et al., 2003) and clay content (Sharma and Awashi, 1997; Andrades et al., 2001; Fernandes et al., 2003) were reported to have positive correlations to sorption of metalaxyl. The wide variation of K_{foc} (20 to 2536 L $kg^{-}1$) may be explained by form and/or composition of organic matter in the sediment. This is supported by the finding of Rodriguez-Cruz et al. (2009) that higher sorption of metalaxyl was found in lignin (a hydrophobic molecule) than in cellulose (a hydrophilic molecule).

4.5 Conclusion

Sorption of the two pesticides to a natural sediment suggested that these pesticides are weakly sorbed and likely to be relatively mobile in the environment. The results from the sorption experiment quantify sorption behaviour of the pesticides to the stream sediment and can be used to predict behaviour of the pesticide in more complex systems.

CHAPTER 5

5. FATE OF THE PESTICIDES METALAXYL-M AND THIAMETHOXAM IN WATER-SEDIMENT SYSTEMS UNDER CONTROLLED CONDITIONS

5.1 Introduction

Pesticides contaminate water by various routes such as direct application, spray drift, run-off, drainage, waste disposal, industrial, domestic or agricultural effluents and atmospheric deposition. Pesticide from different sources can enter water-sediment systems such as rivers, ponds, lakes or the ocean where the aquatic-sediment systems play a significant role in dissipation of the compounds. The upper water phase is often aerobic whilst the surface layer of sediment can be either aerobic or anaerobic depending on depth of the sediment. However, usually the sediment phase is predominantly anaerobic (Gavrilescu, 2005). Potential transformations of pesticides in water-sediment systems occur via various processes including hydrolysis, photolysis and microbial degradation (Katagi, 2006).

The physico-chemical properties of the pesticide itself influence transformation/degradation in water-sediment systems and partitioning between water and sediment phases. For example, some pesticides including thiamethoxam can be transformed/degraded via hydrolysis (Karmakar et al., 2009, Katagi, 2006) whilst others including metalaxyl are stable in water (Sukul and Spiteller, 2000). Not only physico-chemical properties of the pesticide determine transformation/degradation, but also surrounding conditions such as pH (Karmakar et al., 2009, Guzsvany et al., 2006, Liqing et al., 2006) and presence of photo-induced reactions (Katagi, 2006; Shankar et al., 2007). Environmental conditions influence rate of the transformation/degradation processes and partitioning of pesticides between water and soil/sediment phases.

Chapter 3 reported hydrolysis and photolysis of thiamethoxam which was influenced by pH, and sorption of thiamethoxam and metalaxyl-M to sediment. The K_{oc} values of the two pesticides suggested that they were likely to stay largely in the water phase. Here, artificial water-sediment systems were set up under controlled conditions to investigate rate of dissipation of the two pesticides from water-sediment systems and to examine whether

hydrolysis and sorption behaviour observed in simplified phase experiments in Chapter 3 are able to predict behaviour of the two pesticides in water-sediment systems.

The aim of this study was to investigate the rate of dissipation of the two studied pesticides, metalaxyl-M and thiamethoxam, in water-sediment systems under controlled conditions.

5.2 Material and methods

Pesticides, chemicals and sediment (collected in August 2010) used in this experiment were the same as those used in Chapter 3. The natural water (collected in August 2010) had pH 8.32±0.02 at 22.6^{o}C and DO 7.70±0.16 mg L^{-1}.

The study of fate of two pesticides, metalaxyl-M and thiamethoxam, in water-sediment systems was carried out according to the Organization for Economic Co-Operation and Development (OECD) Guideline 308 (Organisation for Economic Co-operation and Development, 2002).

5.2.1. Experimental conditions

A water-sediment experiment was set up in 150 mL glass bottles. Sediment (8.07±0.02 g dry weight basis) was added to each beaker followed by 80 mL natural water. All jars were covered with a lid to prevent evaporation. All jars were bubbled with oxygen for one minute every three to four days to prevent de-oxygenation. At the beginning of the experiment, sediment was left overnight to settle. The water column was then spiked with 0.8 mL of a pesticide stock solution containing 200 mg L^{-1} thiamethoxam and metalaxyl-M to give a final concentration of 2 mg L^{-1} of each pesticide in overlying water. Natural water with spiked pesticide mixture alone was set up as a control and natural water and sediment without spiked pesticide mixture were blank samples. There were three replicates of treatments, blanks, and controls. The experiment was carried out in the dark for four weeks in a growth cabinet at 20±2^{o}C. Samples were collected after 0, 1, 3, 7, 14, 21, and 28 days.

Three jars were destructively sampled at each sampling interval. At day zero, water alone was collected from a blank and control set to confirm dose levels. Blanks and controls were also sampled destructively at the end of the experiment (at 28 days). Overlying water was

removed as far as possible before sampling sediment. In order to improve extraction efficiency, remaining water was evaporated by air-drying the sediment at 20^{o}C (room temperature) for 48 hours. Thus pesticide in sediment is the sum of that sorbed to particles and that present in sediment pore water. Subsequently, the sediment was extracted for pesticides by adding 20 mL methanol and shaking on a side-to-side shaker at 250 oscillations per minute for an hour. The extractant was collected and analyzed by HPLC.

pH and dissolved oxygen (DO) in water were measured using a pH meter model VWR®sympHony™. The pH probe was calibrated with buffer pH 4 and pH 7 and the dissolved oxygen probe was calibrated with distilled water before performing the measurement each day. pH in water was measured by placing the pH probe in water and waiting until the recording stabilised.

5.2.2. HPLC analysis

Pesticide concentration was determined by HPLC-UV using the same HPLC equipment, column and mobile phases as detailed in Chapter 3. In this study, water and sediment samples were analyzed under gradient conditions. Mobile phases were mixtures of water acidified with 0.1% phosphoric acid and methanol at a constant flow rate of 1 mL min^{-1}. For the first 10 min the mobile phase was composed of 80% acidified water and 20% methanol. For the next 20 min the methanol content was increased to 100%, then over the next 7 min the methanol content was decreased to 20%. The absorbance for metalaxyl-M and thiamethoxam was measured at 215 and 252 nm, respectively. The Agilent 1100 series model was used to record and analyze the area of the peak for calculation of quantitative residue of the pesticides by comparing peak area and retention time of the pesticides with authentic standards.

The limit of detection was the lowest concentration level that could be determined to be different from a blank. Limits of detection were matrix-, method- and instrument-specific. The limit of detection was set at a ratio of three between signal heights of the analyte to noise height of a blank (matrix matching). The limits of detection in water and sediment extracts for thiamethoxam and metalaxyl-M are given in Table 5-1.

Table 5-1 Limits of detection in water and sediment extracts (mean±standard deviation) for metalaxyl-M and thiamethoxam.

Matrices	Water (µg L^{-1})	Sediment extract (µg kg^{-1})
Metalaxyl-M	17±4	55±2
Thiamethoxam	10±3	51±28

5.2.3. Extraction of thiamethoxam and metalaxyl-M from sediment

The overlying water was separated from sediment by slowly pouring. After removing the overlying water from sediment as much as possible, the sediment was still saturated with water. In order to improve extraction efficiency, the water was evaporated by air-drying the sediment at room temperature (20±2°C) for 48 hours. Dried sediment was disaggregated by stirring thoroughly to get a homogeneous matrix for extraction. Subsequently, 10 g of sediment (dry weight basis) was sampled into centrifuge tubes in three replicates for each system. The dry sediment was extracted by adding 20 ml methanol and shaking on a side-to-side shaker at 150 oscillations per minute for one hour. The samples were centrifuged at 2500 rpm for 10 minutes then supernatants were collected and then analyzed by HPLC.

The recovery test was undertaken on sediment spiked to 0.92, 2.29, and 4.58 mg kg^{-1}. The spiked sediment was stirred in order to achieve homogenous pesticide concentration in the sediment and then strained off prior to air-drying at room temperature (20±2°C) for 48 hours and then extracting as described above. The initial amount of spiked pesticide and measured amount of spiked pesticide were used to calculate recovery of the extraction method:

$$\%recovery = 100.\frac{measured\ amount\ of\ spiked\ pesticides}{Initial\ amount\ of\ spiked\ pesticides}$$

The recovery of metalaxyl-M and thiamethoxam at the three concentrations is summarized in Table 5-2. The recovery for extraction of the two pesticide from sediment was within an acceptable range (70-110% of total added pesticide; Organisation for Economic Co-operation and Development, 2002). However, there was a concern that the recovery decreased because

of degradation of pesticide on sediment if the spiked sediment was left for longer periods. Moreover when pesticide sorbed to sediment, a fraction of sorbed pesticide was non-extractable, leading to a reduction in the recovery of pesticide from sediment.

Table 5-2 Recovery of metalaxyl-M and thiamethoxam from sediment spiked at three concentrations (mean±standard deviation).

Pesticides	Spiked pesticide concentration (mg kg^{-1})	Recovery of the pesticide (%±standard deviation)
Metalaxyl-M	0.92	103.1 (±1.0)
	2.29	97.7 (±6.6)
	4.58	89.6 (±7.7)
Thiamethoxam	0.92	90.4 (±1.8)
	2.29	88.2 (±5.5)
	4.58	84.0 (±9.5)

5.2.4. Processing of results

It was assumed that when pesticides were added to the water-sediment system, they were distributed between the two phases with an equilibrium established between the two. In the meantime, there were several processes resulting in transformation and dissipation of pesticide in one or both phases such as hydrolysis, microbial degradation in water, sorption to sediment and degradation in sediment.

ModelMaker version 4.0 (Walker and Crout, 1997) was used to process data from the experiment to simulate pesticide concentration in water and sediment and to fit first-order degradation kinetics of the studied pesticides. Firstly, a simulated model diagram was created based on assumed processes acting on the pesticide once it entered the water-sediment system (Figure 5-1).

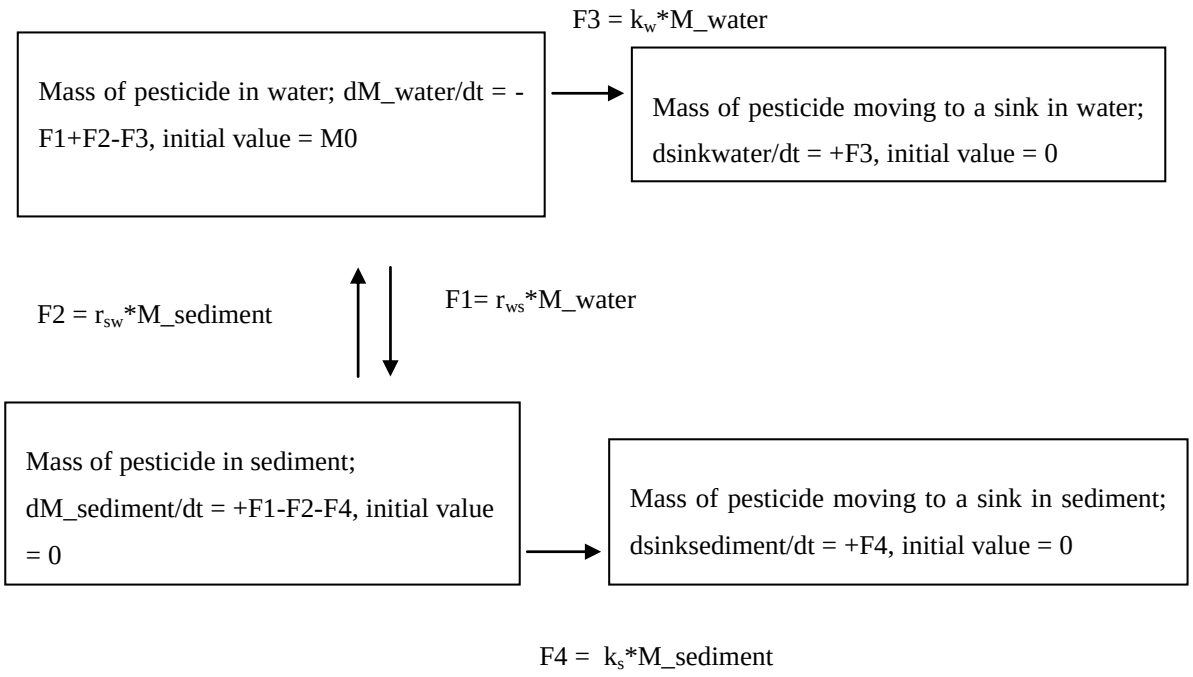

Figure 5-1 Pesticide comparments and assumed processes acting on pesticide once it entered into the water-sediment system.

The model was simulated according to Figure 5-1 where each parameter was defined as follows:

M_water is mass of pesticide in water (µg)

M_sediment is mass of pesticide in water (µg)

Sinkwater is mass of pesticide sink in water (µg)

Sinksediment is mass of pesticide sink in sediment (µg)

k_s is rate constant of dissipation of pesticide in sediment (day^{-1})

k_w is rate constant of dissipation of pesticide in water (day^{-1})

r_{sw} is exchange rate of pesticide from sediment to water (day^{-1})

r_{ws} is exchange rate of pesticide from water to sediment (day^{-1})

Observed data for sampling time (day) and residue (µg) were entered into the model. Initial estimates for k_s, k_w, r_{sw} and r_{ws} were required before running the model; these were taken from previous studies with the pesticides (PPDB, 2009). The model was programmed to find the best values for k_s, k_w, r_{sw} and r_{ws} with respect to the goodness-of-fit statistics (Marquardt optimization: Ordinary least squares) and optimization processes. The weighted sum of squares statistics was used to reach the quantity which minimizes the difference between the model's result and observed data:

$$X^2 = \sum \frac{(m_i - o_i)^2}{E_i^2}$$

where the summation is over all the input data values

o_i is the value of the i^{th} observation

E_i is the error estimate for that observation, and

m_i is the model prediction for that observation.

The half-life of the pesticides was calculated by substituting the first-order rate constant into the following expression

$$t_{\frac{1}{2}} = \frac{ln\ 2}{k}$$

Where $t_{\frac{1}{2}}$ is the half-life (days)

k is the first-order rate constant ($days^{-1}$)

5.3 Results

Dissolved oxygen in the water phase ranged from 2.47±0.24 to 4.60±0.37 mg L^{-1} during the experiment as shown in Figure 5-2. Dissolved oxygen in was initially was 3.37±0.11 mg L^{-1} suggesting that the water phase started depleted in oxygen after the water-sediment system

was set up. During the experiment the dissolved oxygen increased because the water phase of the system was oxygenated every few days; however the dissolved oxygen decreased from day 15 which could result from microbial activity in the system.

pH in the water phase of the system was stable at neutral ranging from 7.60±0.11 to 7.84+0.17 as shown in Figure 5-3.

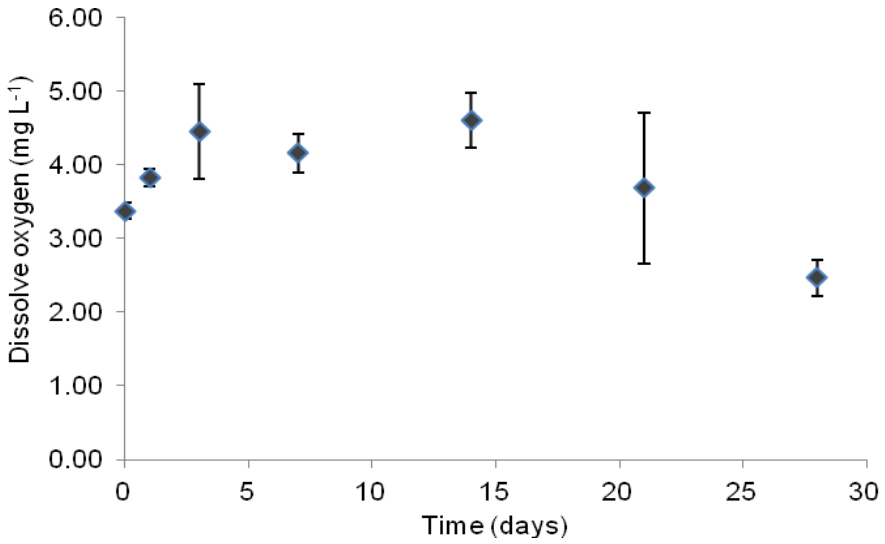

Figure 5-2 Dissolved oxygen in the water phase at each sampling time during the experiment.

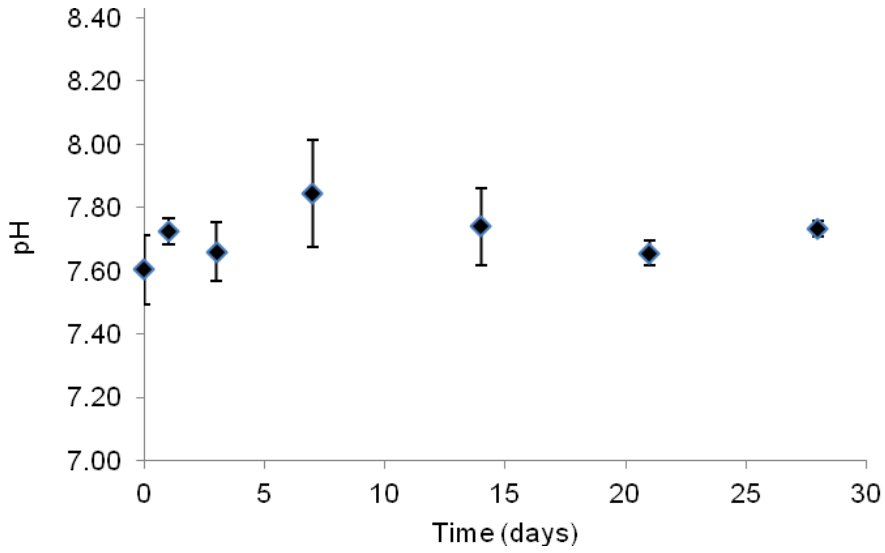

Figure 5-3 pH in the water phase at each sampling time during the experiment

5.3.1. Dissipation of thiamethoxam in the water-sediment system

ModelMaker version 4.0 was used to create a graph showing pesticide residues at each sampling time in the water and sediment phases as shown in Figure 5-4 and Figure 5-5 for thiamethoxam and metalaxyl-M, respectively. Tabulation of modelled values is given in Appendix C-3 for thiamethoxam and Appendix C-4 for metalaxyl-M and optimization statistics are given in Appendix C-5 for thiamethoxam and Appendix C-6 for metalaxyl-M.

Thiamethoxam residues in the water phase decreased from 230±4 µg on day 0 to 35.4±6.8 µg on day 28. Residues in sediment increased rapidly to a peak of 25.5±2.0 µg on day 14 before decreasing slowly to the end of the experiment (Figure 5-4). The prediction line started below observed data points at day 0 because the initial concentration was not fixed as an input to the model. When this value was fixed it was found that the degradation rate in water-sediment system could not be optimised. The prediction line from the model did not fit some observed data in the water/sediment phase. It was possible due to the model tries to fit the prediction line with most of the observed values but there was some variability in observed data.

The dissipation rate of thiamethoxam (excluding photolysis and sorption) from the water phase was obtained by processing the observed data and optimizing using ModelMaker 4.0. The rate constant for dissipation of thiamethoxam from water (±95% confidence interval) was 0.0532±0.0325 $days^{-1}$giving a half-life of thiamethoxam in water of 13.0 days.

The exchange rate of thiamethoxam from water to sediment (±95% confidence interval) was 0.0649±0.0419 day^{-1} and the reverse exchange rate was 0.398±0.304 day^{-1}. The rate constant of dissipation of thiamethoxam from sediment (±95% confidence interval) was 0.0250±0.2410$days^{-1}$ giving a half-life of thiamethoxam in sediment of 27.7 days.

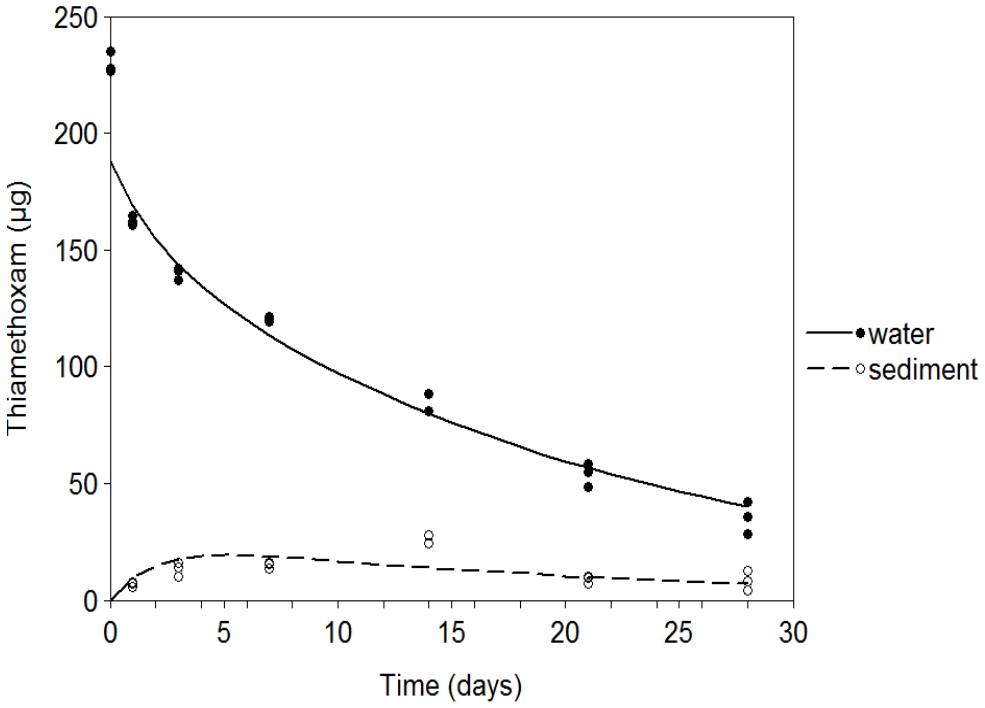

Figure 5-4 Measured and simulated residues of thiamethoxam in the water and sediment phase. Dots represent observed thiamethoxam residues and lines represent predictions from the model.

5.3.2. Dissipation of metalaxyl-M in the water-sediment system

Metalaxyl-M residues in the water phase decreased rapidly from 135±2 µg on day 0 up to day 7; thereafter metalaxyl-M in water gradually decreased to 56.8±3.7 µg on day 28. The residues in sediment increased rapidly to a peak of 25.7±0.3 µg on day 7 before decreasing slowly as shown in Figure 5-5. The rate constant for dissipation of metalaxyl-M from water (±95% confidence interval) was 0.00509±0.00943 $days^{-1}$ giving a half-life of metalaxyl-M in water of 136 days.

The exchange rate of metalaxyl-M between water and sediment (±95% confidence interval) was 0.110±0.013 day^{-1} and the reverse exchange rate was 0.305±0.044 day^{-1}. The rate constant for dissipation of metalaxyl-M from sediment (±95% confidence interval) was 0.0845±0.0365 $days^{-1}$ giving a half-life of metalaxyl-M in sediment of 8.20 days.

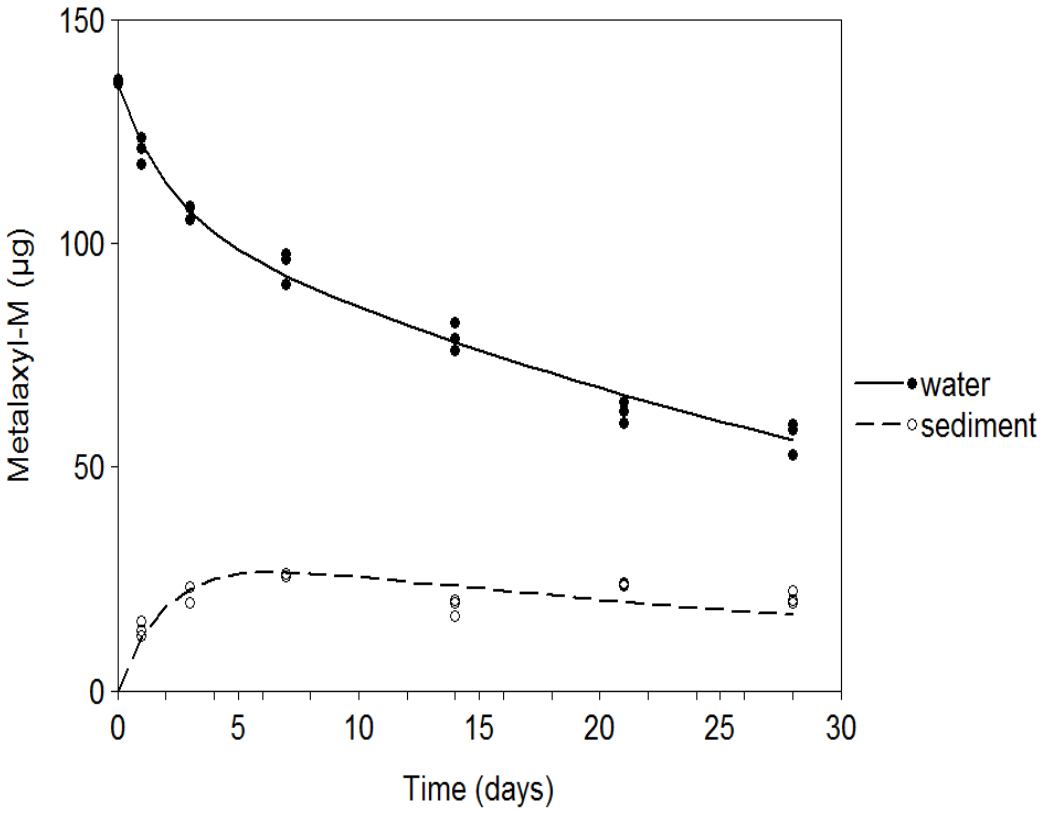

Figure 5-5 Compares measured and simulated residues of metalaxyl-M in the water and sediment phases. Dots represent observed metalaxyl-M residues and lines represent prediction line from the model.

5.4 Discussion

5.4.1. Dissipation of thiamethoxam from the water phase

Dissipation of thiamethoxam from the water phase may have resulted from hydrolysis, microbial degradation in water, sorption to sediment particles and pesticide exchange between water and sediment. Photo-degradation was negligible in the present study because the experiment was carried out under dark conditions. The neutral pH of the water phase suggested that hydrolysis rate would be very low based on the photolysis experiment in Chapter 3 and other studies (Liqing et al., 2006; Karmakar et al., 2009). Hence sorption by sediment and microbial degradation may play the dominant roles in dissipation of thiamethoxam from the water phase.

Sorption to sediment was assumed to have a major role in rapid dissipation in water during the first period because the dissipation rate was high until about 3 days after pesticide addition; subsequently, the rate was slower as thiamethoxam sorption to sediment increased initially then approached equilibrium. Results from the sorption experiment (Chapter 4) were used to estimate that 13.3% of thiamethoxam would sorb to sediment. In fact, maximum sorption was 23.4% of total measured thiamethoxam at day 14. The sorption of thiamethoxam from the calculation and the sorption in a water-sediment system were smaller than the sorption in the water-sediment system. The anomaly may have arisen because of the methodology to separate sediment from overlying water which would have left some pore water within the sediment..

5.4.2. Dissipation of thiamethoxam from the sediment phase

Thiamethoxam sorbed to sediment such that the pesticide concentration in sediment increased until the sorption reached equilibrium. Thiamethoxam in sediment then decreased because of microbial degradation in sediment (Gupta et al., 2008; Karmakar et al., 2006) and pesticide exchange between sediment and water.

A previous study by Karmakar et al. (2006) investigated degradation of thiamethoxam in four different soils; a loamy sand, sandy clay loam, silty clay loam, and sandy loam from India. The degradation was slower in the loamy sand with slightly acidic pH (pH 6.64) compared to degradation of thiamethoxam in the three alkaline soils (pH 7.50-8.10). The authors suggested a plausible transformation of thiamethoxam in soil as given in Figure 5-6. The authors also found a positive relationship between degradation and organic carbon content in the soils.

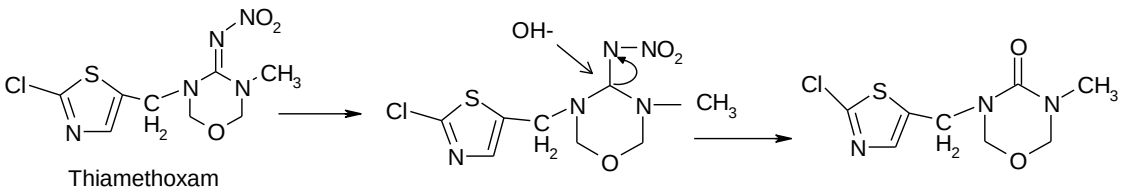

Figure 5-6 Possible transformation pathway for thiamethoxam in soil (Karmakar et al., 2006).

Gupta et al. (2008) studied persistence of thiamethoxam in a sandy loam soil under different moisture conditions (air-dry, field capacity and submerged conditions) at initial concentrations of 1.0 and 10 mg kg^{-1} for 90 days. The study showed that there was a significant difference in persistence with moisture condition with wetter soil giving faster dissipation of thiamethoxam. The dissipation of thiamethoxam was thought to result from microbial degradation. It was explained that microbial activities could be very slow or negligible under insufficient moisture condition (air-dry soil); under adequate moisture condition, the type of microbial population influenced degradation of thiamethoxam as anaerobic microorganisms (submerged soil) were more efficient in degradation of thiamethoxam than aerobic microorganisms (soil at field capacity) (Gupta et al, 2008).

5.4.3. Dissipation of metalaxyl-M from the water phase

Metalaxyl-M was stable under acidic, neutral and slightly alkaline conditions (Sukul and Spiteller, 2000). As the hydrolysis of metalaxyl-M was not significant in the water phase, the possible dissipation mechanisms were sorption to sediment and microbial degradation. The rapid dissipation of metalaxyl-M from the water phase during the first period of the experiment results from metalaxyl-M sorption to sediment. The amount of metalaxyl-M sorbed to sediment in water-sediment systems (21.3%) was lower than that in the sorption study (31.6%) (Chapter 4). As above, the lack of shaking would influence this, but the difference was much greater for metalaxyl-M than for thiamethoxam. In the meantime, some metalaxyl-M was possibly dissipated via microbial degradation as metalaxyl-M residues decreased in the water phase after metalaxyl-M in the sediment phase reached the peak.

5.4.4. Dissipation of metalaxyl-M in the sediment phase

Metalaxyl-M concentration in sediment increased to 7 days and then slowly decreased. The residue trend agreed with the assumption that metalaxyl-M was sorbed by sediment until reaching equilibrium. The peak accounted for about 21.3% of total measured metalaxyl-M at day 7.

Previous studies (Droby and Coffey, 1991; Saha and Sukul, 1997; Sukul and Spiteller, 2001; Sukul et al., 2008) demonstrated that microorganisms are able to degrade metalaxyl. Saha and Sukul (1997) compared dissipation of metalaxyl in sterilized and non-sterilized soil at field capacity (aerobic condition) and under water-logged conditions (anaerobic conditions). Loss of metalaxyl in non-sterilized soil was 52.9 and 43.3% at field capacity and under water-logged conditions, respectively whilst loss of metalaxyl in sterilized soil was 31.5 and 25.2% at field capacity and under water-logged conditions, respectively. The higher loss in non-sterilized soil indicated a significant role of microorganisms in degradation of the compound.

Sukul and Spiteller (2001) confirmed an important role of the microbial population in dissipation of metalaxyl. The authors investigated dissipation of metalaxyl in four different soils (silt, clay, silt loam and sand) under sterilized and non-sterilized conditions. Dissipation of metalaxyl in non-sterilized soil was higher than in sterilized soil. The study found that microbial activity contributed 35.8-57.3% of dissipation and that 5.3-14.7% of dissipation was due to abiotic factors excluding light (the experiment was performed in the dark).

It should be noted that the description of chemical exchange between water and sediment shown in Figure 5-1 is not entirely consistent with the physical process. In reality the exchange between water and sediment will depend on the disequilibrium (gradient in chemical potential or gradient in fugacity).

Chemical will move from water to sediment when the ratio of C_s/ C_w is $<K_d$ and there will be net movement from sediment to water when $C_s/C_w > K_d$. In the model displayed in Figure 5-1, flux from sediment to water depends only on mass of sediment and flux from water to sediment depends only on mass of water. This does not affect the ability of the model to represent concentration changes in water and sediment (see Figures 5-4 and 5-5) but it does affect how the parameters are interpreted.

5.5 Conclusions

Dissipation of the spiked pesticides from water-sediment systems in the dark arose from a number of mechanisms. The main mechanisms were hydrolysis, sorption to sediment and microbial degradation in sediment. Studies reported in Chapters 3 and 4 about factors

influencing dissipation of the pesticides helped to understand the role of each mechanism (hydrolysis and sorption) on dissipation of the pesticides from water-sediment systems.

Sorption of thiamethoxam and metalaxyl-M to sediment in the water-sediment systems was higher than that calculated based on the K_d values. It may be because there was an error in discarding water from the sediment layer such that there was a lot of water left so thiamethoxam in water combined with thiamethoxam in sediment. The dissipation rate for thiamethoxam from water obtained from the model combined all processes contributing to pesticide dissipation from water including hydrolysis and sorption so dissipation rate of thiamethoxam obtained from the model (half-life was 13 days) was faster than the observed hydrolysis rate at similar pH (half-lives ranged from 16 to 27 days at pH 7-8; Chapter 3). The similarity in half-lives suggests that hydrolysis played an important role in dissipation of thiamethoxam from water and sorption to sediment served a minor role which agrees with the prediction based on K_d that thiamethoxam sorbed up to a maximum of 13.3% in sediment.

The water-sediment study showed that a greater proportion of metalaxyl-M was in the water phase than would be predicted from the measured K_d value (Chapter 4). It could be due to non-extractable form of the pesticide sorbed to sediment. Metalaxyl-M in sediment appeared to degrade faster than the residues in the water phase because metalaxyl-M is stable to hydrolysis and there are generally fewer microorganisms in water than in sediment.

CHAPTER 6

6. INFLUENCE OF THE PRESENCE OF PLANTS ON PESTICIDE DISSIPATION FROM WATER-SEDIMENT SYSTEMS

6.1 Introduction

Chapter 5 investigated dissipation of pesticides from water-sediment systems. However, these systems only partially represent dissipation in natural water-sediment systems as real-world systems commonly contain plants. Plants in the systems could be either floating plants, submerged plants and/or rooted plants. Plants play various important roles such as producer, food and habitat in aquatic systems. Plants are not only able to use organic matter, nutrients and CO_2 from soil, water and air, but it is also recognized that they can be involved in dissipation of inorganic (Chaturvedi et al., 2012; Maresova et al., 2012; Materazzi et al., 2012) and organic contaminants (Gregoire et al., 2009).

Plants can influence dissipation of pesticides from water-sediment systems either directly or indirectly. Plants are able to directly take up and then metabolize pesticides from the surrounding water/sediment (Gregoire et al., 2009). The ability to uptake, accumulate and metabolize varies depending on plant species (Bouldin et al., 2005) and pesticide properties such as octanol-water coefficient (log K_{ow}) (Collins et al., 2006; de Carvalho et al., 2007b; Stottmeister et al., 2003) and acidity dissociation constant pKa (Trapp, 2004). Indirect effects of plants could enhance both abiotic and biotic degradation of pesticides. Establishment of plant roots in soil/sediment allows oxygen transport in the root zone supporting aerobic microbial populations to grow and degrade pesticides (Gregoire et al., 2009). Plants in water use up dissolved carbon dioxide via photosynthesis and then they produce CO_2 during respiration causing the diurnal range in pH as a result. Alkaline conditions in water can enhanced hydrolysis of some pesticides such as the neonicotinoid insecticides thiamethoxam (Karmakar et al., 2009) and imidacloprid (Guzsvany et al., 2006), and the organophosphorus insecticide phoxim (Gatidou and Iatrou, 2011).

Potential processes relating to dissipation of organic contaminants from systems containing plants are removal, accumulation, transformation and degradation of organic contaminants

(Salt et al., 1998). Many studies investigated the potential of using plants for pesticide remediation from contaminated water in wetlands (Moore et al., 2006), agricultural drainage ditches (Moore et al., 2001) and vegetated microcosms (Bouldin et al., 2005). Moore et al. (2001) reported distribution of a hydrophilic pesticide (atrazine) and a hydrophobic pesticide (lambda-cyhalothrin) among water, sediment and plants. Mean percentages of atrazine in an agricultural drainage ditch at one hour after simulated runoff (at initial concentration of 28.9 mg L^{-1}) were 37, 2 and 61% in water, sediment and plants, respectively; mean percentages of lambda-cyhalothrin (at initial concentration of 0.46 mg L^{-1}) were 12, 1 and 87% in water, sediment and plants, respectively. The length of agricultural drainage ditch required for mitigation of atrazine/lambda-cyhalothrin to a no-effect concentration (≤20 µg L^{-1}) was 50 m. The study suggested that plants served as an important sorption site taking up pesticide from water runoff as the total percentage of pesticide associated with plants during the study was 42-77% and 61-93% for atrazine and lambda-cyhalothrin, respectively. Moore et al. (2006) found a majority of methyl parathion was in plants for vegetated wetlands and that most of the pesticide was in sediment for non-vegetated wetlands after 10 days of study. A vegetated wetland length to reduce methyl parathion to 0.1% of the initial concentration (8.01 mg L^{-1}) was 18.8 m whilst a length for non-vegetated wetland was 62.9 m; this suggested that vegetated wetlands were about three times more effective in reducing methyl parathion from runoff than non-vegetated wetlands. When contaminated water was passed through a vegetated wetland, it was found that the pesticide concentration decreased to a non-detectable level at a certain distance from the contaminant source depending on water retention time, water runoff, plant contact and vegetative attributes (Moore et al., 2001).

Studies have found that plants are able to take up herbicides and/or insecticides from water runoff (Moore et al., 2001; Bouldin et al., 2005; Moore et al., 2006). Pesticide could be accumulated in the leaf (Bicalho and Langenbach, 2012; Wilson et al., 2001), stems (Gregoire et al., 2009) and/or roots (Bicalho and Langebach, 2012). Wilson et al. (2001) reported that stems and roots of four ornamental plants serve as transportation routes whilst metalaxyl was accumulated in the leaves. Bicalho et al. (2012) found that atrazine was accumulated in the roots and leaves of *Cecropia hololueca* Miq. and *Trema micranta* (L.) Blum.

The aim of this study was to use the model species *Myriophyllum spicatum* to investigate how the presence of plants influences the dissipation of thiamethoxam and metalaxyl-M from water-sediment systems.

6.2 Material and methods

6.2.1. Chemicals and test systems

Pesticides and chemicals used in this experiment were the same as those used and characterized in Chapter 3.

Sediment was collected in December 2010. The sediment was a sandy clay loam with 48.7±3.0% sand, 19.4±0.8% silt and 26.9±5.5% clay (mean±standard deviation). Sediment pH was 7.12±0.03 in distilled water and 7.01±0.01 in 0.01M $CaCl_2$. Total carbon was 5.10±0.05% and total nitrogen was 0.274±0.002%.

Myriophyllum spicatum was collected from an artificial pond at FERA, York. Shoots of the plant were trimmed to 8.0±0.5 cm to give similar fresh biomass. Fresh weight for one shoot was 0.11±0.03 g at the start of the experiment.

Sediment (150 g dry weight) was placed in glass jars and six shoots of *Myriophyllum spicatum* were planted in the sediment in each jar. M4 medium (Table 5-1) was adjusted to pH between 7.5 and 8.0 to allow for optimum growth of *Myriophyllum spicatum* (Maltby et al., 2009), then the medium (600 ml; ratio of 1 g dry weight sediment to 4 ml M4 medium) was added to the jars. The depth of sediment was 3.0±0.3 cm and that of water was 6.0±0.3 cm. The system was maintained under test conditions for a period of one week to allow *M. spicatum* to establish.

Table 6-1 Preparation of M4 Medium (Maltby et al., 2009; the first publication of the M4 medium can be found in Elendt (1990))

Macronutrient stock solutions (single substance)	Amount added to water (g L^{-1})	Concentration (relative to final M4 medium)	Amount of stock solution added to prepare medium (mL L^{-1})
$CaCl_2.2H_2O$	294	1,000-fold	1.0
$MgSO_4.7H_2O$	247	2,000-fold	0.5
KCl	58.0	10,000-fold	0.1
$NaHCO_3$	365	1,000-fold	1.0
$Na_2SiO_3.9H_2O$	50.0	5,000-fold	0.2
$NaNO_3$	2.74	10,000-fold	0.1
KH_2PO_4	1.43	10,000-fold	0.1
K_2HPO_4	1.84	10,000-fold	0.1

6.2.2. Experimental conditions

The experiment was performed at $20\pm1^{o}C$ in a growth chamber model SGC 970 Fitotron (Sanyo, UK) with a cycle of 16 hours light and 8 hours dark. Fluorescent lighting was used to provide a light intensity of 0.0117 kW m^{-2}. This was chosen to provide optimum growth conditions for *Myriophyllum spicatum* (Maltby et al., 2009).

6.2.3. Treatment and application of test substance

At the beginning of the experiment, 12 mL of a 100.3 mg L^{-1} solution of metalaxyl-M and thiamethoxam in water was added to each system to give a final concentration of 2.00 mg L^{-1} of each pesticide in overlying water. There were three replicates of each treatment. All experimental bottles were oxygenated every few days using an aquarium air pump model "airvolution; avmini" to prevent de-oxygenation in the water-sediment systems. An airline from the pump was connected to a glass pipette which was placed just below the surface to allow air bubbles to circulate in the water phase for three minutes without disturbing the sediment.

There were two controls without the spiked pesticides. The first control was a water-sediment system alone and the second control was a water-sediment system containing *Myriophyllum spicatum*. These two controls were set up in three replicates. Six different treatments were set up to investigate individual parameters (light, sediment and plants) which could affect pesticide dissipation (Table 6-2). Treatment A was the simplest system, with the spiked pesticides with M4 medium alone. From the simplest system, one parameter (light/sediment) was added to the systems giving treatment B to separate the effect of photolysis on pesticide dissipation and treatment C to understand the effect of sorption to sediment. More complex systems included two factors to give treatment D to understand the influence of sediment and light on pesticide dissipation and treatment E to understand the influence of light and plants. Treatment F comprised water, light, sediment and plants to quantify dissipation in the full systems.

6.2.4. Test duration, sampling and measurements

The experiment was performed in either light or dark environments for 56 days. Three jars from the respective treatment were sampled destructively at the intervals given in Table 6-2. The pH in water and the sediment phase and dissolved oxygen in water were measured at each interval in the sampled jars. Weight of fresh biomass of the six shoots of *Myriophyllum spicatum* was recorded.

pH and dissolved oxygen in water were measured as described in Section 5.2.1. pH measurement for sediment was made with 1: 2.5 w/v suspensions in (a) water, and (b) 0.01M $CaCl_2$. Air-dried sediment (10 g) was weighed into a 50 mL glass beaker. Distilled water 25 mL was added to the beaker. The sediment was stirred and left to stand for 10 minutes, then stirred again and the pH probe was introduced and pH was recorded when the pH reading was stable. 0.125M $CaCl_2$ (2 mL) was added into the beaker using a micropipette. The solution was stirred, the probe re-introduced and the reading recorded when it stabilised (Avery, 1982). The pH measurement in sediment was checked using a standard soil (obtained from FERA) to confirm correct measurement.

Table 6-2 A summary of experimental treatments, dissipation processes and sampling intervals

Treatment	Light (yes/no)	Sediment (yes/no)	Plant (yes/no)	Pesticide dissipation processes	Sampling interval (days)
A	no	no	no	- Hydrolysis - Microbial degradation in water	0, 28, 56
B	yes	no	no	- Hydrolysis - Microbial degradation in water - Photolysis	0, 28, 56
C	no	yes	no	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment	0, 28, 56
D	yes	yes	no	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis	0, 3, 7, 14, 28, 42, 56
E	yes	no	yes	- Hydrolysis - Microbial degradation in water - Photolysis - Plant uptake - Degradation in plant	0, 28, 56
F	yes	yes	yes	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis - Plant uptake - Degradation in plant	0, 3, 7, 14, 28, 42, 56

6.2.5. Calculation water content in *Myriophyllum spicatum*

Most *Myriophyllum spicatum* fresh weight throughout the experiment was in the range 0.1 to 0.2 g per shoot so *M. spicatum* with fresh weight 0.10±0.05 g per shoot were used for measurement of water content. Triplicate plants were dried using adsorbent tissues. The plants were oven-dried at 60°C for 1 hour and then were re-weighed. The process was repeated until there was no further change in weight. The calculation of water content in *Myriophyllum spicatum* was adopted from that for soil (Avery and Bascomb, 1982):

$$\%water\ content\ (g\ g^{-1}) = 100.\frac{mass\ of\ fresh\ biomass\ (g) - mass\ of\ oven\ dry\ biomass\ (g)}{mass\ of\ fresh\ biomass\ (g)}$$

The water content of *Myriophyllum spicatum* (±standard deviation) was 96.55±1.29% for the plant fresh weight at 0.11±0.05g.

6.2.6. Extraction of thiamethoxam and metalaxyl-M from sediment

Extraction of thiamethoxam and metalaxyl-M from sediment was performed as described in Section 5.2.3

6.2.7. Extraction of metalaxyl-M and thiamethoxam from *Myriophyllum spicatum*

Six shoots of *Myriophyllum spicatum* were rinsed with distilled water to remove sediment and/or pesticide solution from the plant surface and then the plants were dried using absorbent tissue. The plant was ground into small pieces using a glass motar. Methanol was added in a ratio of 10 ml MeOH per 1 g of the plants (wet weight) and this was then shaken on a side-to-side shaker at 150 oscillations per minute for 30 minutes. The samples were centrifuged at 2500 rpm for 10 minutes. Supernatants were decanted.

Before the plant extract was cleaned-up and concentrated by solid phase extraction technique (SPE), the extract was dried under N_2 flow, then re-dissolved in 1 mL of 20:80 (MeOH:H_2O).

The SPE cartridge used was a Strata-x 33μm polymeric reversed phase, 200 mg/ 3 mL (Strata TM, Phenomenex product). The cartridge was connected to a 24-port model, Supelco-Visiprep^{TM} solid phase extraction vacuum manifold. The cartridge was conditioned with 3 mL MeOH followed by 3 mL water, then 1 mL of the plant extract in 20:80 (MeOH:H_2O) was loaded onto the cartridge. 3 mL water was used for rinsing and then the pesticides were eluted using 3 mL MeOH. The eluate was dried under N_2 flow and re-dissolved in 0.2 mL of 50:50 (MeOH:H_2O).

A recovery test for the clean-up and concentration of the two pesticides using solid phase extraction was performed in triplicate at three concentrations (0.2, 0.5, 2.0 μg mL^{-1}). Plant extract (blank; 3 mL) was spiked with the two pesticides to obtain final concentrations of 0.2, 0.5, and 2.0 μg mL^{-1}), Solid-phase extraction was undertaken immediately as described above. The recovery values of thiamethoxam and metalaxyl-M are summarized in Table 6-3. The recovery showed that most of total added pesticides in plant extract were eluted with MeOH and they were not retained on the sorbent in the solid-phase extraction cartridge.

Table 6-3 Recovery of thiamethoxam and metalaxyl-M from plant extracts at three concentrations (mean±standard deviation)

Pesticide concentration (μg mL^{-1})	Thiamethoxam	Metalaxyl-M
0.2	91.8±1.2	86.6±10.3
0.5	97.4±1.8	84.2±0.8
2.0	108±9	87.6±8.3

6.2.8. HPLC analysis

Pesticide concentration in water and sediment samples was determined by HPLC-UV using an Agilent 1100 Series equipped with a binary pump, an auto sampler, a photodiode array detector (Agilent 1100 Series, G1365B MWD) and a C_{18} reversed-phase column (Supelco Discovery C18, 150 x 4.6 mm, 5 μm). Mobile phases were mixtures of water acidified with

0.1% phosphoric acid and methanol at a constant flow rate of 1 mL min^{-1}. For the first 10 min the mobile phase was composed of 20:80 (MeOH: 0.1% acidified H_2O). For the next 20 min the methanol content was increased to 100%, then for the next 7 min the methanol content was decreased to 20%. The absorbance for metalaxyl-M and thiamethoxam was measured at 215 and 252 nm, respectively. The Agilent 1100 series model was used to record and analyze the area of the peak for calculation of quantitative residue of the pesticides by comparing peak area and retention time of the pesticides with authentic standards.

The HPLC equipment described above was used to determine pesticide concentration in the plant extract. The HPLC condition for analysis of metalaxyl-M was a mobile phase composing 50:50 (MeOH: 0.1% acidified H_2O) at a constant flow rate of 1 mL min^{-1}. The isocratic condition was run for 15 minutes. The area of metalaxyl-M's peak for calculation of quantitative residue of the pesticide was recorded at 215 nm. The HPLC condition to analyze thiamethoxam was a mobile phase composing 15:85 (CH_3CN:0.1% acidified H_2O) at a constant flow rate of 1 mL min^{-1}. The isocratic condition was run for 20 mins.

The limit of detection (LOD) was the lowest concentration level that could be determined to be different from a blank. Limits of detection were matrix-, method- and instrument specific. The limit of detection was determined at a ratio of three for the signal height of the analyte to the noise height of a blank with matrix matching. Limits of detection in M4 medium, sediment extract and *Myriophyllum spicatum* extract for thiamethoxam and metalaxyl-M are summarized in Table 6-4.

Table 6-4 Limits of detection in M4 medium, sediment and *Myriophyllum spicatum* (mean±standard deviation) for metalaxyl-M and thiamethoxam

Matrices	Limit of detection for metalaxyl-M (±standard deviation)	Limit of detection for thiamethoxam (±standard deviation)
M4 medium (mg L^{-1})	0.013 (±0.004)	0.009 (±0.004)
Sediment (mg kg^{-1})	0.055 (±0.002)	0.051 (±0.028)
Myriophyllum spicatum (mg kg^{-1})	6.04 (±0.73)	1.85(+0.12)

6.2.9. Statistical analysis

pH in water of experimental treatment were analysed by two-way anova using Sigma Plot 12.0 to determine differences among treatments. According to pesticide residues in varying treatment and time were not normal distribution, half-live of pesticide with error of Chi^2 in varying treatment were plotted to determine difference in degradation among treatments.

6.3 Results

6.3.1. pH of the water phase

The pH in M4 medium during the experiment ranged from 5.96 to 9.49 as shown in Figure 6-1. For the systems without sediment (treatments A, B and E) the pH value in M4 medium increased to alkaline conditions. There was significant different among treatments ($p<0.001$) and also significant different among varying time ($p<0.001$) (Appendix D-14).

pH in treatment A was similar to that in treatment B whereas the presence of *Myriophyllum spicatum* resulted in more alkaline conditions in treatment E than in treatments A and B. Presumably, the rise in pH in the treatments was a result of photosynthesis activity whereby

CO_2 in solution was used as a carbon source for photosynthesis (Prins et al., 1980). At the time that pH in water was measured, the systems were illuminated so CO_2 was being fixed rather than produced by respiration.

The pH value in treatment F did not change to very alkaline conditions and was similar to the control treatment (H) (data not shown); possibly there was a balance between the effects of photo-synthesis and producing CO_2 via respiration of plants and the microbial population in sediment as the trend of pH in treatments C and D was towards acidic condition

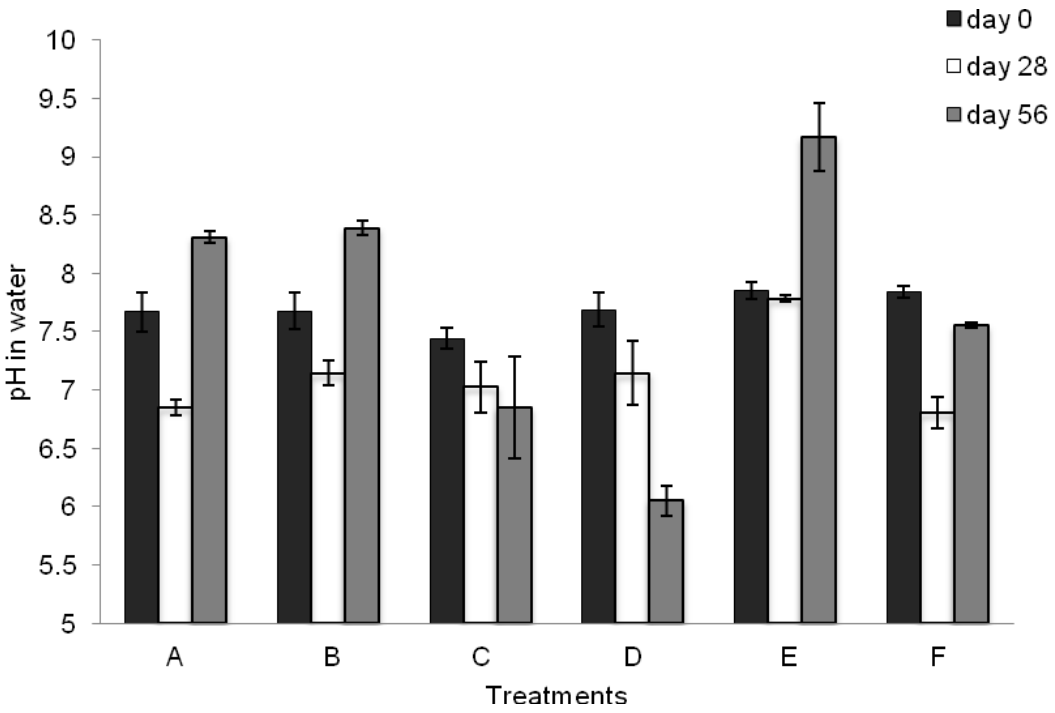

Figure 6-1 Change in pH in M4 medium in different treatments during the experiment (mean±standard deviation; n=3)

6.3.2. Dissipation of thiamethoxam from the water phase

In the presence of plants, the rate of dissipation of thiamethoxam in treatments E and F was faster than the dissipation rate in other treatments without plants as shown in Figure 6-2. The presence of sediment had a positive effect on dissipation of thiamethoxam as the rate of dissipation of thiamethoxam in treatments C and D was faster than that in treatments A and B

(without sediment). The half-life of thiamethoxam in M4 medium was about three times longer in treatment A (without sediment) than in treatment C with presence of sediment (Table 6-5). At 56 days, the thiamethoxam remaining in M4 medium was about 50% of the initial concentration in treatment A whereas thiamethoxam in M4 medium decreased to less than the limit of detection in treatment C.

The rate of dissipation of thiamethoxam in M4 medium decreased in the order treatment E > treatment F > treatment D > treatment C > treatment B > treatment A, as shown in Table 6-5. The details of thiamethoxam residues in each component of all treatments are given in Appendices D-1 to D-6.

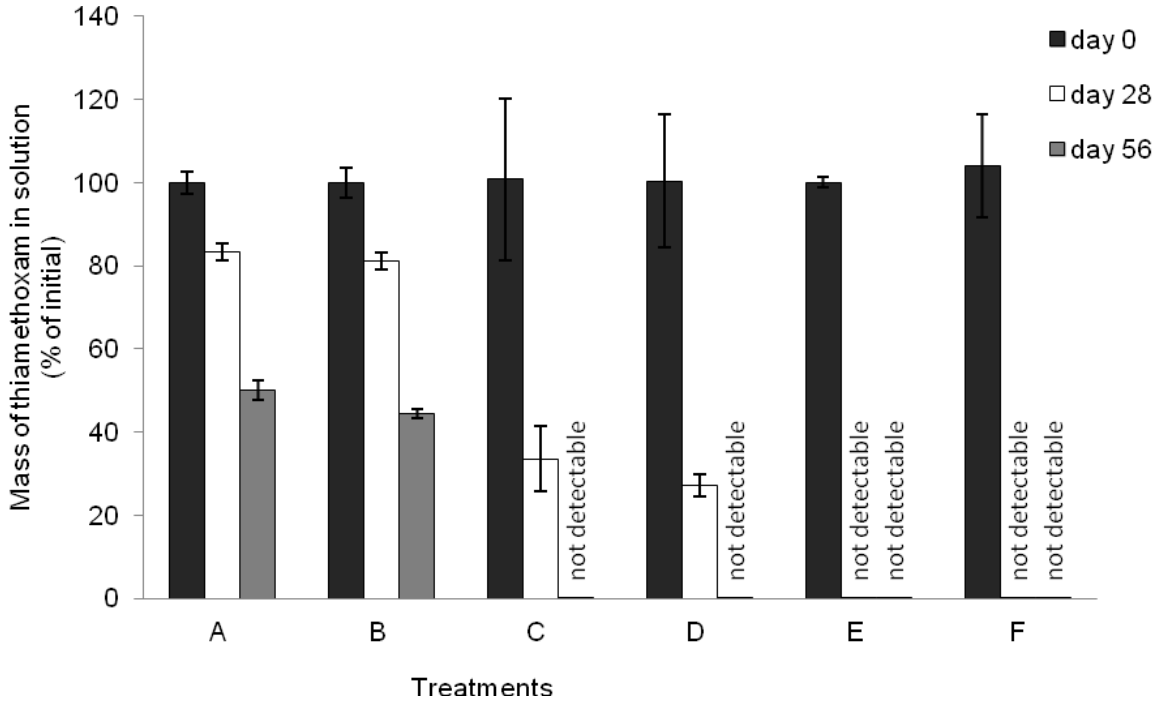

Figure 6-2 Change in concentration of thiamethoxam in solution over time for the six treatments (mean±standard deviation; n=3).

Table 6-5 Assumed processes occurring in the experimental treatments and half-life of thiamethoxam for each treatment, Chi^2 for fit and rate constant of pesticide dissipation obtained by comparing between different experimental treatments

Treatments	Assumed processes related to pesticide dissipation	Half-life (days)	Chi^2 for fit	Rate constant derived by comparing between two treatment (day^{-1})
A	- Hydrolysis - Microbial degradation in water	62.6	6.57	$k_{treatmentA} = \sim k_{hydrolysis} = 0.0111\ day^{-1}$
B	- hydrolysis - microbial degradation in water - Photolysis	54.6	7.59	$k_{treatmentB} - k_{treatmentA} = k_{photolysis}$ $0.0127-0.0111 = 0.00160\ day^{-1}$; Half-life = 433 days
C	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment	15.5	10.3	
D	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis	11.9	11.2	

Table 6-5 (continued) Assumed processes occurring in the experimental treatments and half-life of thiamethoxam for each treatment, Chi^2 for fit and rate constant of pesticide dissipation obtained by comparing between different experimental treatments. Thiamethoxam concentration in treatment E was below the detection limit after day 0 so the detection limit concentration (9 µg L^{-1}) of thiamethoxam was used to calculate half-life in treatment E

Treatments	Assumed processes related to pesticide dissipation	Half-life (days)	Chi^2 for fit	Rate constant derived by comparing between two treatment (day^{-1})
E	- Hydrolysis - Microbial degradation in water - Photolysis - Plant uptake - Degradation in plant	0.465	1.88	
F	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis - Plant uptake - Degradation in plant	1.13	2.36	

6.3.3. Dissipation of thiamethoxam from water-sediment systems

Figure 6-3 shows the change in concentration of thiamethoxam whilst Figure 6-4 shows the same data but expressed as mass of thiamethoxam. Thiamethoxam gradually decreased from 2.01±0.32 mg L^{-1} on day 0 to a non-detectable concentration on day 56 in the water phase of the systems without plants (Figure 6-3). The residues in sediment increased to a peak of 0.449±0.080 mg kg^{-1} on day 14 before decreasing to a non-detectable concentration by day 28.

In the systems containing plants, thiamethoxam residues in the water phase decreased dramatically from 1.73±0.25 mg L^{-1}at day 0 to a non-detectable concentration on day 7 and the highest peak of thiamethoxam residues in sediment was 0.0213±0.0073 mg kg^{-1} on day 14 before decreasing to a non-detectable concentration. The residues in the plants increased to a peak of 5.97±8.13 mg kg^{-1} on day 7.

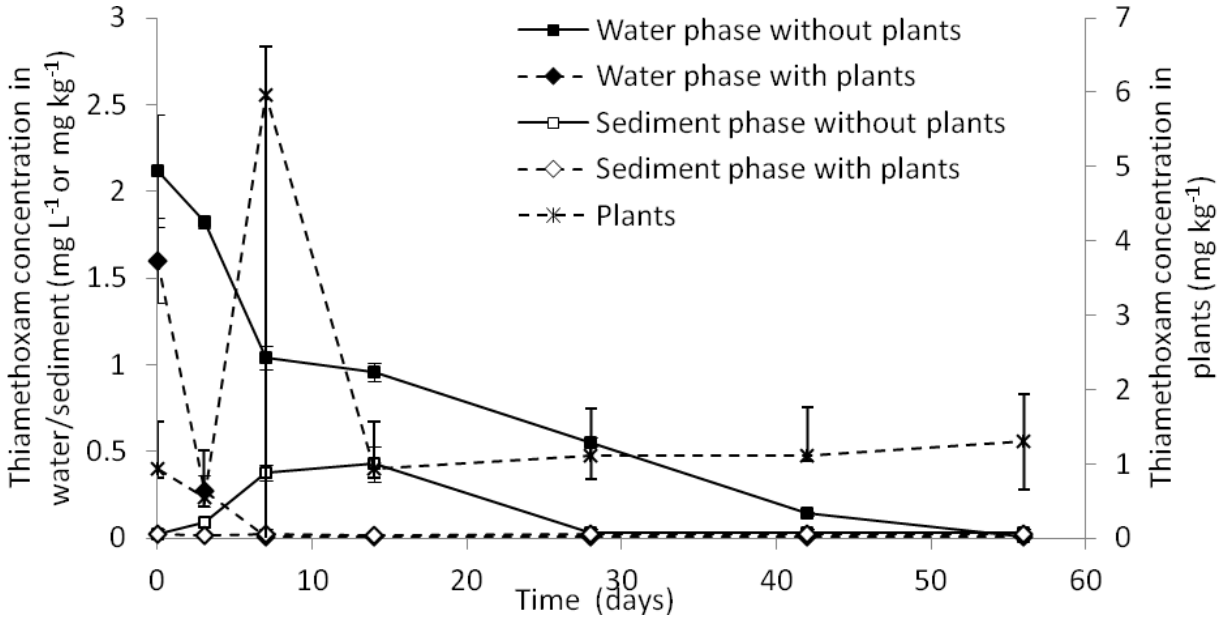

Figure 6-3 Change in concentration (mean ± standard deviation; n=3) of thiamethoxam in the water, sediment and plant phases between two systems with and without *Myriophyllum spicatum.*

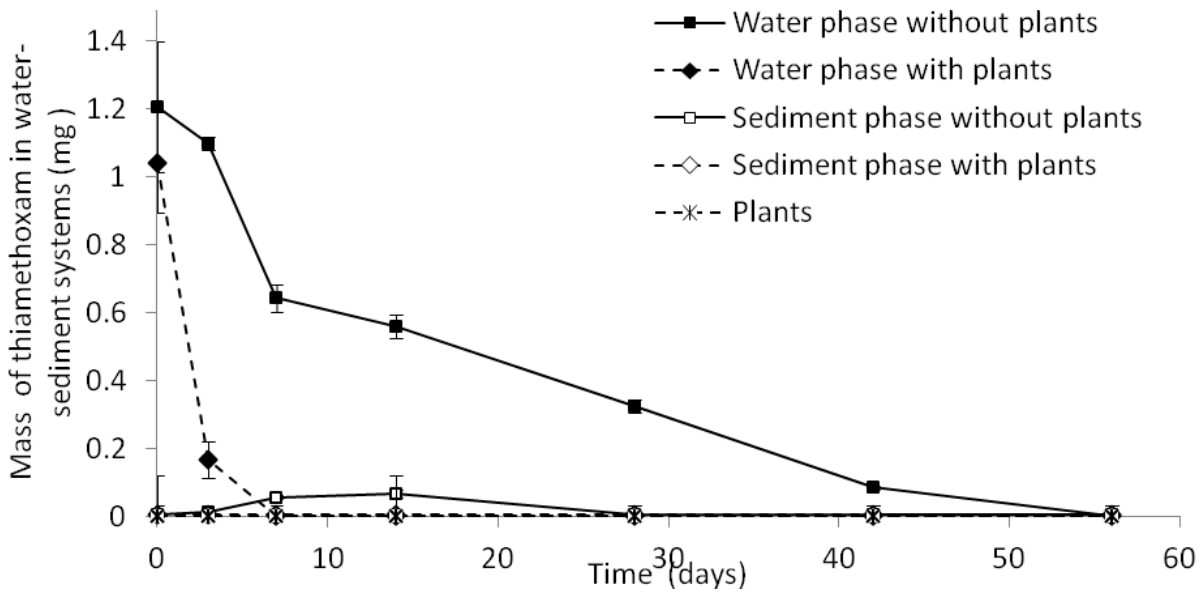

Figure 6-4 Change in mass (mean±standard deviation; n=3) of thiamethoxam in the water sediment and plant phases between two systems with and without *Myriophyllum spicatum.*

The initial mass of thiamethoxam in the systems without plants was 1.20±0.32 mg in the water phase and the mass was below the limit of detection in sediment (Figure 6-4). The maximum mass of thiamethoxam in sediment was 0.08±0.07 mg at day 14; thereafter the mass decreased to below the limit of detection. At the maximum mass of thiamethoxam in sediment, the ratio of mass in water to mass in sediment was 8.3 to 1.

Initial mass of thiamethoxam in the water-sediment system with plants was 1.04±0.25 mg in the water phase and the mass of thiamethoxam in sediment was below the limit of detection throughout the experiment. At day 3, total mass of thiamethoxam decreased by 87% to 0.17±0.09 mg in the system. The maximum mass of thiamethoxam in plants was 0.000852±0.001292 mg.

6.3.4. Dissipation of metalaxyl-M from the water phase

Loss due to volatilization was probably not significant due to the low vapour pressure of metalaxyl at 0.75 mPa (25^{o}C) and comparatively high water solubility of 7.1-8.4 g L^{-1} (PPDB, 2009; Sukul and Spiteller, 2000).

In the presence of sediment, mass of metalaxyl-M in water decreased over 60% and about 50% after 28 days in treatments F, C and D, respectively (Figure 6-5). The rate of dissipation of metalaxyl-M was faster in the treatment containing plants (treatment F) compared to treatments C and D. In water-sediment systems containing plants (treatment F), metalaxyl-M in M4 medium decreased by more than 65% after 28 days and decreased further to a non-detectable concentration after 56 days of the experiment (Figure 5-5). Comparing water-sediment treatments (D and F), Figure 6-5 shows that dissipation of metalaxyl-M in M4 medium in treatment F containing plants was faster than in treatment D (no plants). At 56 days after pesticide application, nearly 40% of metalaxyl-M remained in M4 medium in the treatment without plants whereas in the treatment containing the plants, the pesticide decreased to a non-detectable concentration.

Rate of dissipation of metalaxyl-M in M4 medium decreased in the order treatment F > treatment C > treatment D > treatment E > treatment B > treatment A (Table 6-6). The details of metalaxyl-M residues in each component of all treatments are given in Appendices D-7 to D-13.

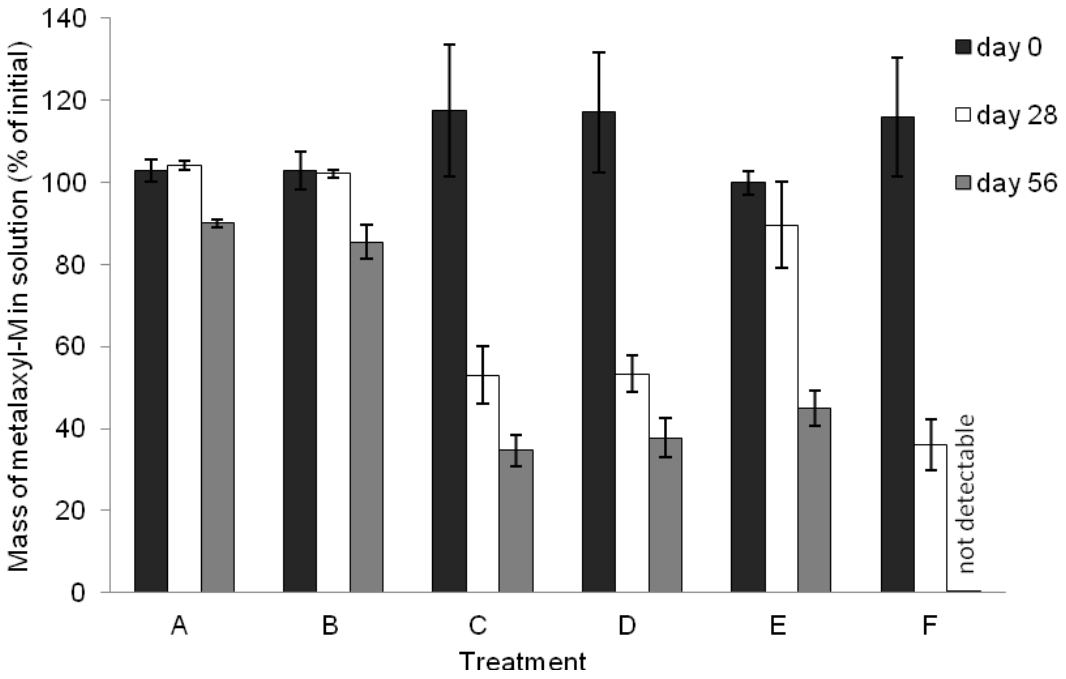

Figure 6-5 Percentage metalaxyl-M (mean±standard deviation; n=3) remaining in M4 medium among experimental treatments at three sampling interval times.

Table 6-6 Assumed processes occurring in the experimental treatments and half-life of metalaxyl-M for each treatment, Chi^2 for fit and rate constant of metalaxyl-M dissipation obtained by comparing between different experimental treatments

Treatment	Assumed processes related to pesticide dissipation	Half-life (days)	Chi^2 for fit	Rate constant derived by comparing between two treatment (day^{-1})
A	- Hydrolysis - Microbial degradation in water	310	3.31	$k_{treatmentA} = \sim k_{hydrolysis} = 0.00223\ day^{-1}$
B	- hydrolysis - microbial degradation in water - Photolysis	221	3.57	$k_{treatmentB} - k_{treatmentA} = k_{photolysis}$ $0.00313 - 0.00223 = 0.0009\ day^{-1}$; Half-life = 770 days
C	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment	28.2	0.970	
D	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis	33.0	13.3	

Table 6-6 (continued) Assumed processes occurring in the experimental treatments and half-life of metalaxyl-M for each treatment, Chi^2 for fit and rate constant of metalaxyl-M dissipation obtained by comparing between different experimental treatments

Treatment	Assumed processes related to pesticide dissipation	Half-life (days)	Chi^2 for fit	Rate constant derived by comparing between two treatment (day^{-1})
E	- Hydrolysis - Microbial degradation in water - Photolysis - Plant uptake - Degradation in plant	59.4	11.6	
F	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis - Plant uptake - Degradation in plant	13.3	15.0	

6.3.5. Dissipation of metalaxyl-M from water-sediment systems

Figure 6-6 shows change in concentration of metalaxyl-M whilst Figure 6-7 shows the same data but expressed as mass of metalaxyl-M. The water-sediment systems without the plants had metalaxyl-M concentration of 1.71±0.55 mg L^{-1} in water at day 0 and the residues in sediment increased to a peak of 0.904±0.177 mg kg^{-1} in the systems without the plants on day 7 (Figure 6-6). Concentration in sediment then decreased to a non-detectable concentration after 42 days.

Metalaxyl-M residues in the water phase decreased gradually from 2.31±0.29 mg L^{-1} on day 0 to a non-detectable concentration on day 56 in the water-sediment systems containing *Myriophyllum spicatum*. The residues in sediment increased to a peak of 1.39±0.25 mg kg^{-1} in the systems containing the plants and then decreased to a non-detectable concentration thereafter. The peak of metalaxyl-M residues in the plants was 15.74±2.74 mg kg^{-1} on day 14.

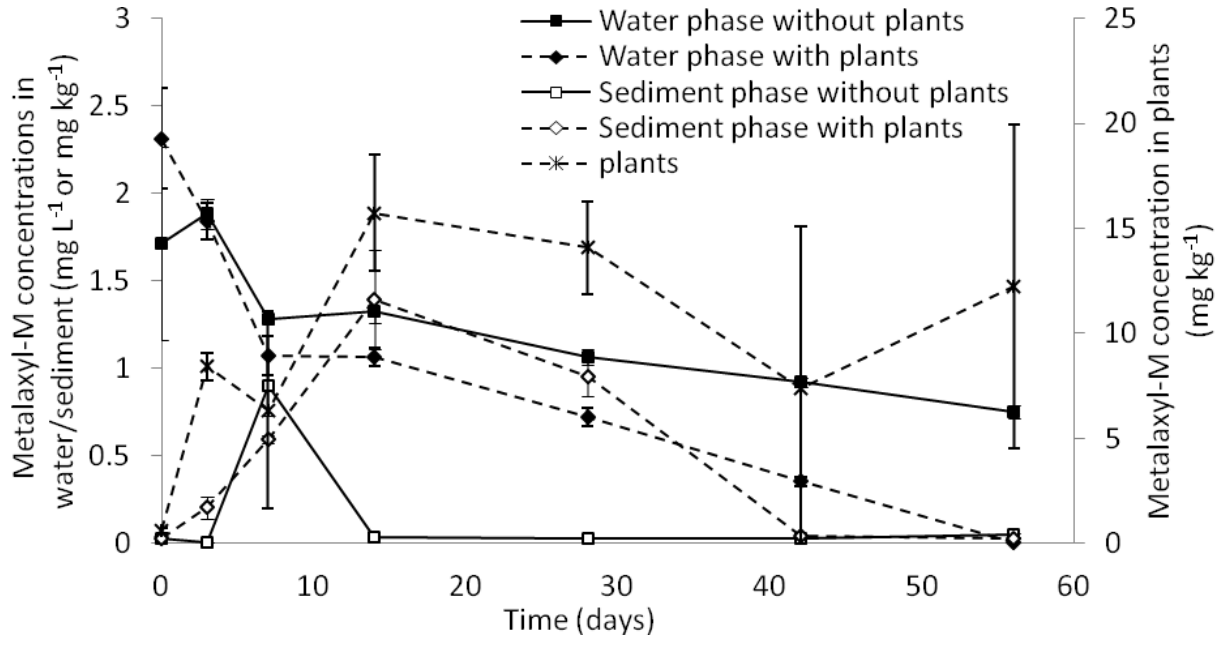

Figure 6-6 Change in concentration (mean±standard deviation; n=3) of metalaxyl-M in the water, sediment and plant phases between two systems with and without *Myriophyllum spicatum.*

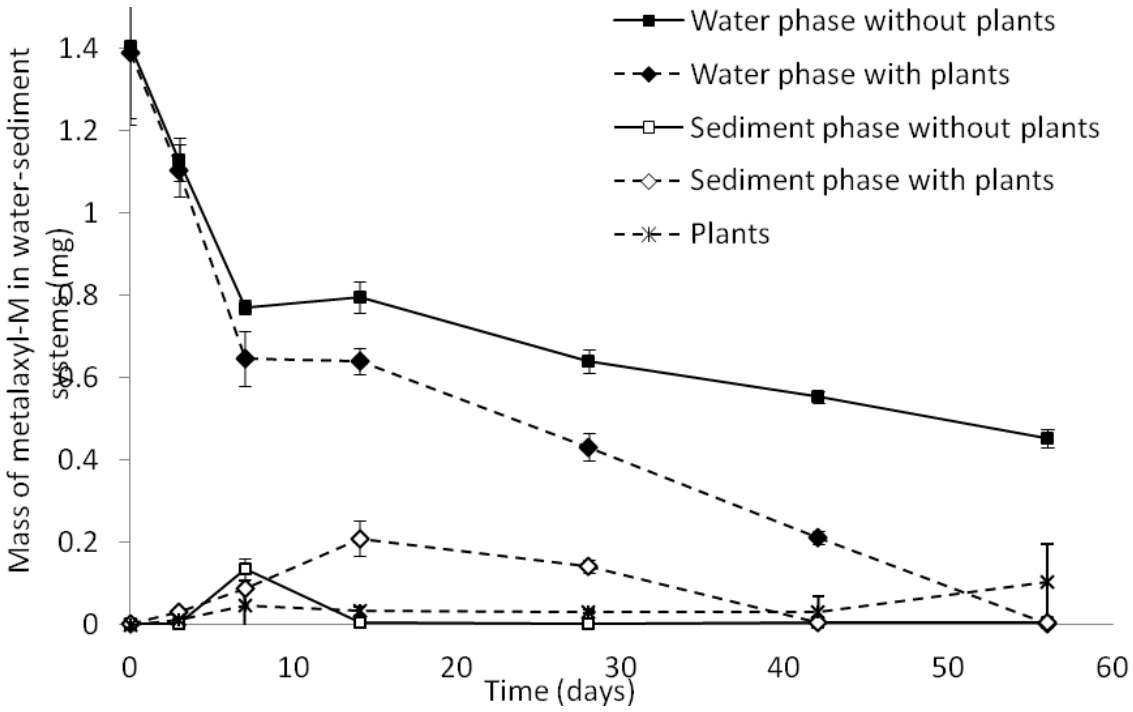

Figure 6-7 Change in mass (mean±standard deviation; n=3 in water) of metalaxyl-M in the water, sediment and plant phases between two systems with and without *Myriophyllum spicatum*.

The initial mass of metalaxyl-M in the systems without plants was 1.40±0.17 mg. At the end of the experiment (day 56), the mass of metalaxyl-M remaining in water and sediment was 0.453±0.023, 0.00705±0.00125 mg, respectively (Figure 6-7). The maximum mass of metalaxyl-M in sediment was at day 14 giving the ratio mass in water to mass in sediment of 5.7 to 1.

The initial mass of metalaxyl-M in systems with plants was 1.39±0.17 mg. Mass of metalaxyl-M continuously decreased to below the limit of detection at day 56. The maximum mass of metalaxyl-M in the sediment phase was 0.209±0.043 mg at day 7; thereafter the pesticide decreased to below the limit of detection at day 56 as shown in Figure 6-7. The ratio of mass of metalaxyl-M in water to that in sediment at the maximum metalaxyl-M in sediment was 3.1 to 1. The maximum mass of metalaxyl-M in the plants was 0.104±0.093 mg on day 56.

6.4 Discussion

6.4.1. Thiamethoxam

The presence of plants contributed to three processes of dissipation of thiamethoxam, namely (i) uptake by plants as the pesticide was found in plant extracts, (ii) enhanced hydrolysis and photolysis, and (iii) enhanced biodegradation as the rhizosphere supports microbial degradation and root exudates may degrade the two pesticides. This study did not collect data on biodegradation because of limitations in budget which prevented use of radioactive compounds. In treatments containing plants (treatment E and F), pH of water became more alkaline resulting in faster hydrolysis and photolysis rate.

The hydrolysis rate of thiamethoxam in treatments A and B was similar because pH values in these treatments were both neutral. This assumption was supported by previous studies showing that hydrolysis of thiamethoxam under neutral conditions is slow (Chapter 3, Liqing et al., 2006 and Karmakar et al., 2009).

Sediment also influenced dissipation of thiamethoxam as rate of dissipation in treatments C and D in the presence of sediment was faster than that without sediment (treatments A and B). The maximum observed amount of thiamethoxam in sediment (<0.07%) was smaller than the predicted amount (13.3%) based on a calculation using the K_d equation and K_d value (1.63 L kg^{-1}, Section 4.2). Again, it is likely that sorption of thiamethoxam to sediment in this experiment was lower than the predicted amount from K_d because only the top layer of sediment was directly in contact with pesticide whilst sediment was shaken in the sorption experiment (Section 4.2) meaning all sediment was in contact with pesticide.

Light had a minor effect on rate of dissipation of thiamethoxam as rate of dissipation of thiamethoxam in the treatments in the presence of light was a little bit faster than that in treatments without light (treatment A (a half-life was 62.6 days) compared to treatment B (a half-life was 54.6 days), and treatment C (a half-life was 15.5 days) compared to treatment D (a half-life was 11.9 days)) regardless of the presence of sediment.

Comparing photolysis of thiamethoxam in the "Suntest" (Section 3.1) and that in the growth chamber, half-lives of thiamethoxam from the "Suntest" (0.34$\pm$0.01 day at pH 7.0, 0.40$\pm$0.06

day at pH 8.0) showed a much faster rate of photolysis than the rate in the growth chamber. There were a number of possibilities that contributed to high photolysis in the previous experiment. Light intensity from the xenon lamp in the "Suntest" (1.27 kW m^{-2}) was much higher than that in the growth chamber (0.0117 kW m^{-2}). The spectrum of light from the xenon lamp ("Suntest") ranged 300-1500 nm whilst that from the fluorescent lamp ranged 300-700 nm. Temperature in the "Suntest" was higher (30 ± 2^{o}C) than in the growth chamber (20 ± 1^{o}C). The container could be a subsidiary reason in that the quartz tube used in the photolysis experiment in the "Suntest" did not absorb UV light whilst the glass jars used in the water-sediment experiment had potential to absorb some UV light.

6.4.2. Metalaxyl-M

Sukul and Spiteller (2000) stated that metalaxyl is stable to hydrolysis at a pH range from pH 1 to pH 9 at 20^{o}C. The pH in M4 medium across all experimental treatments was in the range 6.0 to 9.5 so it can be assumed that hydrolysis of metalaxyl-M was negligible.

The rate of dissipation of metalaxyl-M was faster in the presence of sediment than that in equivalent treatments without sediment. For instance, the half-life of metalaxyl-M in M4 medium was about nine times longer in treatment A (without sediment) than in treatment C in the presence of sediment (Table 6-6). This demonstrates an effect of sediment on dissipation from the aqueous phase. After 56 days of the experiment, the thiamethoxam concentration in M4 medium was more than 80% of the initial concentration in treatment A whereas in treatment C only about 30% of initial metalaxyl-M remained in solution (Figure 6-5). The maximum observed amount of metalaxyl-M in sediment (15.0%) was again smaller than the expected amount (31.6%) based on calculation using K_d equation and K_d value (1.83 L kg^{-1}, Section 4.2).

Dissipation of metalaxyl-M from water-sediment-plant systems was faster than in the other treatments. It is assumed that in the presence of sediment, dissipation of metalaxyl-M from the water phase could be either from metalaxyl-M sorption to sediment, uptake by plants (Wilson et al., 2001; Zaki et al., 1981), or microbial degradation (Saha and Sukul, 1997; Sukul et al., 2008). It is possible that the presence of plants gave favourable conditions for the

microorganisms as roots of plants de-aggregate sediment allowing aeration and/or dead leaves are a source of food for microorganisms.

Metalaxyl-M residues found in plants in this study were consistent with those in previous studies showing that plants are able to take up metalaxyl. Metalaxyl was taken up by roots (Wilson et al., 2001; Zaki et al., 1981) and then distributed within the plants and accumulated in the leaves (Wilson et al., 2001). The authors suggested from plant tissue analysis that after 1 day of exposure, metalaxyl mainly accumulated in the leaves of *Myriophyllum aquaticum* Vell whilst very little metalaxyl was accumulated in the stems and roots. This evidence supported an assumption that metalaxyl was transported via stems and roots in parrotfeather, sweetflag and canna. The finding in other plants such as soybean (Gupta et al., 1985) and tomato (Zaki et al., 1981) also supported the assumption. Metabolic products of metalaxyl were different depending on plant species, metabolic pathways and enzymes (Sukul and Spiteller, 2000). For example, transformation of metalaxyl can occur via various processes such as aryl hydroxylation, ester cleavage, O-dealkylation and N-dealkylation (Businelli et al., 1984; Owen and Donzel, 1986). Wilson et al. (2001) reported different ability of four plants (sweetflag (*Acorus gramineus* Sol. Ex Aiton), canna (*Canna hybrid* L. 'Yellow King Humbert'), parrot feather (*Myriophyllum aquaticum* Vell.) and pickerelweed (*Pontederai cordata* L.) to remove metalaxyl from solution. The reduction of metalaxyl in solution at day 7 of the exposure period was 16, 60, 31, and 50% for sweetflag, canna, parrot feather and pickerelweed, respectively.

Presence of light in the growth chamber did not contribute to the rate of dissipation of metalaxyl-M because of half-lives of metalaxyl-M for treatments A (dark) and B (light) suggesting persistent of metalaxyl-M in water phase. More than 80% of metalaxyl-M remained in M4 medium in both treatments without sediment (treatment A and B) at the end of the experiment (Figure 6-5). Sukul and Spiteller (2000) reported that λ_{max} of metalaxyl is 196 nm in aqueous solution and that there is no absorption above 290 nm. The emission wavelength of the fluorescent lamps was 300-700 nm which was not absorbed by metalaxyl molecules (Sukul and Spiteller, 2000). There was no significant difference in half-lives of metalaxyl-M in treatments C and D, suggesting that the presence of light in the growth chamber was not an important factor for degradation of metalaxyl-M in sediment.

6.5 Conclusions

This experiment provided information on the distribution of thiamethoxam and metalaxyl-M among water, sediment and plants including dissipation of thiamethoxam and metalaxyl-M in each component in the systems with and without plants. The results demonstrate that plants have an important role in dissipation of thiamethoxam and metalaxyl-M. It suggests that in water-sediment systems with plants, dissipation of the pesticides will be faster than in equivalent systems without plants. Plants contributed to both direct and indirect effects on dissipation of pesticide; the direct effect was via uptake by plants and the indirect effect was a change in pH to more alkaline condition resulting in faster hydrolysis and photolysis of thiamethoxam. Uptake by the plants was small in terms of mass but would be a greater proportion of the total in natural systems with a greater mass of plants.

Distribution of thiamethoxam residues in water-sediment systems was similar for all treatments in that most of the residues were located in the water phase whilst smaller amounts sorbed to sediment in agreement with the low K_d value (Section 4.2). Sorption of thiamethoxam to sediment was less than predicted based on a calculation from the K_d value. The strength of influencing factors on dissipation of thiamethoxam from the water-sediment systems with/without plants are in the order plants > sediment > light. Calculated photolysis (Table 6-5) at pH 7.0-8.5 showed that the photolysis rate of thiamethoxam was very low whilst photolysis in the systems with plants could be accelerated by alkaline conditions (Section 3.1). Light intensity in the growth chamber was constant and selected for optimum growth of *Myriophyllum spicatum* whilst the spectrum of wavelengths from sunlight is very different from that from the fluorescent light; also light intensity under the outdoor conditions fluctuates so photolysis of the pesticide under laboratory and outdoor conditions could be different.

The distribution of metalaxyl-M in water-sediment systems also agreed with its low K_d value in general. Most of the metalaxyl-M residues were located in the water phase. The strength of influencing factors on dissipation of metalaxyl-M from the water-sediment systems with/without plants are in the order sediment > plants > light. As metalaxyl-M was stable to hydrolysis and photolysis, microorganisms served an important role in dissipation of metalaxyl-M from sediment. The fastest dissipation of metalaxyl-M was in a system with

sediment and plants as this could provide favourable conditions for growth of microorganisms. However the experiment did not investigate microdegradation of the pesticide, the role of microorganisms was assumed base on literature reviews.

CHAPTER 7

7. PESTICIDE DISSIPATION FROM WATER-SEDIMENT SYSTEMS IN VESSEL UNDER OUTDOOR CONDITIONS

7.1 Introduction

Dissipation of pesticides measured in laboratory experiments has often been used to predict dissipation of pesticides in the field. Most research investigated dissipation of pesticides in single compartments under constant conditions for factors such as temperature and light intensity in order to explain behaviour of pesticides in natural systems. There were many pesticide studies in single components; either water, soil or sediment (Banerjee et al., 2008; Campbell et al., 2005; Carbo et al., 2007; Liqing et al., 2006). Under field conditions, most factors are not constant especially weather conditions, and natural systems are multi-component containing water, soil, sediment, plants and animals. There is variation in either abiotic parameters (weather condition, light intensity, heterogeneous composition of sediment, and surface interactions between air-liquid-solid phases) and/or biotic parameters (number of species and population) that contributes to the difference between dissipation of pesticide in laboratory and field experiments. Physico-chemical properties of the pesticide determine the role of environmental factors. In many cases, differences between dissipation of pesticide in laboratory and field systems were found (Dinelli et al., 2000; Mazanti et al., 2003; PerrinGanier et al., 1996). Generally, dissipation of pesticide under field conditions was faster than that under laboratory conditions both in water (Mazanti et al., 2003) and soil (Dinelli et al., 2000; PerrinGanier et al., 1996). Studies on three pesticides in aquaria and outdoor pond systems showed a similar dissipation rate of chlorpyrifos whilst half-lives for atrazine were 150 and 27-48 days under indoor and outdoor conditions, respectively (Mazanti et al., 2003). Half-lives for metolachlor were 55 and 12-20 days under indoor and outdoor condition, respectively (Mazanti et al., 2003).

A study comparing behaviour of pesticides in water-sediment systems in the laboratory and field (Bromilow et al., 2006) showed that dissipation of eight pesticides in water-sediment systems in the laboratory was slower than in the field. In the field experiment, hot and dry weather over summer accelerated degradation of the pesticides (chlorotoluron, isoproturon,

pendimethalin, mecoprop) compared to degradation in winter. Pesticide properties (especially lipophilicity) contributed to partition of pesticide in both sediment and plants. Lipophilic pesticides (chlorpyrifos, pendimethalin and permethrin) moved into 2.5 cm depth of the sediment within 30 days while others (isoproturon and chlorotoluron) remained largely in the water. Lipophilicity was also positively correlated with uptake into aquatic plants (*Lemma major*). Pesticide uptake by plants in the field was two-to threefold higher than uptake in the laboratory. Uptake by the plants was a small amount compared to sorption to sediment and the amount of dissolved pesticides in water. The authors suggested that laboratory systems gave a reasonably accurate prediction of field behaviour for some pesticides including isoproturon, chlorotoruron, chlopyrifos, and pendimethalin but for others including permethrin and difenoconazole, laboratory estimates could possibly overestimate persistence in the field and movement into soil/sediment. Beulke et al. (2005) compared degradation of two pesticides (cyanazine and bentazone) based on half-lives derived at constant temperature (15 or 25^{o}C) and moisture content (40 or 70% soil moisture content) in a clay loam soil and half-lives measured under fluctuating conditions (temperature 15/25^{o}C, moisture content 40/70%). The results showed that degradation obtained under static conditions gave a reasonable prediction of the degradation under fluctuating conditions. However, there is a need for more work with a wider range of pesticides and test conditions before concluding that laboratory experiments can mimic degradation of pesticide under field conditions (Beulke et al., 2005).

The TOXSWA model describes fate of pesticides entering into single field water systems such as ditches, ponds or streams (Adriaanse et al., 2002; Beltman and Adriaanse, 1999). The model considers four processes: (i) transportation of pesticide by advection and dispersion in both water and sediment layers; (ii) transformation of pesticide as a function of temperature in water and sediment; (iii) sorption to sediment, suspended solid and macrophytes; and (iv) volatilization as a function of temperature (Figure 7-1).

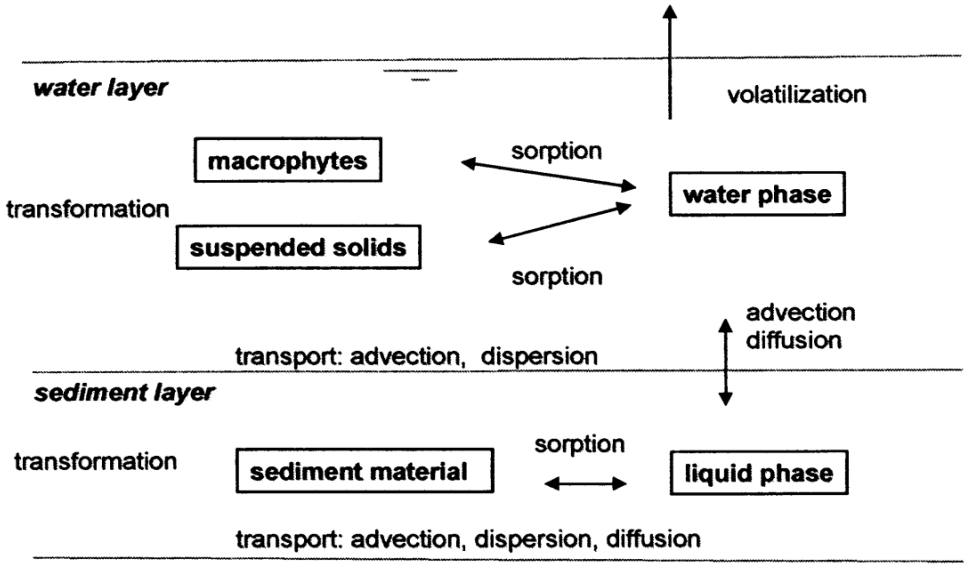

Figure 7-1 Processes govern pesticide fate in water-sediment system in TOXSWA (Adriaanse et al., 2002).

The TOXSWA model predicts the concentration of pesticide as a function of time and distance (or depth for sediment) in a water body and sediment. The model assumes a constant pesticide concentration in the vertical direction of the water column, whilst the pesticide concentration can be varied in the horizontal direction. In the sediment layer, the pesticide concentration is assumed to vary in both the horizontal and vertical distance.

Transformation of pesticide in TOXSWA depends on temperature. The transformation is calculated via:

$$k(T) = k\ (T_{ref})\ \exp\ [\frac{E}{R.T_{ref}.T}(T - T_{ref})]$$

Where T is temperature (K), T_{ref} is reference temperature (K), k is a transformation rate coefficient (d^{-1}), E is molar Arrhenius activation energy (J mol^{-1}) and R is the universal gas constant (~8.3144 J mol^{-1} K^{-1})

Volatilization of pesticide is calculated using the Van't Hoff equation as:

$$P(T) = P(T_{ref}) \exp[-\frac{\Delta H_P}{R}(\frac{1}{T} - \frac{1}{T_{ref}})]$$

where P is saturated vapour pressure of substance (Pa) and ΔH_P is enthalpy of vaporization (J mol^{-1})

The Van 't Hoff equation is also used to calculate effect of temperature for solubility of pesticide in water as:

$$C_{sol}(T) = c_{sol}(T_{ref}) \exp\left[-\frac{\Delta H_{sol}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

where C_{sol} is solubility of substance in water (g m^{-3}) and ΔH_{sol} is enthalpy of dissolution (J mol^{-1})

The output of model simulation is concentration/mass of pesticide in water, macrophytes (optional) and sediment as a function of time and distance (depth for sediment) and distribution of pesticide among water, suspended solid, dissolved sediment, sorbed to sediment and macrophytes.

Sediment in the simulated water-sediment system is divided into subsystems. The model assumes that there is no lateral interaction among each sediment subsystem in the horizontal layer and that the vertical is subdivided. Input transformation rates in TOXSWA are overall transformation in water and sediment phases. In water, the rate is a combination of hydrolysis, photolysis and biodegradation. Moreover, it is not possible to vary transformation rate caused by e.g. change in pH of water, and intensity of light. The results obtained from the model are dictated by the input data so careful selection of the input data, laboratory experiment and/or measured field data is required to get acceptable results.

The aim of this study was to investigate dissipation of the two pesticides from water-sediment systems in vessel under outdoor conditions and compare behaviour with that in water-sediment under laboratory conditions. The work also investigates whether using experimental

data from the laboratory as input to the TOXSWA model can give a reasonable prediction for fate of the pesticide in water-sediment systems under outdoor condition.

7.2 Materials and methods

7.2.1. Chemicals and test systems

The pesticides, chemicals, M4 medium (growth medium), plants (*Myriophyllum spicatum)* and sediment used in this experiment were the same as those used and characterized in Section 6.2.1. Water-sediment systems for all treatments (Table 7-1) were set up similarly to those described in Section 6.2.1.

7.2.2. Experimental conditions

The experiment was performed outdoors at FERA, York (54^{o} 0' 53"N 0^{o} 58' 13"E). A WS-HP1, Delta-T Devices automatic weather station was located within 200 m of the experiment. The weather station measured rainfall, wind speed, air temperature, soil temperature, relative humidity and solar radiation at an hourly interval (detail in Appendix Table E-1). Treatments and application of test substance were similar to the experiment in Chapter 6. The experimental time was decreased to 28 days because it was expected that dissipation of the two pesticides under outdoor conditions would be faster than under laboratory conditions as reported for previous studies (Mazanti et al., 2003; Perrin-Ganier et al., 1996; Dinelli et al., 2000). A summary of experimental treatments and sampling intervals is given in Table 7-1 excluding two control treatments (no pesticide in the system); treatment G was a water-sediment system without pesticides and treatment H was a water-sediment-plant system without pesticides.

Table 7-1 Summary of experimental treatments, dissipation processes and sampling intervals

Treatment	Light (yes/no)	Sediment (yes/no)	Plants (yes/no)	Pesticide dissipation processes	Sampling interval (days)
A	no	no	no	- Hydrolysis - Microbial degradation in water	0, 14, 28
B	yes	no	no	- Hydrolysis - Microbial degradation in water - Photolysis	0, 14, 28
C	no	yes	no	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment	0, 14, 28
D	yes	yes	no	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis	0, 7, 14, 28
E	yes	no	yes	- Hydrolysis - Microbial degradation in water - Photolysis - Plant uptake - Degradation in plant	0, 1, 3, 5, 7
F	yes	yes	yes	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis - Plant uptake - Degradation in plant	0, 1, 3, 5, 7

7.2.3. Sampling and measurements

The experiment was performed under outdoor conditions for 28 days from 9th August 2011 (day 0) until 6th September 2011. Three jars from the respective treatment were sampled destructively at the intervals given in Table 7-1 and the sampling time was midday$\pm$1 hours. The pH in water and sediment phases and dissolved oxygen in water were measured at each

interval in the sampled jars. The weight of fresh biomass of the six shoots of *Myriophyllum spicatum* was recorded.

Water content of *Myriophyllum spicatum* was calculated as described in Section 6.2.5. Water content of *Myriophyllum spicatum* (±standard deviation) was 90.6±0.25% for plants with fresh weight of 0.11±0.03g.

Extraction of thiamethoxam and metalaxyl-M from sediment and plants and HPLC analytical conditions were as described in Sections 6.2.6 – 6.2.8.

7.2.4. Simulation of the fate of pesticides using TOXSWA

TOXSWA model version 1.0 (release date March 22nd, 1999) was used to simulate fate of pesticides in water-sediment systems. The model was written by M. Van Elswijk (SERC) and revised by G.F. van Laar (Q-Ray). TOXSWA predicts fate of pesticides via a simulation that combines a scenario and a set of pesticide parameters. Required input data for pesticide and water-sediment characteristics (scenario) are given in Appendices E-17 and E-18, respectively.

The scenario for the water-sediment system (treatment F) used characteristics of the experimental water-sediment systems which were set up in glass bottles with 10 cm diameter. The height of the water layer was 6 cm from the top layer of sediment and the sediment layer height was 3 cm.

A half-life for thiamethoxam in water was obtained by using average radiation from day 0 to day 3 (0.114 kW m^{-2}) coupled with the photolysis rate constant from laboratory studies at pH 10 (10.6 day^{-1}) and light intensity of the xenon lamp in the Suntest system (1.27 kW m^{-2}). The half-life for modelling was calculated as:

$$Corrected\ dissipation\ rate\ constant\ in\ water\ phase = \frac{photolysis\ rate\ constant\ at\ pH\ 10.\ average\ light\ intensity\ under\ field\ conditions}{light\ intensity\ in\ the\ Suntest}$$

$$Corrected\ dissipation\ rate\ constant\ in\ water\ phase = \frac{(10.6)(0.114)}{1.27} = 0.95\ day^{-1}$$

From the calculation above, the half-life of thiamethoxam in water used for modelling treatment F in outdoor condition was 0.73 days. The half-life in sediment was obtained from Chapter 5 (27.7 days).

The half-life of metalaxyl-M in the water phase was obtained from the water-sediment study reported in Chapter 5. This experiment excluded photolysis and hydrolysis of metalaxyl-M, so the half-life was corrected with the hydrolysis rate constant at the same pH (hydrolysis rate at pH 10 is ca. 0.058 day^{-1}, Sukul and Spittler, 2000) and the photolysis rate constant of metalaxyl-M under field conditions (the dissipation rate constant of treatment B minus the dissipation rate of treatment A; Table 7-3). The corrected half-life of metalaxyl-M was calculated as:

$$\begin{aligned} Corrected\ photolysis\ rate\ constant\ of\ metalaxyl-M\ in\ water \\ = dissipation\ rate\ in\ water + hydrolysis\ rate\ constant\ at\ pH\ 10 \\ + photolysis\ rate\ constant \end{aligned}$$

Corrected rate constant of metalaxyl-M in water = 0.00509 + 0.058 + 0.00186 = 0.065 day^{-1}

The corrected rate constant of degradation for metalaxyl-M in water equated to a half-life of 10.7 days. A half-life in sediment was obtained from Chapter 5 (8.20 days).

7.2.5. Calculation goodness fit for TOXSWA's prediction and observed data

Model efficiency (EF) was employed to calculate goodness fit for TOXSWA's prediction and observed data (Boesten et al., 2006). Model efficiency was calculated as:

$$EF = 1 - \frac{\sum_{i=1}^{n}(C_i - O_i)^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2}$$

Where n = total number of observations

O_i = i^{th} observed value (with i = 1, 2,..., n)

C_i = i^{th} value calculated with selected model (with i = 1, 2, ...,n)

$\bar{O}$ = mean of all observed values

Value of EF can be from minus infinity to +1. The larger values indicate better agreement. For EF < 0, it suggests that the mean of the observed data is a better predictor of the observed values than the model (Boesten et al., 2006). For EF > 0, it indicates the fraction of the total variance of the data set that can be explained by the model.

7.3 Results

7.3.1. Weather data: temperature and solar radiation, during the experiment

Daily average air temperature during the experiment (day 0 to 28) was in the range 11.5 to 19.7^{o}C as shown in Figure 7-2. The minimum and maximum air temperature were 7.1^{o}C and 25.4^{o}C, respectively (full detail of the temperature is given in Appendix E-1). Daily average solar radiation during the experiment (day 0 to 28) ranged from 0.031 to 0.186 kW m^{-2} as shown in Figure 7-3. Detail of the solar radiation is given in Appendix E-1.

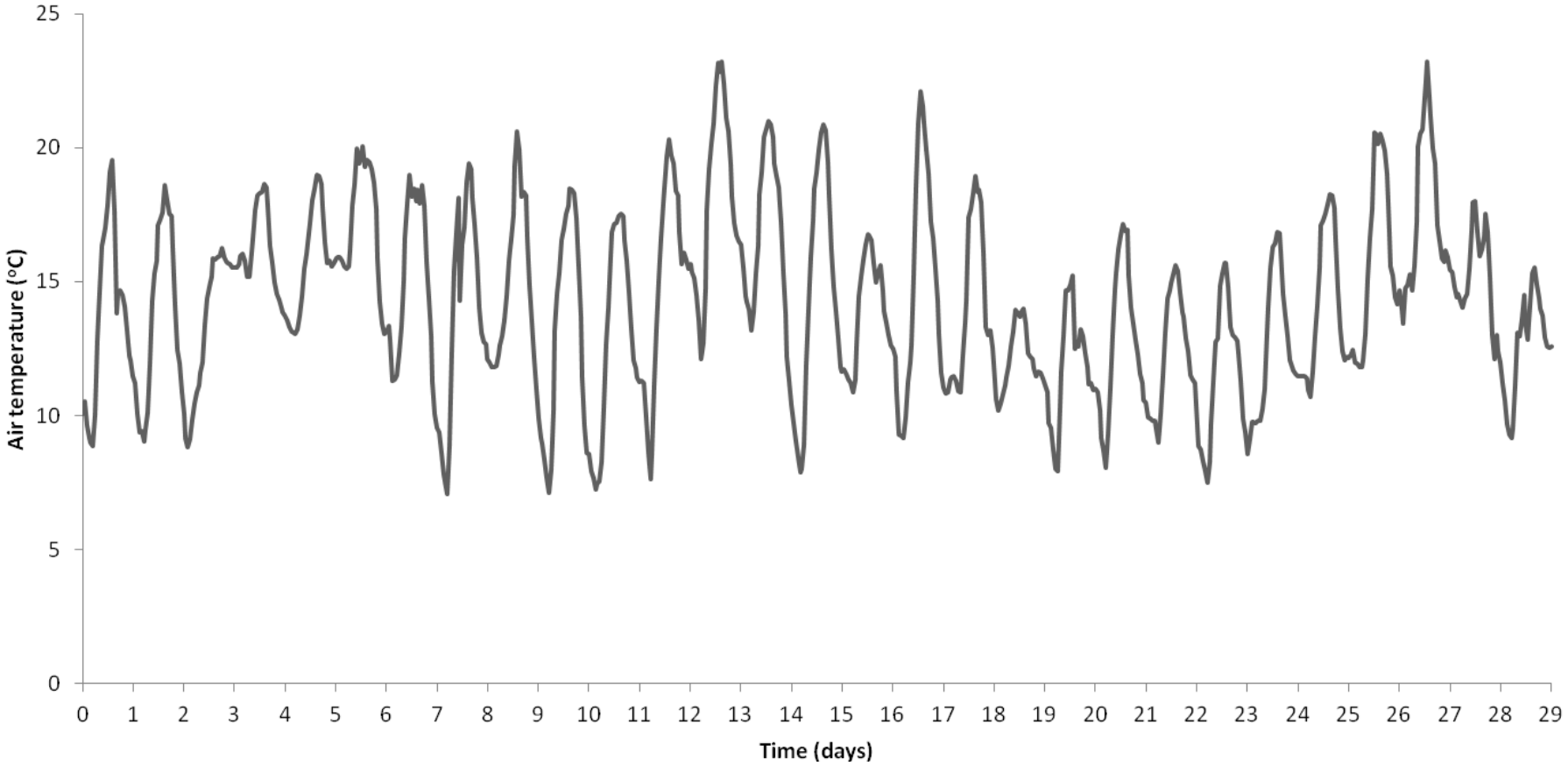

Figure 7-2 Change in air temperature during the experiment (day 0 is 9th August 2011).

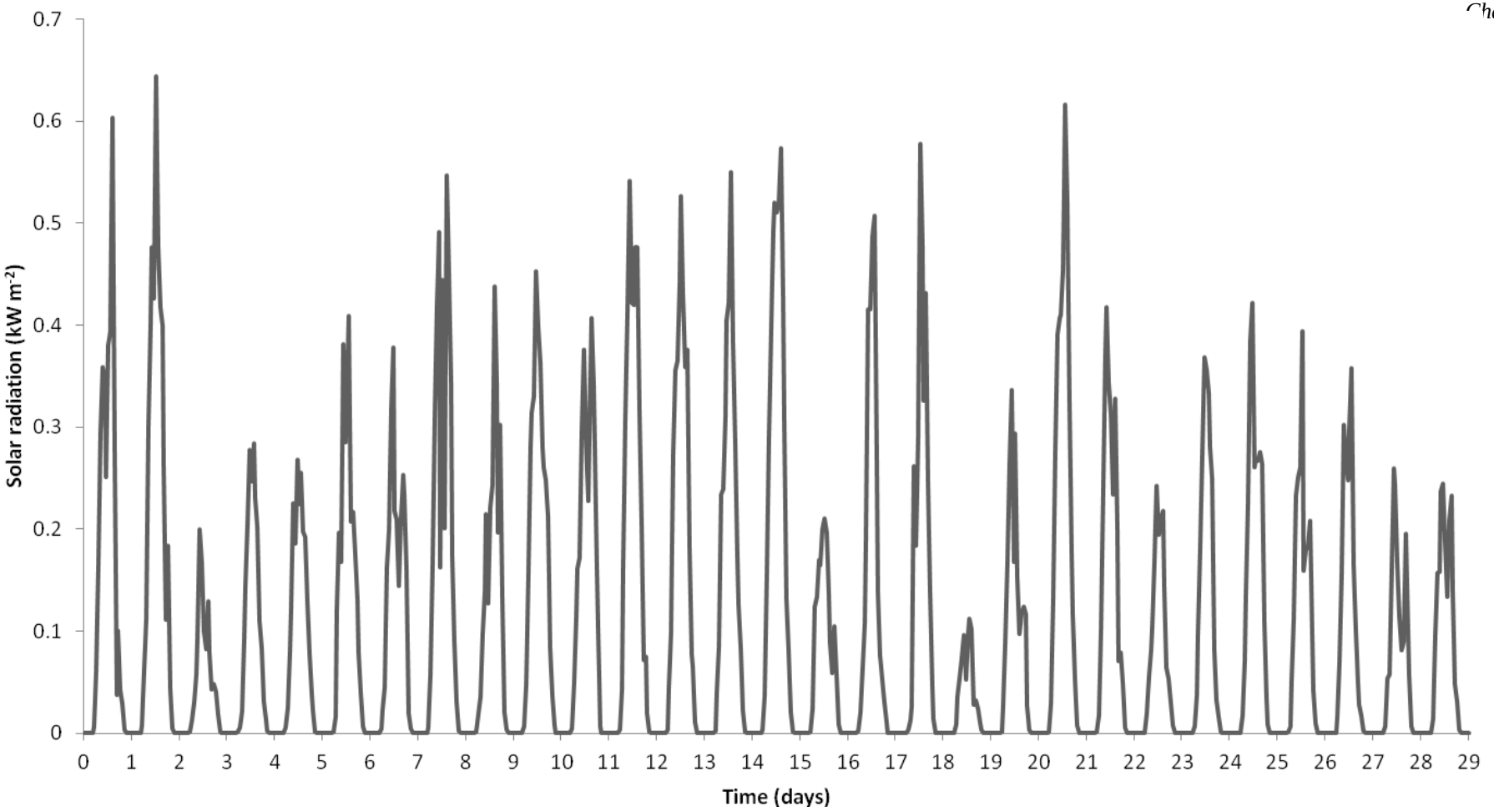

Figure 7-3 Change in solar radiation during the experiment (day 0 is 9th August 2011).

7.3.2. pH in the water phase of the experimental treatments

The pH in M4 medium during the experiment ranged from 7.95 to 9.49 as shown in Figures 7-4 and 7-5. pH was significantly different between treatments ($p<0.001$) and also significant different over time ($p<0.001$) (Appendices E-14, E-15 and E-16). For the systems without sediment (treatments A, B and E), the pH was alkaline throughout the study as shown in Figures 7-4 and 7-5. pH in treatment A was similar to that in treatment B regardless of the presence of light, whereas the presence of *Myriophyllum spicatum* resulted in more alkaline conditions in treatment E. As pH measurements were made at midday$\pm$1 hours on the sampling day, the elevated pH in the presence of plants resulted from photosynthesis that removed CO_2 from the solution (Prins et al., 1980), thus reducing the acidity in the water. For the systems with sediment (treatments C and D), the pH in treatment D was more alkaline than treatment C (Figure 7-4). There are a number of possibilities for this observation including a formation of photolysis products from algae as this experiment used natural sediment which may contain microorganisms and algae.

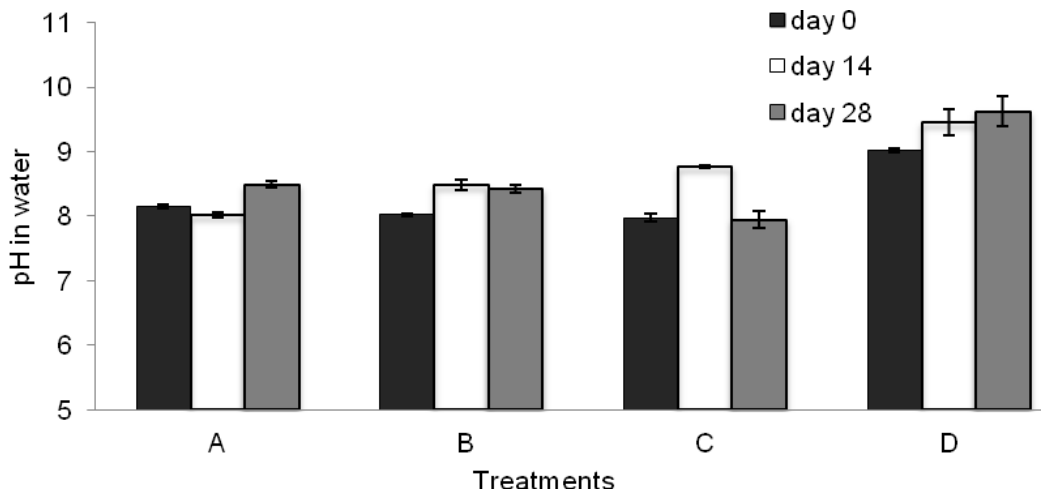

Figure 7-4 Change in pH in M4 medium in different treatments without the plants during the experiment (mean$\pm$standard deviation; n=3).

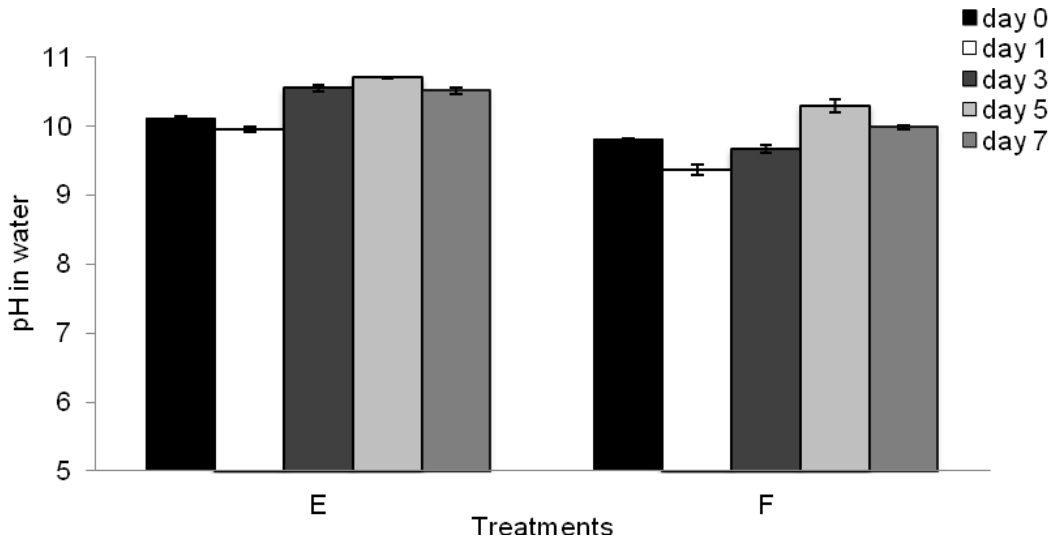

Figure 7-5 Change in pH in M4 medium in different treatments with the plants during the experiment (mean±standard deviation; n=3).

7.3.3. Dissipation of thiamethoxam from the water phase

In the presence of light, the dissipation rate of thiamethoxam in treatments B, D, E and F was faster than dissipation in equivalent treatments without light (treatments A and C) as shown in Figure 7-6 and 7-7. This confirms that light is a dominant influence on dissipation of thiamethoxam from the water phase under outdoor conditions (Chapter 3, Liqing et al., 2006 and Karmakar et al, 2000).

In the presence of plants, the dissipation rate of thiamethoxam in the treatments containing plants was much faster than the others. Thiamethoxam concentration was dramatically decreased within 3 to 5 days of the pesticide application as shown in Figure 7-6 and 7-7.

Rate of dissipation of thiamethoxam in M4 medium was calculated according to single first-order kinetics. The calculation was close to observed data and the statistic test (Chi^2) for fitting passed for all treatments (Table 7-2). The details of thiamethoxam residues in each component of all treatments are given in Appendices E-2 to E-7.

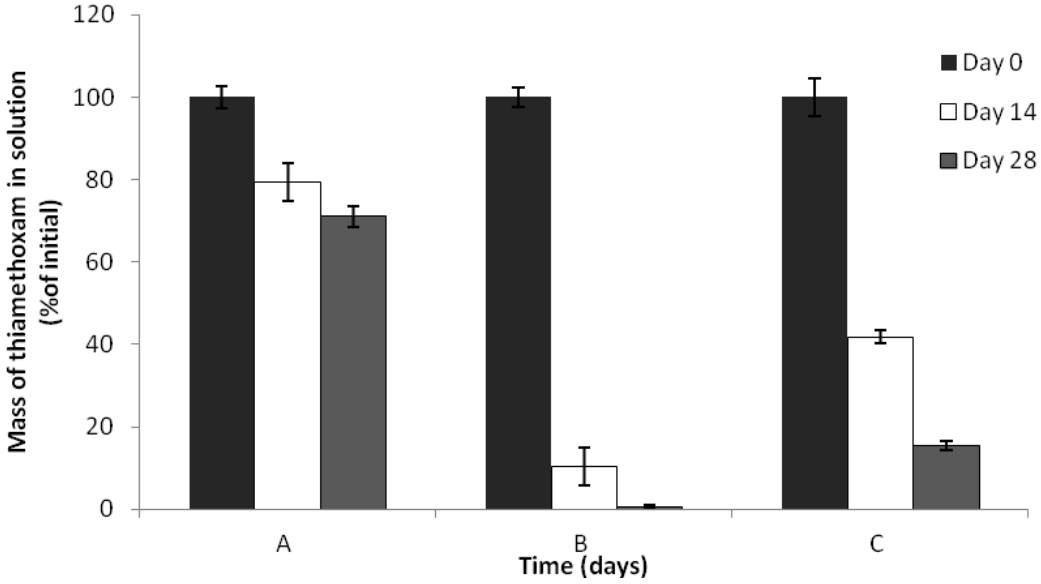

Figure 7-6 Change in concentration of thiamethoxam in solution over time for the treatments A, B and C (mean±standard deviation; n=3).

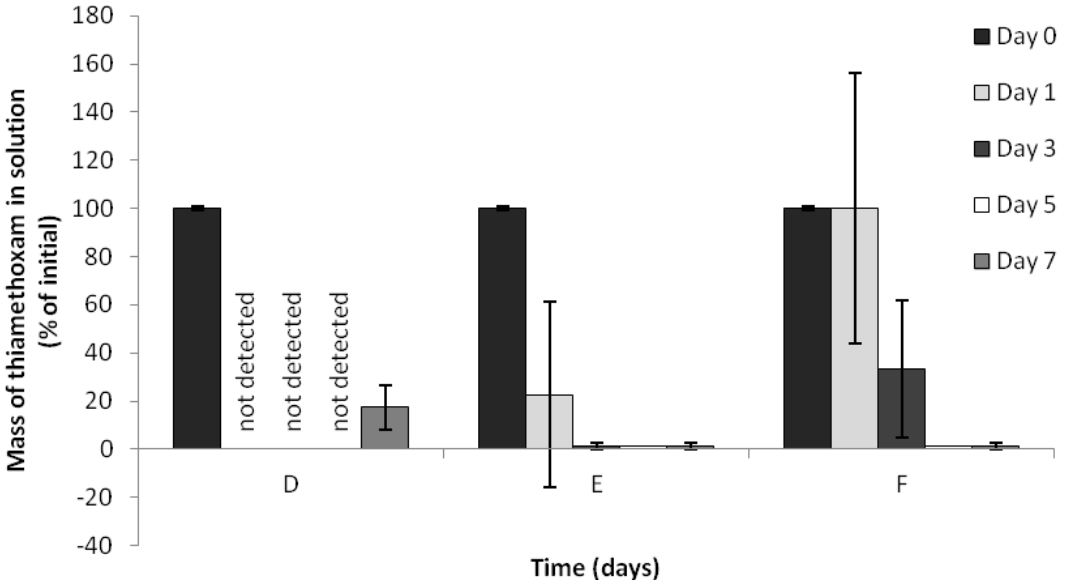

Figure 7-7 Change in concentration of thiamethoxam in solution over time for the treatments D, E and F (mean±standard deviation; n=3).

Table 7-2 Assumed processes occurring in the experimental treatments and half-life of thiamethoxam for each treatment, Chi^2 for fit and rate constants for pesticide dissipation obtained by comparing different experimental treatments

Treatment	Assumed processes related to pesticide dissipation	Half-life (days)	Chi^2 for fit	Rate constants derived by comparing between two treatments (day^{-1})
A	- Hydrolysis - Microbial degradation in water	54.5	2.41	$k_{treatmentA} = \sim k_{hydrolysis} = 0.0127\ day^{-1}$
B	- hydrolysis - microbial degradation in water - Photolysis	4.28	0.733	$k_{treatmentB} - k_{treatmentA} = k_{photolysis}$ $0.162 - 0.0127 = 0.149\ day^{-1}$; Half-life = 4.65 days
C	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment	10.4	1.60	
D	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis	2.69	3.96	

Table 7-2 (continued) Assumed processes occurring in the experimental treatments and half-life of thiamethoxam for each treatment, Chi^2 for fit and rate constants for pesticide dissipation obtained by comparing different experimental treatments

Treatment	Assumed processes related to pesticide dissipation	Half-life (days)	Chi^2 for fit	Rate constant derived by comparing between two treatment (day^{-1})
E	- Hydrolysis - Microbial degradation in water - Photolysis - Plant uptake - Degradation in plant	0.465	1.69	
F	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis - Plant uptake - Degradation in plant	3.59	14.0	

7.3.4. Dissipation of thiamethoxam in water-sediment systems

Figure 7-8 shows the change in concentration of thiamethoxam, whereas Figure 7-10 shows the same data but expressed as mass of thiamethoxam. Thiamethoxam in the water phase in the systems without plants gradually decreased from 1.38±0.02 mg L^{-1} on day 0 to a non-detectable concentration on day 14. Residues in sediment increased to a peak of 0.0182±0.0126 mg kg^{-1} on day 7 before decreasing to a non-detectable concentration at day 28 (Figure 7-8).

In the systems containing plants, thiamethoxam residues dramatically decreased to a non-detectable concentration at day 5 and thiamethoxam residues in sediment phase fluctuated, through to seven days after which residues were non-detectable. The highest thiamethoxam concentration detected in sediment was 0.0231±0.0219 mg kg^{-1} at day 1. Thiamethoxam concentrations showed large variability in plant residues, possibly associated with differences in mass and physiology of individual plants. The highest value was 0.617±0.534 mg kg^{-1} on day 1 and 5.

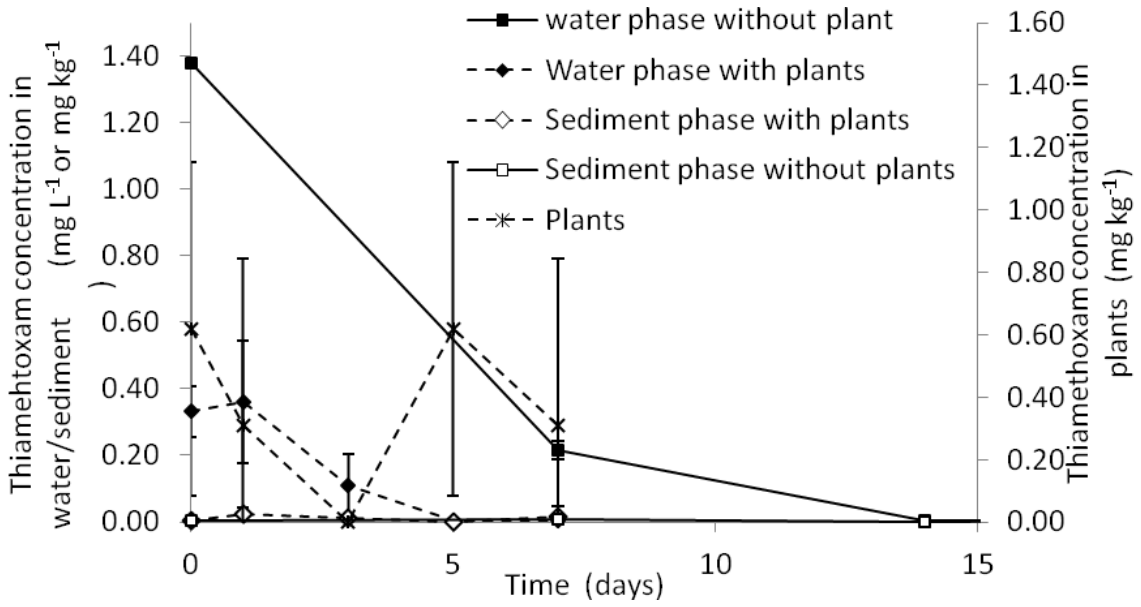

Figure 7-8 Change in concentration (mean±standard deviation; n=3) of thiamethoxam in the water, sediment and plant phases of systems with and without *Myriophyllum spicatum.* All concentrations on day 28 were smaller than the respective limit of detection.

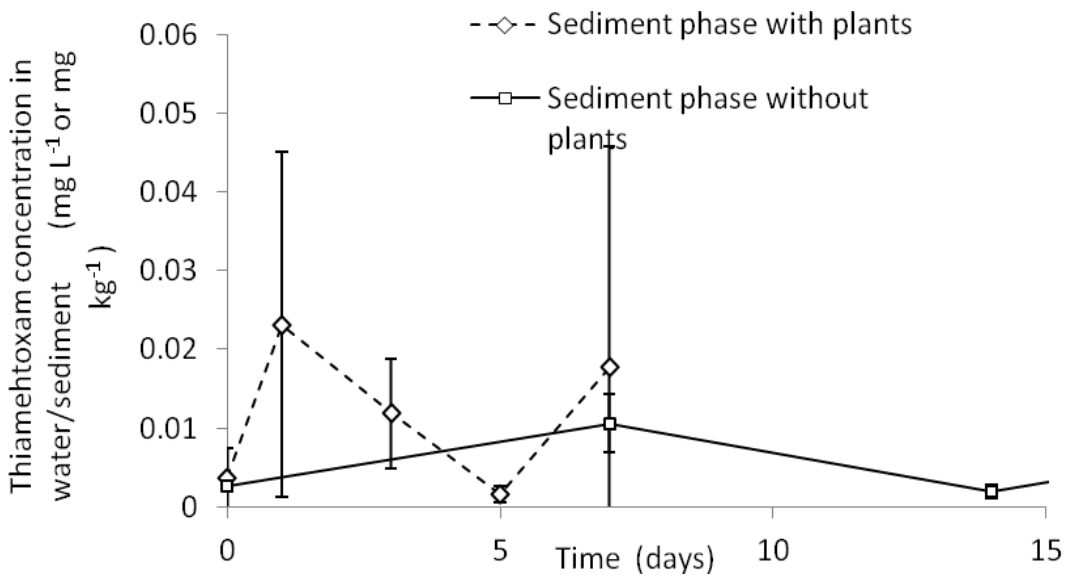

Figure 7-9 Change in concentration (mean±standard deviation; n=3) of thiamethoxam in the sediment of systems with and without *Myriophyllum spicatum.* All concentrations on day 28 were smaller than the respective limit of detection. Data for the pesticide concentration in Figure 7-9 is the same as shown in Figure 7-8.

The initial mass of thiamethoxam in water-sediment systems with the plants was 0.331±0.077 mg in the water phase. Initial mass of thiamethoxam was smaller than the target mass (1.2 mg). It is possible that the very alkaline conditions in the water phase resulted in degradation of thiamethoxam when it was applied to the systems. The two pesticides were prepared as a mix in a batch so the concentration of metalaxyl-M in the same treatment can be used to check the expected initial concentration and that the stock solution was added correctly to the systems. The concentration of thiamethoxam in other treatments matched the expected initial concentration of thiamethoxam. The mass of thiamethoxam was very low in sediment throughout the experiment with the highest mass being 0.0231±0.0219 mg at day 1 as shown in Figure 7-10. The ratio of mass of thiamethoxam in water to that in sediment at the maximum mass of thiamethoxam in sediment was 15.6:1. The low accumulated mass in sediment results from the physico-chemical properties (solubility and K_d) of thiamethoxam meaning that the pesticide is predominantly located in water. The mass of thiamethoxam in plants was negligible as the total mass of plants in the system was very small.

The initial mass of thiamethoxam in the systems without plants was 0.828±0.011 mg in the water phase and 0.00261±0.00069 in sediment. The maximum mass of thiamethoxam in sediment was 0.0106±0.0037 mg at day 7; thereafter the mass decreased to below the limit of detection as shown in Figure 7-10. At the maximum mass of thiamethoxam in sediment, the ratio of mass of thiamethoxam in water to that in sediment was 13.5:1.

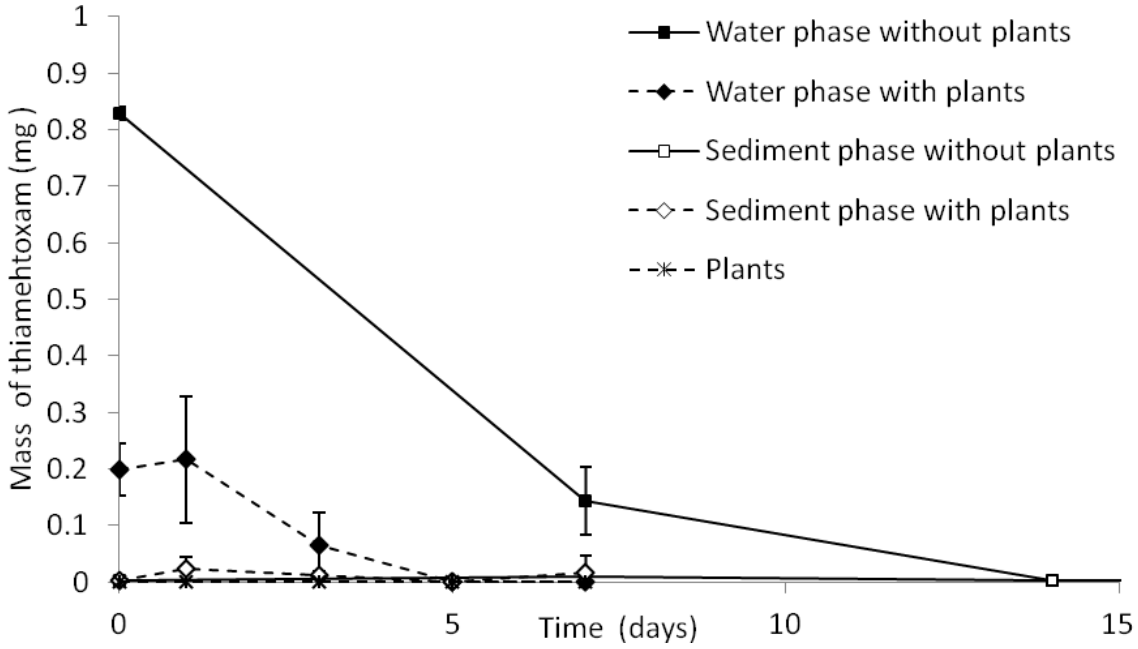

Figure 7-10 Change in mass (mean±standard deviation; n=3) of thiamethoxam in the water, sediment and plant phases of systems with and without *Myriophyllum spicatum*.

7.3.5. TOXSWA prediction for thiamethoxam in the water-sediment-plants system

Mass of thiamethoxam predicted by TOXSWA corresponded with most of the measured data in water except at day 0 (Figure 7-11). The model overestimated mass of thiamthoxam in plants at day 0 and day 1 and then measured thiamethoxam corresponded with the prediction from day 3 onwards. The prediction overestimated mass of the pesticide in sediment throughout.

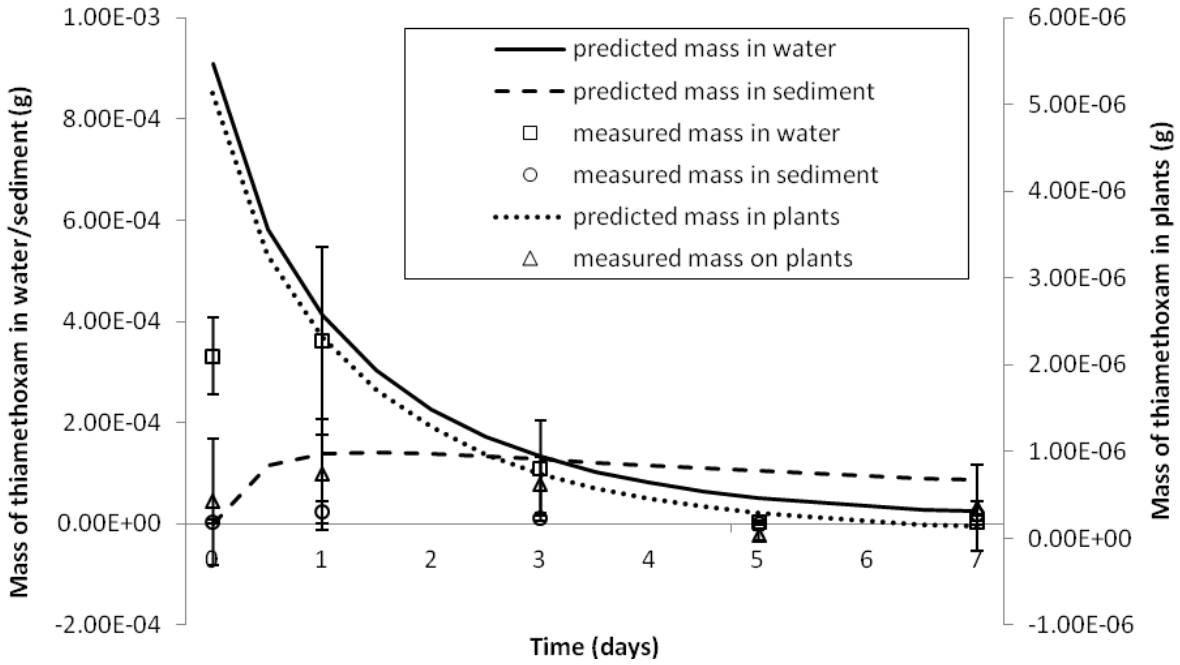

Figure 7-11 Comparison between TOXSWA prediction and measured mass of thiamethoxam in water-sediment system with plants under outdoor conditions at average temperature 14.9°C. Observed data was from treatment F.

7.3.6. Dissipation of metalaxyl-M from the water phase

Presence of plants and sediment were potentially two important influences on dissipation of metalaxyl-M from the water phase as dissipation of metalaxyl-M in treatments without sediment (treatment A and B) was slower than from the remaining treatments (Figure 7-12). Similarly to dissipation of thiamethoxam, the dissipation of metalaxyl-M from the water phase was faster in the treatments containing the plants (treatment E and F) than the remainder (treatments A, B, C and D) (Figure 7-12 and 7-13).

Dissipation of metalaxyl-M in treatments A (no radiation and no sediment), B (in presence of radiation and no sediment), C (no radiation and in presence of sediment) and D (in presence of radiation and sediment) suggested that both radiation and sediment accelerated dissipation of metalaxyl-M. Sediment had an influence on dissipation of metalaxyl-M (Figure 7-12) that was larger than that from radiation (comparing treatment B and treatment D).

In the presence of sediment and without plants, the dissipation rate of metalaxyl-M in treatment C (no radiation, having sediment) was higher than the dissipation rate in treatment A (no radiation and no sediment). The dissipation rate of metalaxyl-M in treatment B (radiation but no sediment) compared to that in treatment D (radiation plus sediment) that the rate the latter higher than in the former. It is likely that there are more microorganisms in the upper layer of sediment than in water. In contrast, the dissipation rate in treatment E (no sediment, but with plants) was less than the dissipation rate in treatment F (having sediment and plants). The faster dissipation in treatment E may arise from hydrolysis under more alkaline conditions in treatment E during the experiment as Sukul and Spiteller (2000) reported that the half-life of metalaxyl was 200 days at pH 5 and 7, and 12 days at pH 10. In this case, the sediment acted to buffer the change in water pH associated with photosynthesis.

The dissipation rate of metalaxyl-M in M4 medium decreased in the order treatment E > F > D > C > B > A as shown in Table 7-3. The details of metalaxyl-M residues in each component of all treatments are given in Appendices E-8 to E-13.

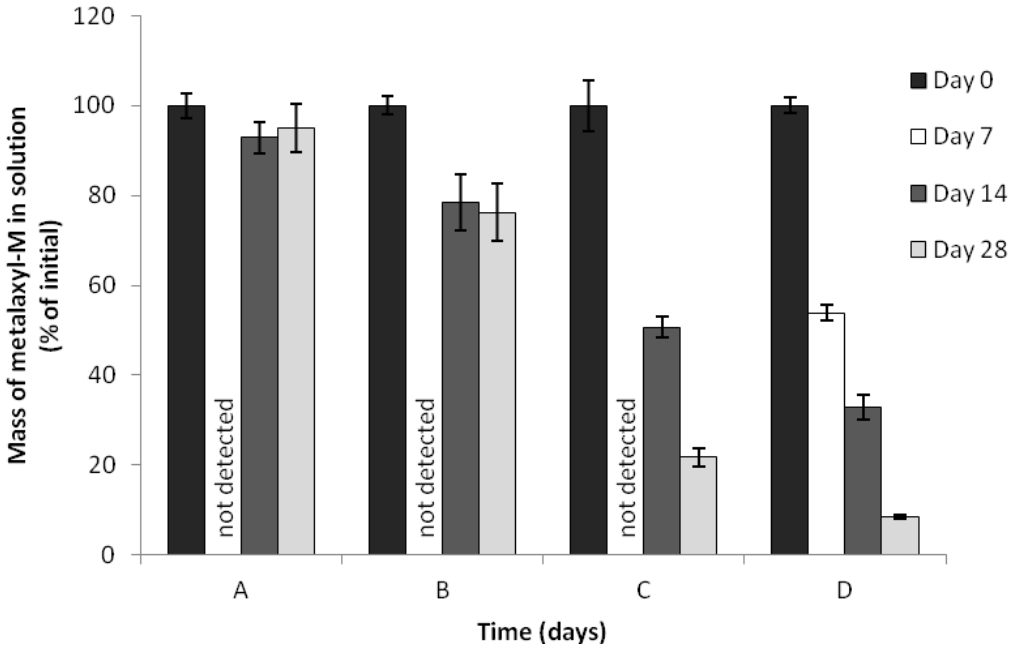

Figure 7-12 Change in concentration of metalaxyl-M in solution over time for the treatments A, B, C and D (mean±standard deviation; n=3).

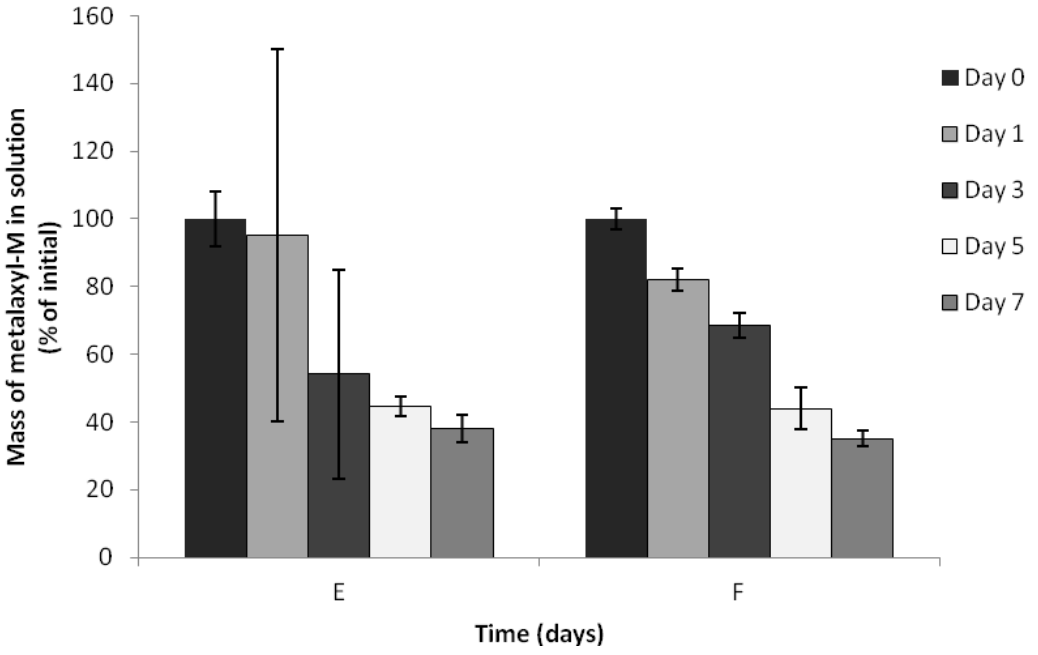

Figure 7-13 Change in concentration of metalaxyl-M in solution over time for the treatments E and F (mean±standard deviation; n=3).

Table 7-3 Assumed processes occurring in the experimental treatments and half-life of metalaxyl-M for each treatment, Chi^2 for fit and rate constant of metalaxyl-M dissipation obtained by comparing different experimental treatments

Treatments	Assumed processes related to pesticide dissipation	Half-life (days)	Chi^2 for fit	Rate constant derived by comparing between two treatment (day^{-1})
A	- Hydrolysis - Microbial degradation in water	372	2.00	$k_{treatmentA} = \sim k_{hydrolysis} = 0.00186\ day^{-1}$
B	- Hydrolysis - Microbial degradation in water - Photolysis	66.8	4.34	$k_{treatmentB} - k_{treatmentA} = k_{photolysis}$ $0.0104 - 0.00186 = 0.00854\ day^{-1}$; Half-life = 81.1 days
C	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment	13.4	2.45	
D	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis	8.28	2.38	

Table 7-3 (continued) Assumed processes occurring the experimental treatments and half-life of metalaxyl-M for each treatment, Chi^2 for fit and rate constant of metalaxyl-M dissipation obtained by comparing between different experimental treatments

Treatments	Assumed processes related to pesticide dissipation	Half-life (days)	Chi^2 for fit	Rate constant derived by comparing between two treatment (day^{-1})
E	- Hydrolysis - Microbial degradation in water - Photolysis - Plant uptake - Degradation in plant	4.43	7.88	
F	- Hydrolysis - Microbial degradation in water - Sorption to sediment - Degradation in sediment - Photolysis - Plant uptake - Degradation in plant	4.66	3.77	

7.3.7. Dissipation of metalaxyl-M in water-sediment systems

Figure 7-14 shows change in concentration of metalaxyl-M whilst Figure 7-15 shows the same data but expressed as mass of metalaxyl-M. In the presence of *Myriophyllum spicatum*, metalaxyl-M residues in the water phase decreased from 1.46±0.05 mg L^{-1} on day 0 to 0.512±0.036 mg L^{-1} on day 7. The residues in sediment increased to a maximum of 0.137±0.088 mg kg^{-1} on day 5 in the system containing *Myriophyllum spicatum.* The highest metalaxyl-M concentration detected in the plants was 26.3±4.8 mg kg^{-1} on day 3. The faster decrease in metalaxyl-M in the aqueous phase and less accumulation of metalaxyl-M in sediment in the treatment with the plants suggests that the plants contributed to dissipation of metalaxyl-M from the systems.

The water-sediment systems without the plants had 1.54±0.03 mg L^{-1} metalaxyl-M on day 0 decreasing to 0.831±0.028 mg L^{-1} on day 7 and with 0.130±0.006 mg L^{-1} remaining on day 28. The residues in sediment increased to a maximum of 0.201±0.047 in the systems without the plant on day 14 (Figure 7-14).

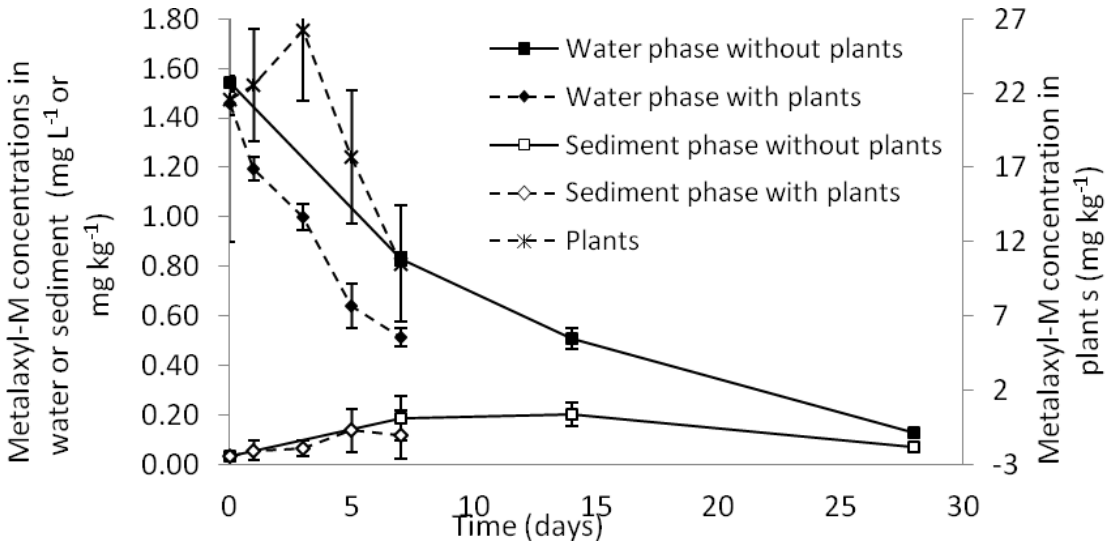

Figure 7-14 Change in concentration (mean±standard deviation; n=3) of metalaxyl-M in the water, sediment and plant phases between two systems with and without *Myriophyllum spicatum*

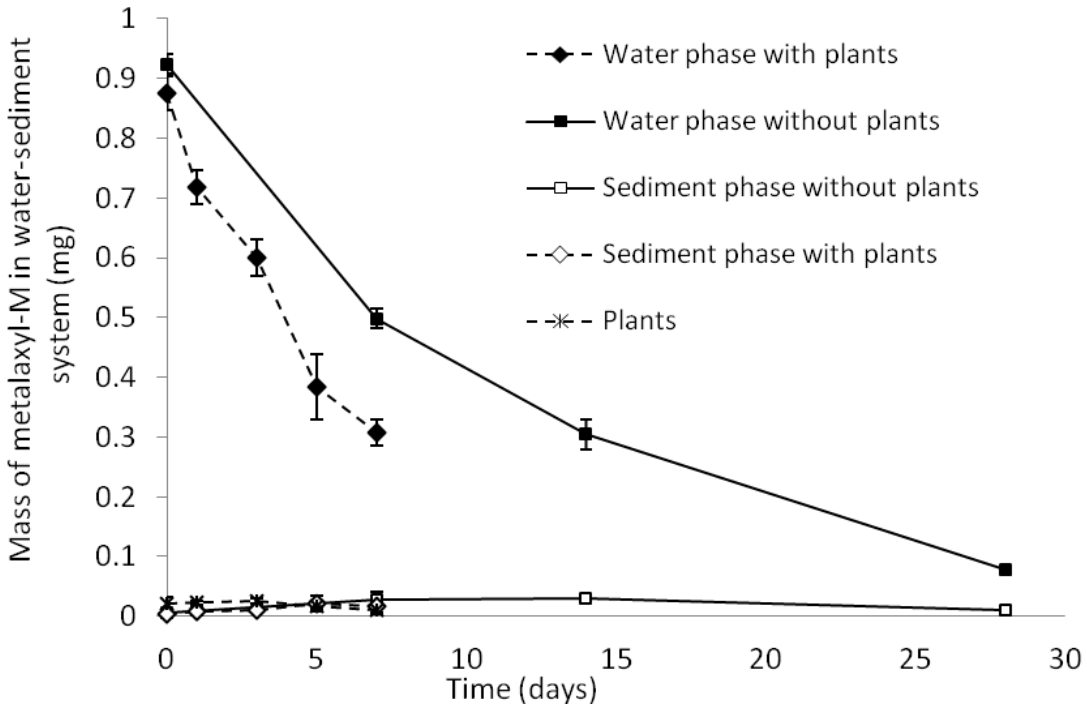

Figure 7-15 Change in mass (mean±standard deviation; n=3 in water) of metalaxyl-M in the water, sediment and plant phases of two systems with and without *Myriophyllum spicatum*

In the presence of the plants, the initial mass of metalaxyl-M in the water-sediment systems was 0.875±0.028 mg. The mass of metalaxyl-M in water decreased steadily to 0.307±0.022 mg at day 7. The maximum mass of metalaxyl-M in sediment was 0.0205±0.0133 mg at day 5 as shown in Figure 7-15. The ratio of metalaxyl-M in water to that in sediment at the maximum metalaxyl-M in sediment was 18.7:1. The maximum mass of metalaxyl-M in plants was 0.0263+0.0048 mg at day 3.

Initial mass of metalaxyl-M in the systems without the plants was 0.924±0.016 mg. At the end of the experiment (day 28), the mass of metalaxyl-M remaining in water and sediment was 0.0782±0.0038, 0.0103±0.0006 mg, respectively. The maximum mass of metalaxyl-M in sediment was at day 14 giving a ratio for mass in water to mass in sediment was 10.1:1.

7.3.8. TOXSWA prediction for metalaxyl-M in the water-sediment-plant system

TOXSWA gave a reasonable prediction for mass of metalaxyl-M in the water phase (Figure 7-16). The predicted mass of metalaxyl-M in sediment was greatly overestimated throughout. The predicted mass of metalaxyl-M in plants was lower than measured data throughout.

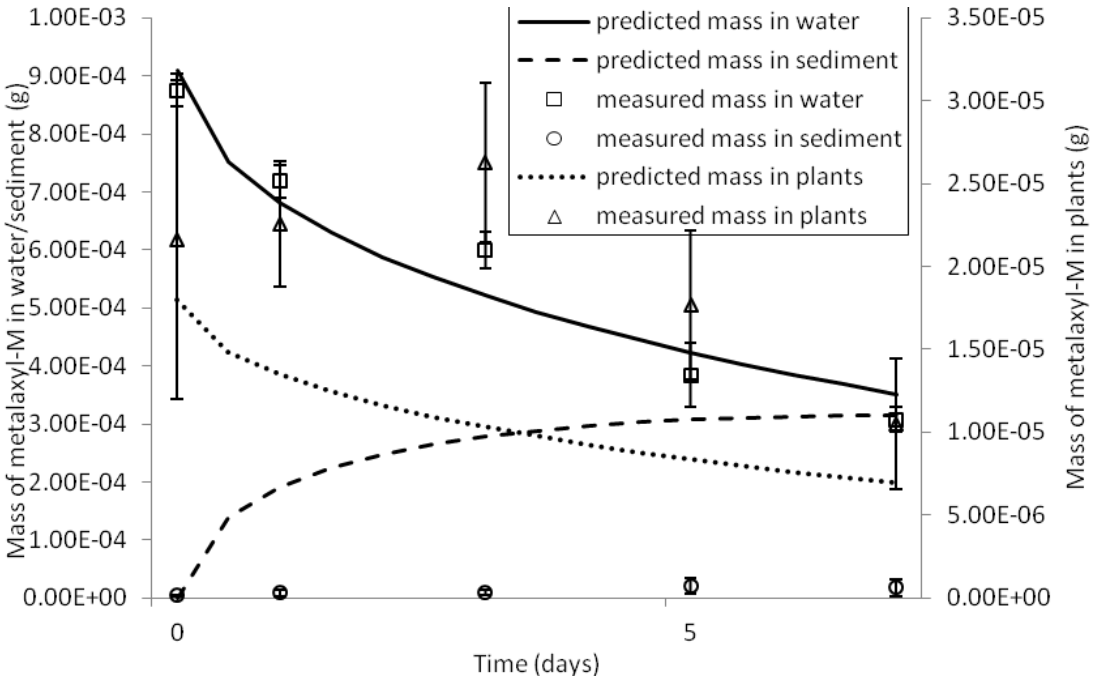

Figure 7-16 Comparison between TOXSWA predictions and measured mass of metalaxyl-M in water-sediment system with plants under outdoor conditions at average temperature 14.9°C. Observed data was from treatment F.

7.4 Discussion

7.4.1. Thiamethoxam

Two of the six treatments included presence of plants, namely treatment E was water-plant systems and treatment F was water-sediment-plant systems. The two treatments were different with respect to presence of sediment and pH (treatment E had more

alkaline conditions). Hydrolysis and photolysis of thiamethoxam are both faster under alkaline conditions and would contribute more to dissipation in treatment E than other treatments (Section 3.1).

In the presence of light, dissipation of thiamethoxam was faster than in the equivalent that treatment in the dark regardless of the presence of sediment. A previous experiment (Section 3.1) showed that thiamethoxam can be degraded rapidly by radiation giving half-lives of thiamethoxam of 0.34±0.01 days at pH 7.0 and 0.40±0.06 days at pH 8.0. These values are shorter than the half-life from this experiment. This results from different light intensity and temperature of the equipment in the earlier experiment. Temperature in the photolysis experiment (30±2^{o}C) was generally higher than that outdoors (in the range of 11.5 to 19.7^{o}C).

Sediment plays only a minor role in dissipation of thiamethoxam because most thiamethoxam residues are located in the water phase. Thiamethoxam is only weakly sorbed and the use of unstirred systems inhibited pesticide contact with sediment at depth. Moreover, thiamethoxam residues in sediment were possibly degraded by microorganisms resulting in a decrease of any residues in the sediment phase (Gupta et al., 2008).

7.4.2. Comparison between dissipation of thiamethoxam in water-sediment systems under laboratory and outdoor conditions

The dissipation of thiamethoxam via hydrolysis in treatment A under field conditions (pH 8.0 to 8.5) was 1.15 times faster than that under laboratory conditions (pH 6.9 to 8.4) as shown in Table 7-4. Thiamethoxam from treatment A (no radiation and no sediment) under field conditions (pH 8.0 to 8.5) reached less than 80% of initial concentration whilst thiamethoxam from the treatment under controlled condition (pH 6.9 to 8.4) remained at more than 80% of initial concentration at day 28. It was assumed that more alkaline conditions in the water phase contributed to faster hydrolysis.

Dissipation of thiamethoxam in treatment B under field conditions was 12.7 times faster than that under laboratory conditions (Table 7-4). It was possible that light intensity around midday was higher than natural light provided wide emission wavelength which support for light absorption of thiamethoxam molecules (200-400 nm) whilst fluorescent lamp in growth chamber provided emission wavelength in range 300-700 nm.

Table 7-4 Half-life for thiamethoxam in treatments under laboratory and outdoor conditions: data are the same as those in Table 6-5 and 7-2.

Treatment	Half-life of thiamethoxam under laboratory condition (days)	Half-life of thiamethoxam under outdoor condition (days)
A (water alone/dark)	62.6	54.5
B (water alone/light)	54.6	4.28
C (water-sediment/dark)	15.5	10.4
D (water-sediment/light)	11.9	2.69
E (water with plants/light)	0.465	0.465
F (water-sediment with plants/light)	1.13	3.59

The dissipation rate of thiamethoxam measured in the presence of sediment but without light (treatment C) in water-sediment systems under outdoor conditions was 1.49 times faster than that under laboratory conditions (Table 7-4). Thiamethoxam from treatment C (no radiation) under outdoor conditions represented about 15% of initial mass at day 28 whilst thiamethoxam from the treatments under laboratory conditions remained at about 40% of initial mass. At peak of thiamethoxam in sediment, the sorption accounted for 0.33 and 0.87% of initial mass under laboratory and outdoor conditions, respectively. The difference in dissipation rate of thiamethoxam in sediment could have been due to fluctuation in temperature being favourable for microbial populations. Additionally, the fresh weight of the plants under outdoor conditions was higher than that under laboratory condition (Figure 7-17).

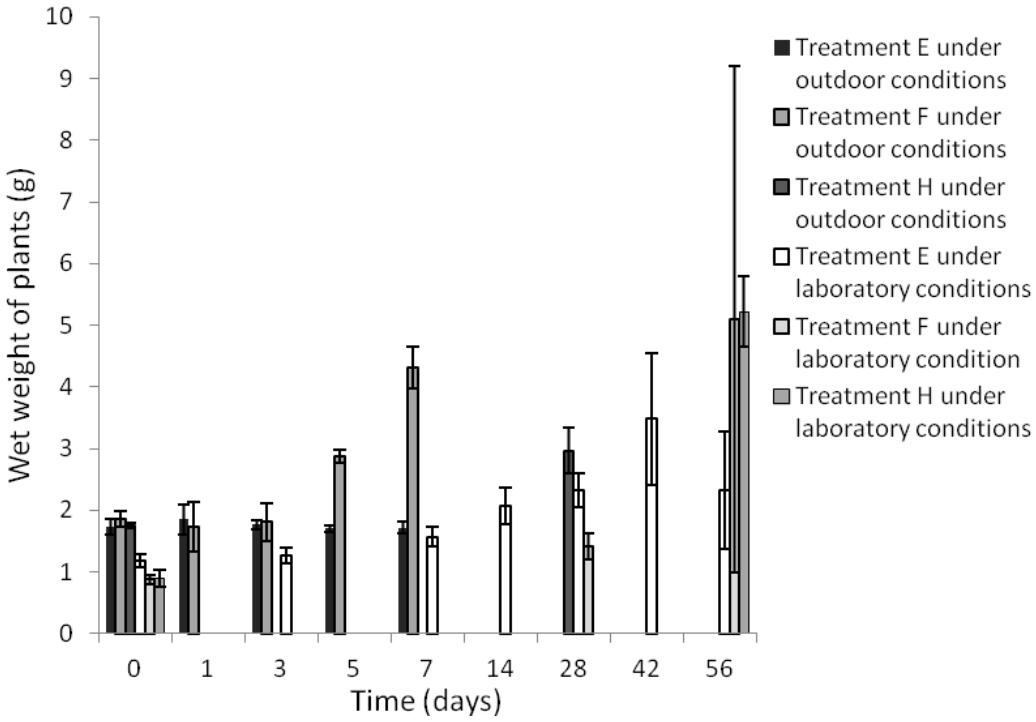

Figure 7-17 Fresh weight of plants in treatments E (water-plants systems spiked with 2 mg thiamethoxam and metalaxyl-M L^{-1}), F (water-sediment-plants systems spiked with 2 mg thiamethoxam and metalaxyl-M L^{-1}) and H (water-sediment-plants without any pesticides) under laboratory and outdoor conditions. Observed data did not collected at the same interval time so there was missing bar in this Figure.

7.4.3. Prediction fate of thiamethoxam in water-sediment systems

The model gave a reasonable prediction of mass of thiamethoxam in water under outdoor conditions when the half-life of thiamethoxam in water was corrected for pH and light intensity. This judgement is based on visual assessment and the model efficiency value of thiamethoxam (-1.81). This suggests that experimental data from single-phase experiments can be coupled with the TOXSWA model to predict thiamethoxam in water-sediment systems with plants. The model overestimated mass of thiamethoxam in plants early in the experiment (day 0 and day 1) and then corresponded with the measured behaviour. The model efficiency value was -84.0 for thiamethoxam in plants. TOXSWA assumes that transfer to plants is from sorption

whereas it seems likely that there was also some uptake into the plants. The model did not give a reasonable prediction in sediment based on the model efficiency for thiamethoxam sorbed to sediment of -124. Sorption to sediment in the vessels under outdoor condition was much less than would be predicted from laboratory water-sediment studies with thiamethoxam in the dark. Sorption of a non-extractable form of thiamethoxam to sediment could be a reason for low measured concentrations in sediment. The rate of dissipation of thiamethoxam from water under outdoor conditions was very rapid and it seems likely that there was insufficient time for the pesticide to transfer to the sediment prior to degradation. There are limitations to the capacity for TOXSWA to simulate fate of pesticide in water-sediment system under outdoor condition. The model does not allow separation of aquatic degradation into separate processes such as hydrolysis, photolysis and microbial degradation, and simulations cannot account for fluctuations in temperature, light intensity or other environmental variables. This is a major limitation to the ability to use models to extrapolate between laboratory and outdoor behaviour. Inclusion of these additional functions could improve the ability of the model to represent fate of pesticides in the field. Figure 7-18 shows an independent prediction of photolysis rate for the calculation of thiamethoxam residues in the water of outdoor conditions (Treatment B). The photolysis rate measured at high light intensity in the "Suntest" was used to calculate photolysis rate in the outdoor using an Microsoft Excel calculation as described in section 7.2.4. The rate constant at pH 8 in natural water (1.73 day^{-1}) was corrected using hourly data for solar radiation for solar radiation in the outdoor in order to predict thiamethoxam concentration under fluctuating solar radiation (outdoor conditions; bold line in Figure 7-18). Figure 7-18 shows that the outdoor measurements were in line with the predicted concentration under outdoor conditions suggesting that laboratory data were able to predict photolysis of thiamethoxam in water (single compartment) under outdoor conditions. This implies that a major requirement is to develop mathematical models that can separate different processes influencing pesticide fate and can respond to changes in environmental conditions (e.g. light/dark cycles).

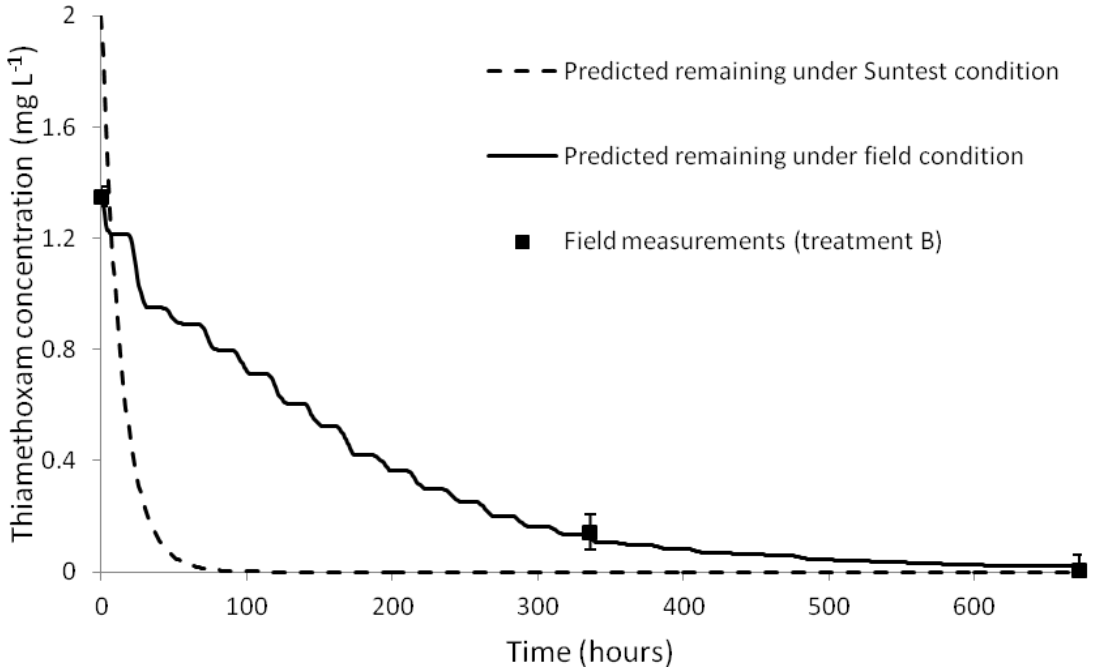

Figure 7-18 Comparison among predictions of thiamethoxam concentrations under Suntest and outdoor condition and outdoor measurement

7.4.4. Metalaxyl-M

Most of the metalaxyl-M residues were located in the water phase whilst a smaller amount of metalaxyl-M was in sediment and plants. The dissipation rate of metalaxyl-M between treatments showed that the influence of different factors on dissipation increased in the order plants > sediment > radiation.

Only a small amount of metalaxyl-M was found in the plants, so the influence of plants on dissipation may not only arise from uptake by plants but also from an indirect effect on hydrolysis due to more alkaline conditions. A previous study (Sukul and Spiteller, 2000) reported that alkaline conditions (Half-lives were 200 days at pH 5 and 7, and 12 days at pH 10) in water resulted in increased hydrolysis of metalaxyl. Treatments E and F had pH close to 10 so hydrolysis of metalaxyl-M would probably have occurred in these systems. One of possibilities is that in the presence of plants supporting microbial degradation. Muratova et al. (2003) reported that the microbial population in vegetated soil was 1.3 times higher than that in non-vegetated soil

resulting in faster degradation of polycyclic aromatic hydrocarbons. Sun et al. (2004) showed that plants not only take up aldicarb but also that degradation is promoted by in the presence of plants. Half-lives of aldicarb were 2.7, 1.7, 1.6 and 1.4 days in soil without plants, soil with cowpea, maize, and mung bean, respectively. Loss of aldicarb via uptake by plants was varied among plant species accounting for 16.2%, 61.5% and 8.0% of total removal of aldicarb in plant-grown soil for cowpea, maize and mung bean, respectively.

Regarding the influence of sediment, it is assumed that not only metalaxyl-M sorption to sediment contributed to dissipation of metalaxyl-M from the water phase, but also that there was some microbial degradation (Saha and Sukul, 1997; Sukul et al., 2008).

7.4.5. Comparison between dissipation of metalaxyl-M in water-sediment systems under laboratory and outdoor conditions

Hydrolysis of metalaxyl-M was assumed negligible in all treatments under laboratory conditions and also in treatments A, B and C under outdoor conditions because the neutral or slightly alkaline conditions in the water phase do not favour hydrolysis of metalaxyl-M (Sukul and Spiteller, 2000).

The rate of photolysis of metalaxyl-M in the experiment under outdoor conditions was 3.3 times higher than that in the experiment under laboratory conditions (Table 7-5). Natural light will comprise more light at a wavelength below 290 nm where light absorption of metalaxyl-M possibly occurs (Sukul and Spiteller, 2000).

Dissipation of metalaxyl-M from the treatment in the presence of sediment but without light (treatment C) under outdoor conditions was 2.15 times faster than that in the growth chamber (Table 7-5). The maximum metalaxyl-M sorption to sediment in treatment C was 14.9% and 6.97% of total applied metalaxyl-M under laboratory and outdoor conditions. In contrast, the dissipation of metalaxyl-M from the water phase under outdoor conditions was faster than that under laboratory condition (Table 7-5), so metalaxyl-M sorption to sediment was not the only process contributing to dissipation. It is clear that microbial degradation also contributed to the dissipation.

Table 7-5 Half-lives for metalaxyl-M in treatments under laboratory and outdoor conditions: data are the same as those in Table 7-6 and 7-3

Treatment	Half-life of metalaxyl-M under laboratory condition (days)	Half-life of metalaxyl-M under outdoor condition (days)
A (water alone/dark)	310	372
B (water alone/light)	221	66.8
C (water-sediment/dark)	28.2	13.4
D (water-sediment/light)	33.0	8.28
E (water with plants/light)	59.4	4.43
F (water-sediment with plants/light)	13.3	4.66

7.4.6. Prediction fate of metalaxyl-M in water-sediment system

There was good correspondence between measured and predicted behaviour in water (TOXSWA). The visual agreement was good and the model efficiency was 0.944. However the model greatly overestimated the mass of metalaxyl-M in sediment. The model efficiency was -1545 indicating that the observed data in sediment may be better explained by the mean of observed mass in sediment than by the model. Concentrations of metalaxyl-M in sediment in the outdoor systems were much smaller than those in equivalent treatments in the growth chambers (Chapter 7). It could be that under outdoor conditions, there was more non-extractable form of metalaxyl-M bound to sediment. The reasons for this discrepancy are unknown and require further study. The model did not give a reasonable prediction mass of metalaxyl-M in plants based on visual assessment and the model efficiency (-2.14). It could be because a prediction of mass in plant by TOXSWA relies on mass of pesticide in water. This was not true in reality because there was no pesticide in plants at initial time and a prediction of mass in plants needs to concern uptake, metabolism and depuration.

7.5 Conclusion

Most of the thiamethoxam and metalaxyl-M residues were found in the water phase in line with the physico-chemical properties of the two pesticides (K_d). However sorption of pesticides to sediment was generally less than predicted based on K_d value (Chapter 4). Varying water-sediment treatments with/without plants showed strength of factors influencing dissipation of thiamethoxam to be: plants > light > sediment. Dissipation of thiamethoxam occurred via hydrolysis, photolysis, microbial degradation and uptake by plants. The presence of plants had a dominant effect because this increased hydrolysis and photolysis rate due to enhanced alkaline conditions and possibly increased microbial degradation. Metalaxyl-M is stable to photolysis and also persistent to hydrolysis in water (PPDB, 2008) so the factors influencing dissipation of metalaxyl-M were different from those for thiamethoxam. The order of factor influence for metalaxyl-M was plants > sediment > light. The results suggest that some photolysis may occur under field conditions (Table 7-5) so dissipation of metalaxyl-M occurred via uptake by plants, microbial degradation, photolysis and hydrolysis. The presence of plants resulted in more alkaline conditions to the extent that it could increase hydrolysis. Plants are able to take up metalaxyl-M and also enhance microbial degradation as plant roots aggregate sediment resulting in increased oxygen at the root zone.

Comparison of dissipation of thiamethoxam and metalaxyl–M under laboratory and field conditions suggested that the hydrolysis rate obtained from laboratory conditions gave a reasonable prediction of hydrolysis in field condition. Light intensity needs to be carefully selected for photolysis experiments in the laboratory in order to obtain a reasonable measure for pesticides in the environment. In general, dissipation of the two pesticides was faster in the outdoor. There were a number of parameters contributing to the discrepancy of parallel systems under laboratory and outdoor conditions (i) difference in wavelength of light, (ii) light intensity, (iii) favourable conditions which enhance microbial degradation or pesticide uptake by plants.

The predicted fate of pesticides in water-sediment systems using TOXSWA showed that experimental data are able to predict fate of selected pesticide in the water phase

in the outdoor but that input data need to be corrected using actual environmental variables (such as light intensity and pH). The model did not give a reasonable prediction of mass of pesticide in sediment and plants. The reason could be that the TOXSWA model did not allow to separate degradation processes in plants and sediment. For plants, the model only accounts for sorption process but in reality, plants are able to take up pesticide and the pesticides could be metaboliseds. In sediment, the model relies on measured concentration in sediment and counts the decrease in concentration as a combined degradation. Some of the pesticide sorbed to sediment could be in non-extractable form which contributed to less measured concentration of pesticides than the concentration of the total sorbed pesticide to sediment.

CHAPTER 8

8. GENERAL CONCLUSIONS

Literature reviews showed that fate of pesticides in the aquatic environment depends on various processes such as photolysis, hydrolysis, volatilisation, microbial degradation, uptake by plants, and sorption to sediment. Environmental conditions affect all these processes. Discrepancies between predictions from models and measured data (Knabel et al., 2012; Beulke et al., 2000), and different behaviour of pesticides under laboratory and field conditions (Dinelli et al., 2000; Mazanti et al., 2003; PerrinGanier et al., 1996) have been reported.

This thesis focused on understanding the fate of two pesticides in water-sediment systems. It started by investigating fate in simple, single-phase systems and built up to more complex systems incorporating a range of phases under outdoor conditions. Comparison between results and limited modelling were used to determine the extent to which simple laboratory experiments can be extrapolated to describe behaviour of pesticides in the outdoor.

8.1 Fate of selected pesticide in single component (water/sediment phase)

Two currently-used pesticides were selected with different physico-chemical properties and degradation; thiamethoxam dissipates via hydrolysis and photolysis and has a low sorption coefficient (K_{oc} = 56.2 L kg^{-1}), whilst metalaxyl-M is stable to hydrolysis and photolysis and has moderate sorption (K_{foc} = 660 L kg^{-1}; PPDB, 2009).

Hydrolysis experiments (Chapter 3) showed that the pH of water strongly influenced the rate of hydrolysis of thiamethoxam with a significant increase at alkaline conditions (above pH 9; $p<0.001$). Photolysis of thiamethoxam was also strongly influenced by pH ($p<0.001$) with the rate of photolysis 4.30 and 3.85 times faster at pH 10 than at pH 9 for pure and natural water, respectively. Thiamethoxam degradation via photolysis has a maximum absorption of light at about 250 nm (Figures 3-6 to 3-9). The presence of nitrate anions significantly ($p<0.05$) decreased

the rate of photolysis of thiamethoxam and this was attributed to a direct competition for absorption of light.

Sorption of thiamethoxam fitted a linear isotherm. The sorption coefficient (K_{oc} = 32.6 L kg^{-1}) showed that thiamethoxam was likely to be present primarily in the water phase (Table 4-1, vanLoon and Duffy, 2005) and the value corresponded with the literature.

Hydrolysis and photolysis experiments were not performed for metalaxyl-M as the pesticide database (PPDB, 2009) suggested it to be stable. However, half-lives of metalaxyl-M for experiments under outdoor conditions (Table 7-5) suggested that photolysis of metalaxyl-M may occur under natural sunlight. The finding highlights the importance of selecting appropriate light intensity and source of light for photolysis experiments in order to determine whether a pesticide will be subjected to photolysis under outdoor conditions.

The sorption coefficient of metalaxyl-M in the sediment (K_{foc} = 35.2 L kg^{-1}) suggested that the pesticide was again likely to be located primarily in the water phase of aquatic systems (vanLoon and Duffy, 2005); the value is smaller than most values in the literature which suggest that metalaxyl-M is moderately sorbed to soil. The natural sediment used in this study was collected from a small stream where there were a lot of decomposed leaves; Different forms of organic matter in soil/sediment could contribute to variation in the K_{foc} value; Rodriguez-Cruz et al. (2009) showed that sorption of metalaxyl to lignin (a hydrophobic molecule) was greater than that to cellulose (a hydrophilic molecule).

8.2 Fate of selected pesticides in water-sediment systems

Experiments in single-component systems (Chapter 3) gave information on the effects of individual factors on the dissipation of pesticides as a first step in studying natural water-sediment systems comprising multiple components and subjected to fluctuating environmental conditions. Dissipation of the two pesticides from water-sediment systems under outdoor conditions was generally faster than that under laboratory conditions. Not only abiotic degradation processes such as hydrolysis and photolysis were contributors to dissipation of pesticide from the experimental water-sediment systems but also biodegradation had a role on dissipation of pesticides from the water-sediment systems, especially in the presence of plants (Susarla et al., 2002; Sun et al., 2004). As there was no study of biodegradation in this work, the role of biodegradation is uncertain and needs further studies in water-sediment systems with and without plants.

Dissipation of thiamethoxam in experimental treatments under laboratory conditions showed the strength of factors influencing dissipation of the pesticide was in the order plants > sediment > light. Presence of plants was the dominant factor influencing fate of thiamethoxam in water-sediment systems even though the mass of thiamethoxam in plants was small (the maximum mass of thiamethoxam in plants was 0.08% of applied mass) in comparison to that in other compartments. Dissipation of thiamethoxam from the water phase in water-sediment system with plants was much faster than that in the system without plants primarily because the rates of photolysis and hydrolysis were greatly accelerated by the alkaline conditions induced by the presence of plants. Literature studies (Susarla et al., 2002; Sun et al., 2004) reported that plants enhance biodegradation via rhizosphere and root exudates so, biodegradation in the experimental water-sediment system with plants could be faster than that in the systems without plants. For this study, difference in biodegradation rate between the system with plants and the system without plants is uncertain. It needs further studies on biodegradation to quantify biodegradation rate in the two systems. In natural water-sediment systems, direct removal of pesticide from water and sediment by uptake or sorption to plants will be greater than reported in this thesis as plant density in natural water bodies (50 - 300 g m^{-2} dry weight basis; Beltman and Adriaanse,

1999) is higher than those used in the current studies (maximum about 44 g m^{-2}). The measured concentration of pesticide in plants showed high variation between replicates and this is most likely associated with differences in the mass and physiology of plants in individual systems.

Strength of factors influencing dissipation of thiamethoxam under outdoor conditions was in order plants ≥ light > sediment. The loss rate of thiamethoxam in water-sediment systems under outdoor conditions was faster than that under laboratory conditions. The higher light intensity under outdoor conditions (daily average ranged 0.031 to 0.186 kW m^{-2}) than that under laboratory conditions (0.0117 kW m^{-2}) contributed to the change in strength of effect because thiamethoxam degraded via photolysis.

Behaviour of metalaxyl-M in water-sediment systems under laboratory conditions corresponded with information from pesticide databases and the literature in that the pesticide was stable to hydrolysis and photolysis but was degraded in sediment via microbial degradation (Saha and Sukul, 1997; Sukul et al., 2008). Unexpectedly, the behaviour of metalaxyl-M in water-sediment systems changed under outdoor conditions. The importance of photolysis and hydrolysis to field behaviour is demonstrated by the half-life of metalaxyl-M in water alone under outdoor conditions (a half-life in water alone with illumination was 66.8 days) compared to that under laboratory conditions (a half-life in water alone with illumination was 221 days, Table 7-5) and the half-lives of treatments E and F under outdoor conditions compared to those in the laboratory (Table 7-5).

8.3 Approach of laboratory data to predict behaviour of pesticide under outdoor conditions

Behaviour of the two selected pesticides in water-sediment system with plants showed that the data from simple systems (water/sediment phase) gave a picture of behaviour of pesticide under specific conditions. In order to approach the behaviour of pesticide in water-sediment systems under outdoor conditions, some parameters such as pH in water, sorption of soil/sediment and light intensity were used to correct dissipation of pesticides measured in the laboratory.

The TOXSWA model was able to give a reasonable prediction in water phase for the two selected pesticides and overestimated the mass of the two pesticides in sediment. The discrepancy between prediction and measured data could be the pesticides in water degrade quickly so there not enough time for sorption to sediment. The discrepancy also found with predicted mass in plants for both pesticides. One possibility that the model assumed only sorption to plants and not concern other possible processes such as uptake.

8.4 Recommendations for further research

1. Only two pesticides were studied in this thesis, so this restricts generalisation of the results. In particular, experiments did not consider a pesticide with high sorption. Initial experiments included propiconazole to address this need, but it was found to have a high detection limit for analysis in water and high toxicity to plants (preliminary tests, data not shown). Further research should include pesticides with stronger sorption and/or compounds with higher volatility.

2. Further data should be collected to improve understanding of the fate of pesticides in water-sediment systems. For example, characterising the form of organic matter in sediment would provide greater depth of understanding of the controls on sorption, particularly for metalaxyl-M where sorption behaviour was different from that expected from the literature. It would be useful to quantify microbial degradation in water-sediment systems to investigate whether rate of microbial degradation varies under laboratory and outdoor conditions and to include and change in degradation rate amongst the treatments. In practice, maintenance of sterile conditions needed to isolate microbial degradation would be very difficult in the field. An alternative option is to use radioactive compound to identify CO_2 produced by microbial mineralisation.

3. The density of plants used in water-sediment systems in this thesis was lower than that expected in natural water bodies. Presence of more plants in the system would have affected both the direct and indirect impacts of the plants on pesticide fate. The plant species used in experiments in this thesis is a submerged plant. Further research

should be undertaken with different types of plants (floating or rooted plants) and/or different species to investigate the influence of plants in changing of the pH of water-sediment systems and to assess variation in pesticide sorption to different plants.

4. It is interesting to do further work under tropical conditions. Environmental conditions such as temperature and light intensity are higher than in this study, so such experiments would investigate whether fate of pesticide in water-sediment systems changes as rates of photolysis, volatilization and microbial activity increase with increasing temperature and solar radiation.

5. Prediction of the fate of pesticide could be undertaken using other models such as EXAMS. The model separate degradation processes in the water phase into hydrolysis, photolysis, redox reactions and biological degradation. EXAMS thus addresses some of the limitations in the TOXSWA model and could be used to generate more precise predictions of fate. However, there are also shortcomings for EXAMS. The model has not been actively developed for 15 years and still operates under MS-DOS with model-specific programming requirements. EXAMS does not include any simulation of plants in water or their influence on pesticide fate. A stronger alternative, would thus be to develop a new model that includes and distinguishes all relevant fate processes, includes plants and their effect on pesticide behaviour, and is able to account for fluctuations in environmental conditions.

6. Scale-up the experiment system to systems such as mesocosms in the field; this will provide a picture of the dissipation of pesticide under field condition.

LIST OF REFERENCES

Adriaanse, P., Allen, R., Gouy, V., Hollis, J., Hosang, J., Jarvis, T., Klein, M., Layton, R., Linders, J., Schafer, H., Smeets, L., Yon, D., 1997. Surface water models and EU registration of plant protection products. (No. 6476/VI/96), European Commission document.

Adriaanse, P.I., Leistra, M., Vink, J.P.M., Brouwer, W.W.M., Tas, J.W., Linders, J.B.H.J., Pol, J.W., 2002. Estimating transformation rates of pesticides, to be used in the TOXSWA model, from water-sediment studies, Alterra-rapport 023. Wageningen, Alterra, Green World research.

Ahmad, F., Iqbal, S., Anwar, S., Afzal, M., Islam, E., Mustafa, T., Khan, Q.M., 2012. Enhanced remediation of chlorpyrifos from soil using ryegrass (Lollium multiflorum) and chlorpyrifos-degrading bacterium Bacillus pumilus C2A1. Journal of Hazardous Materials 237–238, 110–115.

Andrades, M.S., Sánchez-Martín, M.J., Sánchez-Camazano, M., 2001. Significance of soil properties in the adsorption and mobility of the fungicide metalaxyl in vineyard soils. Journal of Agricultural and Food Chemistry 49, 2363–2369.

Avery, B.W. (Editor), 1982. Soil Survey Laboratory Methods. The Soil Survey.

Banerjee, K., Patil, S., Dasgupta, S., Oulkar, D., Adsule, P., 2008. Sorption of thiamethoxam in three Indian soils. Journal of Environmental Science and Health, Part B 43, 151–156.

Bedos, C., Rousseau-Djabri, M.F., Gabrielle, B., Flura, D., Durand, B., Barriuso, E., Cellier, P., 2006. Measurement of trifluralin volatilization in the field: relation to soil residue and effect of soil incorporation. Environmental Pollution 144, 958–966.

Beltman, W.H.J., Adriaanse, P.I., 1999. User's manual TOXSWA 1.2. Simulation of pesticide fate in small surface waters, Technical Document 54. Winand Staring Centre for Integrated Land, Soil and Water Research (SC).

Benoit, P., Perceval, J., Stenrod, M., Moni, C., Eklo, O.M., Barriuso, E., Sveistrup, T., Kvaerner, J., 2007. Availability and biodegradation of metribuzin in alluvial soils as affected by temperature and soil properties. Weed Research 47, 517–526.

Beulke, S., Brown, C.D., Fryer, C.J., Van Beinum, W., 2004. Influence of kinetic sorption and diffusion on pesticide movement through aggregated soils. Chemosphere 57, 481–490.

Beulke, S., Dubus, I.G., Brown, C.D., Gottesburen, B., 2000. Simulation of pesticide persistence in the field on the basis of laboratory data - A review. Journal of Environmental Quality 29, 1371–1379.

Beulke, S., Van Beinum, W., Brown, C.D., Mitchell, M., Walker, A., 2005. Evaluation of simplifying assumptions on pesticide degradation in soil. Journal of Environmental Quality 34, 1933–1943.

Bicalho, S.T.T., Langenbach, T., 2012. Distribution of the herbicide atrazine in a microcosm with riparian forest plants. Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes 47, 505–511.

Bouldin, J.L., Farris, J.L., Moore, M.T., Smith, S., Stephens, W.W., Cooper, C.M., 2005. Evaluated fate and effects of atrazine and lambda-cyhalothrin in vegetated and unvegetated microcosms. Environmental Toxicology 20, 487–498.

Briceño, G., Fuentes, M.S., Palma, G., Jorquera, M.A., Amoroso, M.J., Diez, M.C., 2012. Chlorpyrifos biodegradation and 3,5,6-trichloro-2-pyridinol production by actinobacteria isolated from soil. International Biodeterioration & Biodegradation 73, 1–7.

Bromilow, R., De Carvalho, R., Evans, A., Nicholls, P., 2006. Behavior of pesticides in sediment/water systems in outdoor mesocosms. Journal of Environmental Science and Health, Part B 41, 1–16.

Brown, C.D., Van Beinum, W., 2009. Pesticide transport via sub-surface drains in Europe. Environmental Pollution 157, 3314–3324.

Broznić, D., Milin, Č., 2012. Effects of temperature on sorption-desorption processes of imidacloprid in soils of Croatian coastal regions. Journal of Environmental Science and Health, Part B 47, 779–794.

Burrows, H.D., Canle, M., Santaballa, J.A., Steenken, S., 2002. Reaction pathways and mechanisms of photodegradation of pesticides. Journal of Photochemistry and Photobiology B-Biology 67, 71–108.

Businelli, M., Patumi, M., Marucchini, C., 1984. Identification and determination of some metalaxyl degradation products. Journal of Agricultural and Food Chemistry 32, 644–647.

Caceres, T.C., Megharaj, M., Naidu, R., 2008. Degradation of fenamiphos in soils collected from different geographical regions: The influence of soil properties and climatic conditions. Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes 43, 314–322.

Čadková, E., Komárek, M., Kaliszová, R., Koudelková, V., Dvořák, J., Vaněk, A., 2012. Sorption of tebuconazole onto selected soil minerals and humic acids. Journal of Environmental Science and Health, Part B 47, 336–342.

Campbell, S., Chen, L., Yu, J., Li, Q.X., 2005. Adsorption and analysis of the insecticides thiamethoxam and indoxacarb in Hawaiian soils. Journal of Agricultural and Food Chemistry 53, 5373–5376.

Carbo, L., Martins, E.L., Dores, E.F.G.C., Spadotto, C.A., Weber, O.L.S., De-Lamonica-Freire, E.M., 2007. Acetamiprid, carbendazim, diuron and thiamethoxam sorption in two Brazilian tropical soils. Journal of Environmental Science and Health, Part B 42, 499–507.

Carter, A., 2000. How pesticides get into water - and proposed reduction measures. Pesticide Outlook 11, 149–156.

Chan, K.H., Chu, W., 2009. Riboflavin-sensitized photooxidation of phenylurea herbicide monuron in aqueous peroxide solution. Chemical Engineering Journal 152, 103–109.

Chaturvedi, N., Dhal, N.K., Reddy, P.S.R., 2012. Phytostabilization of iron ore tailings through Calophyllum Inophyllum L. International Journal of Phytoremediation 14, 996–1009.

Chaudhari, S.K., Singh, R., Kundu, D.K., 2008. Rapid Textural Analysis for Saline and Alkaline Soils with Different Physical and Chemical Properties. Soil Science Society of America Journal 72, 431.

Chen, H., He, X., Rong, X., Chen, W., Cai, P., Liang, W., Li, S., Huang, Q., 2009. Adsorption and biodegradation of carbaryl on montmorillonite, kaolinite and goethite. Applied Clay Science 46, 102–108.

Chen, S., Luo, J., Hu, M., Lai, K., Geng, P., Huang, H., 2012. Enhancement of cypermethrin degradation by a coculture of Bacillus cereus ZH-3 and Streptomyces aureus HP-S-01. Bioresource Technology 110, 97–104.

Chiu, T.C., Yen, J.H., Hsieh, Y.N., Wang, Y.S., 2005. Reductive transformation of dieldrin under anaerobic sediment culture. Chemosphere 60, 1182–1189.

Chnirheb, A., Harir, M., Kanawati, B., Fekete, A., El Azzouzi, M., Hertkorn, N., Schmitt-Kopplin, P., 2010. Hydrolysis of mefenpyrdiethyl: an analytical and DFT investigation. Analytical and Bioanalytical Chemistry 398, 2325–2334.

Collins, C., Fryer, M., Grosso, A., 2006. Plant uptake of non-ionic organic chemicals. Environmental Science & Technology 40, 45–52.

Connell, D.W., 2005. Basic concepts of environmental chemistry, second Edition, 2nd ed. CRC Press.

Dams, R.I., Paton, G.I., Killham, K., 2007. Rhizoremediation of pentachlorophenol by Sphingobium chlorophenolicum ATCC 39723. Chemosphere 68, 864–870.

De Carvalho, R.F., Bromilow, R.H., Greenwood, R., 2007a. Uptake of pesticides from water by curly waterweedLagarosiphon major and lesser duckweedLemna minor. Pest Management Science 63, 789–797.

De Carvalho, R.F., Bromilow, R.H., Greenwood, R., 2007b. Uptake and translocation of non-ionised pesticides in the emergent aquatic plant parrot featherMyriophyllum aquaticum. Pest Management Science 63, 798–802.

De Urzedo, A.P.F.M., Diniz, M.E.R., Nascentes, C.C., Catharino, R.R., Eberlin, M.N., Augusti, R., 2007. Photolytic degradation of the insecticide thiamethoxam in aqueous medium monitored by direct infusion electrospray ionization mass spectrometry. Journal of Mass Spectrometry 42, 1319–1325.

Dimou, A.D., Sakkas, V.A., Albanis, T.A., 2005. Metolachlor photodegradation study in aqueous media under natural and simulated solar irradiation. Journal of Agricultural and Food Chemistry 53, 694–701.

Dinelli, G., Accinelli, C., Vicari, A., Catizone, P., 2000. Comparison of the persistence of atrazine and metolachlor under field and laboratory conditions. Journal of Agricultural and Food Chemistry 48, 3037–3043.

Droby, S., Coffey, M., 1991. Biodegradation process and the nature of metabolism of metalaxyl in soil. Annals of Applied Biology 118, 543–553.

Druzina, B., Stegu, M., 2007. Degradation study of selected organophosphorus insecticides in natural waters. International Journal of Environmental Analytical Chemistry 87, 1079–1093.

El Gaini, L., Meghea, A., Bakasse, M., 2010. Phototransformation of pesticide in the presence of moroccan natural phosphate in aqueous solution. Journal of Optoelectronics and Advanced Materials 12, 1981–1985.

El Sebai, T., Devers, M., Lagacherie, B., Rouard, N., Soulas, G., Martin-Laurent, F., 2010. Diuron mineralisation in a Mediterranean vineyard soil: impact of moisture content and temperature. Pest Management Science 66, 988–995.

Fernandes, M.C., Cox, L., Hermosin, M.C., Cornejo, J., 2003. Adsorption-desorption of metalaxyl as affecting dissipation and leaching in soils:role of mineral and organic components. Pest Management Science 59, 545–552.

Gatidou, G., Iatrou, E., 2011. Investigation of photodegradation and hydrolysis of selected substituted urea and organophosphate pesticides in water. Environmental Science and Pollution Research 18, 949–957.

Gavrilescu, M., 2005. Fate of pesticides in the environment and its bioremediation. Engineering in Life Sciences 5, 497–526.

Gerhardt, K.E., Huang, X.-D., Glick, B.R., Greenberg, B.M., 2009. Phytoremediation and rhizoremediation of organic soil contaminants: Potential and challenges. Plant Sci. 176, 20–30.

Gregoire, C., Elsaesser, D., Huguenot, D., Lange, J., Lebeau, T., Merli, A., Mose, R., Passeport, E., Payraudeau, S., Schuetz, T., Schulz, R., Tapia-Padilla, G., Tournebize, J., Trevisan, M., Wanko, A., 2009. Mitigation of agricultural nonpoint-source pesticide pollution in artificial wetland ecosystems. Environmental Chemistry Letters 7, 205–231.

Gupta, J., Erwin, D., Eckert, J., Zaki, A., 1985. Translocation of metalaxyl in soybean plants and control of stem rot caused by Phytophthora-Megasperma F Sp Glycinea. Phytopathology 75, 865–869.

Gupta, S., Gajbhiye, V.T., Gupta, R.K., 2008. Soil dissipation and leaching behavior of a neonicotinoid insecticide thiamethoxam. Bulletin of Environmental Contamination and Toxicology 80, 431–437.

Guth, J.A., Reischmann, F.J., Allen, R., Arnold, D., Hassink, J., Leake, C.R., Skidmore, M.W., Reeves, G.L., 2004. Volatilisation of crop protection chemicals from crop and soil surfaces under controlled conditions-prediction of volatile losses from physico-chemical properties. Chemosphere 57, 871–887.

Guzsvany, V., Csanadi, J., Gaal, F., 2006. NMR study of the influence of pH on the persistence of some neonicotinoids in water. Acta Chimica Slovenica 53, 52–57.

Harrison, R., 1999. Understanding our environment, 3rd ed. Royal Society of Chemistry.

Hemond, H.F., Fechner-Levy, E.J., 1999. Chemical fate and transport in the environment, Second Edition, 2nd ed. Academic Press.

Hiller, E., Cernansky, S., Krascsenits, Z., Milicka, J., 2009. Effect of soil and sediment composition on acetochlor sorption and desorption. Environmental Science and Pollution Research 16, 546–554.

Holvoet, K.M.A., Seuntjens, P., Vanrolleghem, P.A., 2007. Monitoring and modeling pesticide fate in surface waters at the catchment scale. Ecological Modelling 209, 53–64.

Hussain, S., Siddique, T., Arshad, M., Saleem, M., 2009. Bioremediation and phytoremediation of pesticides: recent advances. Critical Reviews in Environmental Science and Technology 39, 843–907.

Jaipieam, S., Visuthismajarn, P., Sutheravut, P., Siriwong, W., Thoumsang, S., Borjan, M., Robson, M., 2009. Organophosphate pesticide residues in drinking water from Artesian Wells and health risk assessment of agricultural communities, Thailand. Human and Ecological Risk Assessment 15, 1304–1316.

Kah, M., Brown, C.D., 2006. Adsorption of ionisable pesticides in soils, in: Ware, G.W., Whitacre, D.M., Albert, L.A., Voogt, P., Gerba, C.P., Hutzinger, O., Knaak, J.B., Mayer, F.L., Morgan, D.P., Park, D.L., Tjeerdema, R.S., Yang, R.S.H., Gunther, F.A. (Eds.), Reviews of Environmental Contamination and Toxicology. Springer New York, New York, NY, pp. 149–217.

Kah, M., Brown, C.D., 2007. Prediction of the adsorption of ionizable pesticides in soils. Journal of Agricultural and Food Chemistry 55, 2312–2322.

Karmakar, R., Singh, S.B., Kulshrestha, G., 2006. Persistence and transformation of thiamethoxam, a neonicotinoid insecticide, in soil of different agroclimatic zones of India. Bulletin of Environmental Contamination and Toxicology 76, 400–406.

Karmakar, R., Singh, S.B., Kulshrestha, G., 2009. Kinetics and mechanism of the hydrolysis of thiamethoxam. Journal of Environmental Science and Health, Part B 44, 435–441.

Kasozi, G.N., Nkedi-Kizza, P., Lib, Y., Zimmerman, A.R., 2012. Sorption of atrazine and ametryn by carbonatic and non-carbonatic soils of varied origin. Environmental Pollution 169, 12–19.

Katagi, T., 2004. Photodegradation of pesticides on plant and soil surfaces, in: Ware, G.W. (Ed.), Reviews of Environmental Contamination and Toxicology, Vol 182. Springer, New York, pp. 1–189.

Katagi, T., 2006. Behavior of pesticides in water-sediment systems, in: Ware, G.W. (Ed.), Reviews of Environmental Contamination and Toxicology, Vol 187. Springer, New York, pp. 133–251.

Kettler, T.A., Doran, J.W., Gilbert, T.L., 2001. Simplified method for soil particle-size determination to accompany soil-quality analyses. Soil Sci. Soc. Am. J. 65, 849–852.

Knaebel, A., Stehle, S., Schaefer, R.B., Schulz, R., 2012. Regulatory FOCUS surface water models fail to predict insecticide concentrations in the field. Environmental Science & Technology 46, 8397–8404.

Kruawal, K., Sacher, F., Werner, A., Müller, J., Knepper, T.P., 2005. Chemical water quality in Thailand and its impacts on the drinking water production in Thailand. Science of The Total Environment 340, 57–70.

Lin, Z., Li, X., Li, Y., Huang, D., Dong, J., Li, F., 2012. Enhancement effect of two ecological earthworm species (Eisenia foetida and Amynthas robustus E. Perrier) on removal and degradation processes of soil DDT. Journal of Environmental Monitoring 14, 1551–1558.

Liqing, Z., Guoguang, L., Dezhi, S., Kun, Y., 2006. Hydrolysis of thiamethoxam. Bulletin of Environmental Contamination and Toxicology 76, 942–949.

Liu, Y., Xu, Z., Wu, X., Gui, W., Zhu, G., 2010. Adsorption and desorption behavior of herbicide diuron on various Chinese cultivated soils. J. Hazard. Mater. 178, 462–468.

Mack, J., Bolton, J.R., 1999. Photochemistry of nitrite and nitrate in aqueous solution: a review. Journal of Photochemistry and Photobiology a-Chemistry 128, 1–13.

Maltby, L., Arnold, D., Arts, G., Davies, J., Heimbach, F., Pickl, C., Poulsen, V., 2009. Aquatic macrophyte risk assessment for pesticides, 1st ed. CRC Press.

Maresova, J., Remenarova, L., Hornik, M., Pipiska, M., Augustin, J., Lesny, J., 2012. Foliar uptake of zinc by vascular plants: radiometric study. Journal of Radioanalytical and Nuclear Chemistry 292, 1329–1337.

Materazzi, S., Canepari, S., Aquili, S., 2012. Monitoring heavy metal pollution by aquatic plants. Environmental Science and Pollution Research 19, 3292–3298.

Matocha, M.A., Krutz, L.J., Reddy, K.N., Senseman, S.A., Locke, M.A., Steinriede, R.W., Palmer, E.W., 2006. Foliar washoff potential and simulated surface runoff losses of trifloxysulfuron in cotton. Journal of Agricultural and Food Chemistry 54, 5498–5502.

Mazanti, L., Rice, C., Bialek, K., Sparling, D., Stevenson, C., Johnson, W.E., Kangas, P., Rheinstein, J., 2003. Aqueous-phase disappearance of atrazine, metolachlor, and chlorpyrifos in laboratory aquaria and outdoor macrocosms. Archives of Environmental Contamination and Toxicology 44, 67–76.

McCarthy, A.M., Bales, J.D., Cope, W.G., Shea, D., 2007. Modeling pesticide fate in a small tidal estuary. Ecological Modelling 200, 149–159.

Milz, B., Bin Idros, I., Spangenberg, B., 2012. Limits of quantification of some neonicotinoid insecticides measured by thin-layer chromatography. Journal of Liquid Chromatography & Related Technologies 35, 1404–1414.

Monkiedje, A., Spiteller, M., 2002. Sorptive behavior of the phenylamide fungicides, mefenoxam and metalaxyl, and their acid metabolite in typical Cameroonian and German soils. Chemosphere 49, 659–668.

Moore, M.T., Bennett, E.R., Cooper, C.M., Smith, S., Farris, J.L., Drouillard, K.G., Schulz, R., 2006. Influence of vegetation in mitigation of methyl parathion runoff. Environmental Pollution 142, 288–294.

Moore, M.T., Bennett, E.R., Cooper, C.M., Smith, S., Shields, F.D., Milam, C.D., Farris, J.L., 2001. Transport and fate of atrazine and lambda-cyhalothrin in an agricultural drainage ditch in the Mississippi Delta, USA. Agriculture Ecosystems & Environment 87, 309–314.

Morrica, P., Trabue, S., Anderson, J.J., Lawler, S., Seccia, S., Fidente, P., Swain, R.S., Mattson, S.L., 2004. Kinetics and mechanism of cymoxanil degradation in buffer solutions. Journal of Agricultural and Food Chemistry 52, 99–104.

Muhamad, H., Ismail, B.S., Sameni, M., Mat, N., 2011. Adsorption study of C-14-paraquat in two Malaysian agricultural soils. Environmental Monitoring and Assessment 176, 43–50.

Muratova, A.Y., Turkovskaya, O.V., Hubner, T., Kuschk, P., 2003. Studies of the efficacy of alfalfa and reed in the phytoremediation of hydrocarbon-polluted soil. Applied Biochemistry and Microbiology 39, 599–605.

Murthy, H.M.R., Manonmani, H.K., 2007. Aerobic degradation of technical hexachlorocyclohexane by a defined microbial consortium. Journal of Hazardous Materials 149, 18–25.

Navarro, S., Barba, A., Segura, J.C., Oliva, J., 2000. Disappearance of endosulfan residues from seawater and sediment under laboratory conditions. Pest Management Science 56, 849–854.

Nelieu, S., Kerhoas, L., Sarakha, M., Einhorn, J., 2004. Nitrite and nitrate induced photodegradation of monolinuron in aqueous solution. Environmental Chemistry Letters 2, 83–87.

Organisation for Economic Co-operation and Development, 2000. Test No. 106: adsorption-desorption using a batch equilibrium method. OECD Publishing, [Paris].

Organisation for Economic Co-operation and Development, 2002. Test No. 308: aerobic and anaerobic transformation in aquatic sediment systems. OECD Publishing, [Paris].

Organisation for Economic Co-operation and Development, 2008. Test No. 316: phototransformation of chemicals in water-direct photolysis. OECD Publishing, [Paris].

Owen, W., Donzel, B., 1986. Oxidative-degradation of chlortoluron, propiconazole, and metalaxyl in suspension-cultures of various crop plants. Pesticide Biochemistry and Physiology 26, 75–89.

Padovani, L., Capri, E., 2005. Chlorpyrifos-methyl dissipation in a small adjacent water body following application to citrus. Chemosphere 58, 1219–1229.

Panuwet, P., Siriwong, W., Prapamontol, T., Ryan, P.B., Fiedler, N., Robson, M.G., Barr, D.B., 2012. Agricultural pesticide management in Thailand: status and population health risk. Environmental Science & Policy 17, 72–81.

Patakioutas, G.I., Albanis, T.A., 2004. Runoff of herbicides from cropped and uncropped plots with different slopes. International Journal of Environmental Analytical Chemistry 84, 103–121.

Peña, A., Rodríguez-Liébana, J.A., Mingorance, M.D., 2011. Persistence of two neonicotinoid insecticides in wastewater, and in aqueous solutions of surfactants and dissolved organic matter. Chemosphere 84, 464–470.

Peng, X., Wang, J., Fan, B., Luan, Z., 2009. Sorption of endrin to montmorillonite and kaolinite clays. Journal of Hazardous Materials 168, 210–214.

PerrinGanier, C., Breuzin, C., Portal, J.M., Schiavon, M., 1996. Availability and persistence of isoproturon under field and laboratory conditions. Ecotoxicology and Environmental Safety 35, 226–230.

Peters, R., Kelsey, J.W., White, J.C., 2007. Differences in p,p ’-DDE bioaccumulation from compost and soil by the plants Cucurbita pepo and Cucurbita maxima and the earthworms Eisenia fetida and Lumbricus terrestris. Environmental Pollution 148, 539–545.

Pinna, M.V., Pusino, A., 2012. Direct and indirect photolysis of two quinolinecarboxylic herbicides in aqueous systems. Chemosphere 86, 655–658.

Plianbangchang, P., Jetiyanon, K., Wittaya-areekul, S., 2009. Pesticide use patterns among small-scale farmers: a case study from Phitsanulok, Thailand. Southeast Asian Journal of Tropical Medicine and Public Health 40, 401–410.

Polati, S., Gosetti, F., Gianotti, V., Gennaro, M.C., 2006. Sorption and desorption behavior of chloroanilines and chlorophenols on montmorillonite and kaolinite. Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes 41, 765–779.

Poolpak, T., Pokethitiyook, P., Kruatrachue, M., Arjarasirikoon, U., Thanwaniwat, N., 2008. Residue analysis of organochlorine pesticides in the Mae Klong River of Central Thailand. Journal of hazardous materials 156, 230–239.

PPDB, 2009. The Pesticide Properties Database (PPDB) developed by the Agriculture & Environment Research Unit (AERU), Univerisity of Hertfordshire, funded by UK national sources and the EU-funded FOOTPRINT project (FP6-SSP-022704). [WWW Document]. PPDB: Pesticide properties database. URL http://www.herts.ac.uk/aeru/footprint (accessed 10.7.12).

Quilbe, R., Rousseau, A.N., Lafrance, P., Leclerc, J., Amrani, M., 2006. Selecting a pesticide fate model at the watershed scale using a multi-criteria analysis. Water Quality Research Journal of Canada 41, 283–295.

Racke, K.D., Skidmore, M., Hamilton, D.J., Unsworth, J.B., Miyamoto, J., Cohen, S.Z., 1999. Pesticide fate in tropical soils. Pesticide Science 55, 219–220.

Ramezani, M., Oliver, D.P., Kookana, R.S., Gill, G., Preston, C., 2008. Abiotic degradation (photodegradation and hydrolysis) of imidazolinone herbicides. Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes 43, 105–112.

Rani, R., Juwarkar, A., 2012. Biodegradation of phorate in soil and rhizosphere of Brassica juncea (L.) (Indian Mustard) by a microbial consortium. International Biodeterioration & Biodegradation 71, 36–42.

Renaud, F.G., Brown, C.D., Fryer, C.J., Walker, A., 2004. A lysimeter experiment to investigate temporal changes in the availability of pesticide residues for leaching. Environ. Pollut. 131, 81–91.

Riise, G., Lundekvam, H., Wu, Q.L., Haugen, L.E., Mulder, J., 2004. Loss of pesticides from agricultural fields in SE Norway - runoff through surface and drainage water. Environmental Geochemistry and Health 26, 269–276.

Rodríguez-Cruz, M.S., Valderrábano, M., Del Hoyo, C., Sánchez-Martín, M.J., 2009. Physicochemical study of the sorption of pesticides by wood components. Journal of Environment Quality 38, 719.

Saha, T., Sukul, P., 1997. Metalaxyl—its persistence and metabolism in soil. Toxicological & Environmental Chemistry 58, 251–258.

Salt, D.E., Smith, R.D., Raskin, I., 1998. Phytoremediation. Annual Review of Plant Physiology and Plant Molecular Biology 49, 643–668.

Samoh, A.N.H., Ibrahim, M.S., 2008. Organochlorine Pesticide Residues in the Major Rivers of Southern Thailand. Malaysian Journal of Analytical Sciences.

Shankar, M.V., Nelieu, S., Kerhoas, L., Einhorn, J., 2007. Photo-induced degradation of diuron in aqueous solution by nitrites and nitrates: Kinetics and pathways. Chemosphere 66, 767–774.

Sharma, D., Awasthi, M.D., 1997. Adsorption and movement of metalaxyl in soils under unsaturated flow conditions. Plant and Soil 195, 293–298.

Stottmeister, U., Wiessner, A., Kuschk, P., Kappelmeyer, U., Kastner, M., Bederski, O., Muller, R.A., Moormann, H., 2003. Effects of plants and microorganisms in constructed wetlands for wastewater treatment. Biotechnology Advances 22, 93–117.

Sukul, P., Majumder, A., Spiteller, M., 2008. Microbial population and their activities in soil as influenced by metalaxyl residues. Fresenius Environmental Bulletin 17, 103–110.

Sukul, P., Spiteller, M., 2000. Metalaxyl: Persistence, degradation, metabolism, and analytical methods. Reviews of Environmental Contamination and Toxicology 164, 1–26.

Sukul, P., Spiteller, M., 2001. Influence of biotic and abiotic factors on dissipating metalaxyl in soil. Chemosphere 45, 941–947.

Sun, H.W., Xu, J., Yang, S.H., Liu, G.L., Dai, S.G., 2004. Plant uptake of aldicarb from contaminated soil and its enhanced degradation in the rhizosphere. Chemosphere 54, 569–574.

Sun, K., Gao, B., Ro, K.S., Novak, J.M., Wang, Z., Herbert, S., Xing, B., 2012. Assessment of herbicide sorption by biochars and organic matter associated with soil and sediment. Environmental Pollution 163, 167–173.

Susarla, S., Medina, V.F., McCutcheon, S.C., 2002. Phytoremediation: An ecological solution to organic chemical contamination. Ecol. Eng. 18, 647–658.

Tan, K.H., 1994. Environmental Soil Science. Marcel Dekker Inc.

Trapp, S., 2004. Plant uptake and transport models for neutral and ionic chemicals. Environmental Science and Pollution Research 11, 33–39.

Triantafyllidis, V., Hela, D., Dimopoulos, P., Albanis, T., 2006. Imidacloprid losses in surface runoff from plots cultivated with tobacco. International Journal of Environmental Analytical Chemistry 86, 185–194.

Ukpebor, J.E., Halsall, C.J., 2012. Effects of dissolved water constituents on the photodegradation of fenitrothion and diazinon. Water Air and Soil Pollution 223, 655–666.

Van Wesenbeeck, I., Driver, J., Ross, J., 2008. Relationship between the evaporation rate and vapor pressure of moderately and highly volatile chemicals. Bulletin of Environmental Contamination and Toxicology 80, 315–318.

vanLoon, G.W., Duffy, S.J., 2005. Environmental chemistry: a global perspective, 2nd ed. Oxford University Press, USA.

Wainwright, J., Mulligan, M. (Eds.), 2004. Environmental modelling: finding simplicity in complexity, 1st ed. Wiley.

Walker, A., Crout, N., 1997. ModelMaker: user manual version 3. Cherwell Scientific Publishing.

Wang, X., Li, Y., Dong, D., 2008. Sorption of pentachlorophenol on surficial sediments: the roles of metal oxides and organic materials with co-existed copper present. Chemosphere 73, 1–6.

Wauchope, R.D., Yeh, S., Linders, J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kordel, W., Gerstl, Z., Lane, M., Unsworth, J.B., 2002. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Management Science 58, 419–445.

Wilson, P.C., Whitwell, T., Klaine, S.J., 2001. Metalaxyl toxicity, uptake, and distribution in several ornamental plant species. Journal of Environmental Quality 30, 411–417.

Xie, H., Zhu, L., Xu, Q., Wang, J., Liu, W., Jiang, J., Meng, Y., 2011. Isolation and degradation ability of the DDT-degrading bacterial strain KK. Environmental Earth Sciences 62, 93–99.

Xu, G., Li, F., Wang, Q., 2007. Effect of humic acids on photodegradation of chloroacetanilide herbicides under UV irradiation. Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes 42, 165–171.

Yeo, H.-G., Choi, M., Sunwoo, Y., 2004. Seasonal variations in atmospheric concentrations of organochlorine pesticides in urban and rural areas of Korea. Atmospheric Environment 38, 4779–4788.

Zaki, A., Zentmyer, G., Lebaron, H., 1981. Systemic translocation of C-14-labeled metalaxyl in tomato, avocado, and Persea-Indica. Phytopathology 71, 509–514.

Zheng, W., Liu, W.P., 1999. Kinetics and mechanism of the hydrolysis of imidacloprid. Pesticide Science 55, 482–485.

Zheng, W., Yates, S.R., Papiernik, S.K., 2008. Transformation kinetics and mechanism of the sulfonylurea herbicides pyrazosulfuron ethyl and halosulfuron methyl in aqueous solutions. Journal of Agricultural and Food Chemistry 56, 7367–7372.

APPENDICES

Appendices A: Observed data for photolysis experiments (Chapter 3)

Appendix A-1 Photolysis rate constants and calculated half-lives of thiamethoxam in pure and natural water with varying nitrate concentration

Water type	Nitrate concentration (mg L^{-1})	$k_{photolysis}$ (day^{-1})	Chi^2 for fit	Photolysis half-life (days)
pure	0	3.01	0.755	0.231
water	25	2.62	0.557	0.266
	100	2.39	0.502	0.291
natural	0	2.09	4.43	0.334
water	25	2.01	0.799	0.347
	100	2.02	1.55	0.343

Appendix A-2 Measured rate constant of overall reaction, measured hydrolysis rate constant and calculated photolysis rate constant and half-life of thiamethoxam in pure water with varying pH.

Water type	$k_{overall}$ (day^{-1})	Chi^2 for fit	$k_{hydrolysis}$ (day^{-1})	$k_{photolysis}$ (day^{-1})	Half-life (calculated from photolysis reaction (days)
Pure water pH 5 (pH 4.45)	2.14	0.73	0.0222	2.11	0.328
Pure water pH 7 (pH 7.02)	1.74	0.57	0.0438	1.70	0.408
Pure water pH 8 (pH 8.01)	1.97	0.63	0.0254	1.94	0.357
Pure water pH 9 (pH 9.03)	3.08	1.35	0.547	2.53	0.274

Pure water pH 10 (pH 10.02)	14.0	1.74	3.06	10.9	0.0636

Appendix A-3 Measured rate constant of overall reaction, measured hydrolysis rate constant and calculated photolysis rate constant and half-life of thiamethoxam in natural water with varying pH.

Water type	$k_{overall}$ (day^{-1})	Chi^2 for fit	$k_{hydrolysis}$ (day^{-1})	$k_{photolysis}$ (day^{-1})	Half-life (calculated from photolysis reaction (days)
Natural water pH 5 (pH 5.10)	1.72	1.17	0.0121	1.71	0.405
Natural water pH 7 (pH 7.00)	2.00	1.52	0.00750	1.99	0.348
Natural water pH 8 (pH 8.04)	1.75	1.10	0.0196	1.73	0.401
Natural water pH 9 (pH 9.00)	3.09	1.84	0.343	2.75	0.252
Natural water pH 10 (pH 10.01)	13.7	1.63	3.08	10.6	0.0654

Appendices B: Sediment particle size determinations, and observed data for sorption experiment (Chapter 4)

Appendix B-1 Sediment particle size determinations

Introduction

Soil particle-size (%sand, silt and clay) is important information for any experiment relating to soil or sediment. Soil particle-size relates to soil properties such as soil-water retention, leaching, erosion potential and sorption. There are several methods for particle-size analysis for example including hydrometer and pipette methods (Avery et al., 1982). Kettler et al. (2001) developed a soil particle-size determination method name 'rapid method' by analysing six different soil samples. Later, Chaudhari et al. (2008) confirmed the rapid method by analyzing 100 saline and alkaline soil samples. Kettler et al. (2001) and Chaudhari et al. (2008) evaluated the rapid method by comparison against a standard pipette method for the same soils (Table B-1). The authors claimed that the rapid method provides a reliable soil particle-size determination with similar results to the pipette method.

Table B-1 Linear regression equation relating measured sand, silt and clay fraction using the hydrometer, particulate organic matter (POM) and rapid method to the pipette method (Kettler et al., 2001 and Chaudhari et al., 2008).

Fraction	Hydrometer vs. pipette		POM vs. pipette		Rapid vs. pipette	
	Equation	R^2	Equation	R^2	Equation	R^2
Sand	y=0.93x+1.44	0.98	Y=0.98x+0.92	0.99	Y=0.99x+0.26	0.99
	-	-	Y=1.02x	0.99	Y=1.02x	0.99
Silt	y=0.87+5.33	0.88	Y=0.96+1.61	0.98	Y=1.01x+0.37	0.99
	-	-	Y=0.99x	0.98	0.999x	0.99
Clay	y=0.90x+2.86	0.95	Y=0.95x+1.04	0.99	Y=1.01x+1.04	0.99
	-	-	Y=0.95x	0.93	Y=0.96X	0.97

Note: (-) is information was not given.

Method

Air-dried (<2 mm) sediment samples in three replicate (15 g) were mixed with 3% (by weight) hexametaphosphate solution (90 mL) and then the flasks were shaken on a reciprocating shaker at 120 revolutions min^{-1} for 2 hours. Afterwards the mixtures were sieved through a 0.063-mm sieve to separate sand particles. The sand particles were rinsed and oven dried at 105^{o}C to constant weight. The sand content in the sample was calculated as:

$$\%sand = \frac{Oven\ dry\ sand\ mass}{sample\ mass\ corrected\ for\ moisture\ content}.100$$

The mixture solution was transferred to a one litre beaker and stirred for 30 minutes to get a homogeneous suspension. The beakers were left undisturbed for 4 hours at room temperature (20±2^{o}C) for silt sedimentation. Afterwards, the liquid phase in the beakers was discarded. The settled silt was dried in the beaker at 105^{o}C to constant weight. Silt content in the soil sample was calculated as:

$$\%silt = \frac{Oven\ dry\ silt\ mass}{Sample\ mass\ corrected\ for\ moisture\ content}.100$$

The clay content was determined by subtraction: %clay = 100 – (%sand + %silt)

Results

The amount of sand measured in three replicates was 7.68, 6.36 and 7.86 g giving sand content in the sediment of 51.2, 42.4 and 52.4%, respectively. The amount of measured silt from the three replicates was 2.88, 2.81, and 3.03 g giving silt in the sediment of 19.2, 18.7 and 20.2%, respectively. Calculated clay fraction in the sediment was 29.6, 38.9 and 27.4% for three replicates. The sediment was composed of (mean±standard deviation) 48.7±5.5%, 19.4±0.8%, 32.0±6.1% for sand, silt and clay, respectively.

Appendix B-2 Thiamethoxam residues in sorption test systems varying in water-sediment ratio (1:10, 1:5, 1:4, and 1:2)

Sample	Initial Total Pesticide per Tube (mg)	Pesticide per mL (no sorption) in sol. (mg)	Measured Pesticide After 3-Days (mg/l)	Total Pesticide in Solution (mg)	Total TMX in Soil (mg)	Sorption (%)	Average % Sorption	Standard deviation
2 g soil	0.020	0.0010	0.62	0.012	0.0075	37.7		
2 g soil	0.020	0.0010	0.57	0.011	0.0086	43.0	40.5	2.67
2 g soil	0.020	0.0010	0.59	0.012	0.0082	40.8		
4 g soil	0.020	0.0010	0.48	0.0096	0.010	51.8		
4 g soil	0.020	0.0010	0.49	0.0099	0.010	50.6	51.3	0.65
4 g soil	0.020	0.0010	0.48	0.0097	0.010	51.5		
5 g soil	0.020	0.0010	0.47	0.0095	0.011	52.6		
5 g soil	0.020	0.0010	0.48	0.0096	0.010	51.8	52.6	0.87
5 g soil	0.020	0.0010	0.46	0.0093	0.011	53.5		
10 g soil	0.020	0.0010	0.36	0.0072	0.013	64.0		
10 g soil	0.020	0.0010	0.35	0.0070	0.013	64.9	63.5	1.80
10 g soil	0.020	0.0010	0.39	0.0077	0.012	61.5		

Appendix B-3 Metalaxyl-M residues in sorption test system varying in water-sediment ratio (1:10, 1:5, 1:4, and 1:2)

Sample	Initial Total Pesticide per Tube (mg)	Pesticide per mL (no sorption) in sol. (mg)	Measured Pesticide After 3-Days (mg L^{-1})	Total Pesticide in Solution (mg)	Total MET in Soil (mg)	Sorption (%)	Average % Sorption	Standard deviation
2 g soil	0.020	0.0010	0.65	0.013	0.0070	35.1		
2 g soil	0.020	0.0010	0.57	0.011	0.0087	43.4	42.1	6.47
2 g soil	0.020	0.0010	0.52	0.010	0.0096	47.9		
4 g soil	0.020	0.0010	0.47	0.0094	0.011	52.8		
4 g soil	0.020	0.0010	0.49	0.0098	0.010	50.9	51.7	0.98
4 g soil	0.020	0.0010	0.49	0.0097	0.010	51.4		
5 g soil	0.020	0.0010	0.38	0.0075	0.012	62.5		
5 g soil	0.020	0.0010	0.44	0.0088	0.011	55.8	58.7	3.43
5 g soil	0.020	0.0010	0.42	0.0084	0.012	57.8		
10 g soil	0.020	0.0010	0.33	0.0066	0.013	67.0		
10 g soil	0.020	0.0010	0.30	0.0060	0.014	69.9	69.4	2.19
10 g soil	0.020	0.0010	0.29	0.0058	0.014	71.2		

Appendix B-4 Thiamethoxam (TMX) residues in solution and in sediment for the main sorption study

Sample	Initial total TMX per tube (mg)	TMX per mL (no sorption) in solution (mg)	Measured TMX after 4-Days (mg L^{-1})	Total thiamethoxam in Solution (mg)	Actual total thiamethoxam in sediment (mg)	%Sorption	Average %Sorption	Standard deviation	TMX in soil (mg kg^{-1})	TMX in solution (ug mL^{-1})
TMX 0.2 mg L^{-1}_1	0.00400	0.000200	0.113	0.00226	0.00174	43.5	47.1	9.3	0.180	0.113
TMX 0.2 mg L^{-1}_2	0.00400	0.000200	0.120	0.00240	0.00160	40.1			0.165	0.120
TMX 0.2 mg L^{-1}_3	0.00400	0.000200	0.085	0.00169	0.00231	57.6			0.238	0.0847
TMX 0.5 mg L^{-1}_1	0.0100	0.000500	0.294	0.00588	0.00412	41.2	41.8	1.2	0.425	0.294
TMX 0.5 mg L^{-1}_2	0.0100	0.000500	0.284	0.00568	0.00432	43.2			0.445	0.284
TMX 0.5 mg L^{-1}_3	0.0100	0.000500	0.295	0.00590	0.00410	41.0			0.423	0.295
TMX 1 mg L^{-1}_1	0.0200	0.00100	0.556	0.0111	0.00889	44.4	47.5	2.8	0.917	0.556
TMX 1 mg L^{-1}_2	0.0200	0.00100	0.501	0.0100	0.0100	49.9			1.03	0.501
TMX 1 mg L^{-1}_3	0.0200	0.00100	0.518	0.0104	0.00963	48.2			0.994	0.518
TMX 1.5 mg L^{-1}_1	0.0300	0.00150	0.889	0.0178	0.0122	40.7	43.7	2.6	1.26	0.889
TMX 1.5 mg L^{-1}_2	0.0300	0.00150	0.827	0.0165	0.0135	44.9			1.39	0.827
TMX 1.5 mg L^{-1}_3	0.0300	0.00150	0.819	0.0164	0.0136	45.4			1.41	0.819
TMX 2 mg L^{-1}_1	0.0400	0.00200	1.17	0.0234	0.0166	41.6	44.0	2.6	1.72	1.17
TMX 2 mg L^{-1}_2	0.0400	0.00200	1.06	0.0213	0.0187	46.8			1.93	1.06
TMX 2 mg L^{-1}_3	0.0400	0.00200	1.13	0.0226	0.0174	43.5			1.79	1.13

Appendix B-5 Metalaxyl-M (MET) residues in solution and in sediment for the main sorption study

Sample	Initial total MET per tube (mg)	MET per mL (no sorption) in solution. (mg)	Measured MET after 4-Days (mg L^{-1})	Total MET in solution (mg)	Total MET in Soil (mg)	%Sorption	Average %Sorption	Standard deviation	MET in Soil (mg kg^{-1})	MET in solution (µg mL^{-1})
met 0.2 mg L^{-1}_1	0.0040	0.00020	0.127	0.00253	0.00147	36.7	58.3	19.2	0.151	0.127
met 0.2 mg L^{-1}_2	0.0040	0.00020	0.0704	0.00141	0.00259	64.8			0.267	0.070
met 0.2 mg L^{-1}_3	0.0040	0.00020	0.0534	0.00107	0.00293	73.3			0.302	0.053
met 0.5 mg L^{-1}_1	0.010	0.00050	0.199	0.00398	0.00602	60.2	56.9	3.4	0.621	0.199
met 0.5 mg L^{-1}_2	0.010	0.00050	0.233	0.00466	0.00534	53.4			0.551	0.233
met 0.5 mg L^{-1}_3	0.010	0.00050	0.214	0.00427	0.00573	57.3			0.591	0.214
met 1 mg L^{-1}_1	0.020	0.0010	0.457	0.00915	0.0109	54.3	51.4	2.5	1.12	0.457
met 1 mg L^{-1}_2	0.020	0.0010	0.499	0.0100	0.0100	50.1			1.03	0.499
met 1 mg L^{-1}_3	0.020	0.0010	0.502	0.0100	0.0100	49.8			1.03	0.502
met 1.5 mg L^{-1}_1	0.030	0.0015	0.793	0.0159	0.0141	47.1	47.3	0.5	1.46	0.793
met 1.5 mg L^{-1}_2	0.030	0.0015	0.783	0.0157	0.0143	47.8			1.48	0.783
met 1.5 mg L^{-1}_3	0.030	0.0015	0.797	0.0159	0.0141	46.9			1.45	0.797
met 2 mg L^{-1}_1	0.040	0.0020	1.12	0.0224	0.0176	43.9	45.5	1.4	1.81	1.12
met 2 mg L^{-1}_2	0.040	0.0020	1.08	0.0216	0.0184	46.0			1.90	1.08
met 2 mg L^{-1}_3	0.040	0.0020	1.07	0.0213	0.0187	46.6			1.92	1.07

Appendices C: Supporting data for water-sediment systems experiment (Chapter 5)

Appendix C-1 Observed thiamethoxam (µg) in water and in sediment at selected time intervals (days)

Time (days)	Thiamethoxam in water (µg)			Thiamethoxam in sediment (µg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
0	235	228	227	Not detected	Not detected	Not detected
1	165	162	161	5.70	6.93	7.41
3	137	141	142	10.2	16.1	13.8
7	121	120	119	13.8	15.3	16.0
14	80.9	81.1	88.5	27.8	24.4	24.2
21	54.7	58.5	48.7	9.42	9.88	6.99
28	42.1	35.6	28.4	12.7	8.19	3.98

Appendix C-2 Observed metalaxyl-M (µg) in water and in sediment at selected time intervals (days)

Time (days)	Metalaxyl-M in water (µg)			Metalaxyl-M in sediment (µg)		
	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
0	136	132	136	Not detected	Not detected	Not detected
1	121	124	118	12.3	13.4	15.4
3	105	108	108	19.5	23.2	19.7
7	90.8	96.3	97.5	26.0	25.7	25.5
14	78.6	76.0	82.3	20.3	19.7	16.8
21	64.4	59.9	62.6	24.1	23.8	23.5
28	52.6	59.6	58.2	19.7	22.2	20.1

Appendix C-3 Calculated thiamethoxam (µg) in water and in sediment from ModelMaker, version 4.0

Time (days)	Thiamethoxam in water from model (µg)	Thiamethoxam in sediment from model (µg)
0	187	0
1	169	9.42
2	155	14.7
3	144	17.5
4	134	18.8
5	127	19.2
6	120	19.1
7	113	18.7
8	108	18.1
9	102	17.4
10	97.3	16.7
11	92.6	16.0
12	88.1	15.2
13	83.9	14.5
14	79.9	13.8
15	76.0	13.2
16	72.4	12.6
17	68.9	12.0
18	65.6	11.4
19	62.5	10.8
20	59.5	10.3

Appendix C-3 (Continued) Calculated thiamethoxam (µg) in water and in sediment from ModelMaker, version 4.0

Time (days)	Thiamethoxam in water from model (µg)	Thiamethoxam in sediment from model (µg)
21	56.6	9.84
22	53.9	9.37
23	51.3	8.92
24	48.9	8.49
25	46.5	8.09
26	44.3	7.70
27	42.2	7.33
28	40.2	6.98

Appendix C-4 Calculated metalaxyl-M in water and in sediment from ModelMaker, version 4.0

Time (days)	Metalaxyl-M in water from model (µg)	Metalaxyl-M in sediment from model (µg)
0	135	0
1	122	11.7
2	113	18.6
3	107	22.7
4	102	24.9
5	98.6	26.0
6	95.5	26.5
7	92.7	26.5
8	90.2	26.3
9	87.9	26.0
10	85.7	25.5

Appendix C-4 (Continued) Calculated metalaxyl-M in water and in sediment from ModelMaker, version 4.0

Time (days)	Metalaxyl-M in water from model (µg)	Metalaxyl-M in sediment from model (µg)
11	83.7	25.0
12	81.7	24.4
13	79.8	23.9
14	77.9	23.4
15	76.1	22.8
16	74.3	22.3
17	72.6	21.8
18	70.9	21.3
19	69.3	20.8
20	67.7	20.3
21	66.1	19.9
22	64.5	19.4
23	63.1	19.0
24	61.6	18.5
25	60.2	18.1
26	58.8	17.7
27	57.4	17.3
28	56.1	16.9

Appendix C-5 Optimization statistics for the thiamethoxam in water-sediment study simulated with ModelMaker version 4.0

Statistic parameter	Model	Residual	Total
Degree of freedom	3	35	38
Weighted sum of squares	1.82×10^{5}	6.50×10^{3}	1.89×10^{5}
Mean square	6.08×10^{4}	1.86×10^{2}	N/A
Total uncorrected sum of squares	-	-	3.77×10^{5}
r^2	-	-	0.966
F	-	-	3.27×10^{2}
P	-	-	1.40×10^{-21}
Q	-	-	N/A

Appendix C-6 Optimization statistics for the metalaxyl-M in water-sediment study simulated with ModelMaker version 4.0

Statistic parameter	Model	Residual	Total
Degree of freedom	3	35	38
Weighted sum of squares	6.79×10^{4}	3.76×10^{2}	6.82×10^{4}
Mean square	2.26×10^{4}	10.7	N/A
Total uncorrected sum of squares	-	-	2.09×10^{5}
r^2	-	-	0.994
F	-	-	2.10×10^{3}
P	-	-	1.74×10^{-05}
Q	-	-	N/A

Appendices D: Pesticide residues in three components; water, sediment, plants in laboratory experiment. (Chapter 6)

Pesticide concentration (thiamethoxam and metalaxyl-M) in water, sediment and plants in treatments G and H (control treatments) are not shown because all measured concentrations were below the detection limit. Any sample were concentration below detection limit is defined as a half of detection limit concentration in water, sediment and plants if use the concentration at limit detection, the sample with below detection limit concentration could result in high concentration than sample at very low concentration

Appendix D-1 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water in treatment A

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment A-day0_1D	2.00	2.06	2.02	0.06	No sediment			No plants		
Treatment A-day0_2D	2.00	1.97								
Treatment A-day0_3D	2.00	1.97								
Treatment A-day28_1D	2.00	1.67	1.67	0.01						
Treatment A-day28_2D	2.00	1.66								
Treatment A-day28_3D	2.00	1.67								
Treatment A-day56_1D	2.00	1.08	1.03	0.07						
Treatment A-day56_2D	2.00	0.983								
Treatment A-day56_3D	2.00	0.938								

Appendix D-2 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water in treatment B

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment B-day0_1L	2.00	1.92	1.97	0.08	No sediment			No plants		
Treatment B-day0_2L	2.00	2.03								
Treatment B-day0_3L	2.00	2.05								
Treatment B-day28_1L	2.00	1.59	1.60	0.02						
Treatment B-day28_2L	2.00	1.61								
Treatment B-day28_3L	2.00	1.66								
Treatment B-day56_1L	2.00	0.875	0.881	0.009						
Treatment B-day56_2L	2.00	0.887								
Treatment B-day56_3L	2.00	0.903								

Appendix D-3 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water and sediment in treatment C

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment C-day0_1D	2.00	1.94	2.19	0.35	0.0255	0.0255	0.0280	No plants		
Treatment C-day0_2D	2.00	2.44			0.0255					
Treatment C-day0_3D	2.00	1.67			0.0255					
Treatment C-day28_1D	2.00	0.657	0.652	0.006	0.0255	0.0255	0.0280			
Treatment C-day28_2D	2.00	0.648			0.0255					
Treatment C-day28_3D	2.00	0.708			0.0255					
Treatment C-day56_1D	2.00	0.00450	0.00450	0.00400	0.0255	0.0255	0.0280			
Treatment C-day56_2D	2.00	0.00450			0.0255					
Treatment C-day56_3D	2.00	0.00450			0.0255					

Appendix D-4 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water and sediment in treatment D

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment D-day0_1L	2.00	1.86	2.12	0.32	0.0255	0.0255	0.0280	No plants		
Treatment D-day0_2L	2.00	2.38			0.0255					
Treatment D-day0_3L	2.00	1.79			0.0255					
Treatment D-day3_1L	2.00	1.85	1.82	0.03	0.0726	0.0929	0.0301			
Treatment D-day3_2L	2.00	1.79			0.128					
Treatment D-day3_3L	2.00	1.84			0.0785					
Treatment D-day7_1L	2.00	1.07	1.04	0.07	0.375	0.377	0.045			
Treatment D-day7_2L	2.00	1.00			0.423					
Treatment D-day7_3L	2.00	1.14			0.334					
Treatment D-day14_1L	2.00	1.00	0.958	0.053	0.498	0.428	0.100			
Treatment D-day14_2L	2.00	0.921			0.357					
Treatment D-day14_3L	2.00	0.877			0.492					
Treatment D-day28_1L	2.00	0.533	0.553	0.029	0.0255	0.0255	0.0280			
Treatment D-day28_2L	2.00	0.573			0.0255					
Treatment D-day28_3L	2.00	0.515			0.0255					
Treatment D-day42_1L	2.00	0.151	0.143	0.011	0.0255	0.0255	0.0280			
Treatment D-day42_2L	2.00	0.135			0.0255					
Treatment D-day42_3L	2.00	0.132			0.0255					
Treatment D-day56_1L	2.00	0.00450	0.00450	0.00400	0.0255	0.0255	0.0280			
Treatment D-day56_2L	2.00	0.00450			0.0255					
Treatment D-day56_3L	2.00	0.00450			0.0255					

Appendix D-5 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water and plants in treatment E

Sample ID	Added TMX ($mg\ L^{-1}$)	TMX in water ($mg\ L^{-1}$)	Mean	STDEV	TMX in sediment ($mg\ kg^{-1}$)	Mean	STDEV	TMX in plants ($mg\ kg^{-1}$)	Mean	STDEV
Treatment E-day0_1L	2.00	1.01	1.02	0.02	No sediment			11.6	6.96	5.46
Treatment E-day0_2L	2.00	1.03						8.39		
Treatment E-day0_3L	2.00	1.01						0.926		
Treatment E-day28_1L	2.00	0.00450	0.00450	0.00400				0.851	0.901	0.043
Treatment E-day28_2L	2.00	0.00450						0.926		
Treatment E-day28_3L	2.00	0.00450						0.926		
Treatment E-day56_1L	2.00	0.00450	0.00450	0.00400				0.926	0.926	0.120
Treatment E-day56_2L	2.00	0.00450						0.926		
Treatment E-day56_3L	2.00	0.00450						0.926		

Appendix D-6 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water, sediment and plant in treatment F

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment F-day0_1L	2.00	1.52			0.0255			0.926		
Treatment F-day0_2L	2.00	1.69	1.60	0.25	0.0255	0.0255	0.0098	0.926	0.926	0.12
Treatment F-day0_3L	2.00	2.00			0.00856			0.926		
Treatment F-day3_1L	2.00	0.366			0.0169			0.425		
Treatment F-day3_2L	2.00	0.181	0.274	0.092	0.0133	0.0151	0.0063	0.656	0.540	0.115
Treatment F-day3_3L	2.00	0.282			0.0255			0.548		
Treatment F-day7_1L	2.00	0.00450			0.0255			0.926		
Treatment F-day7_2L	2.00	0.00450	0.00450	0.00400	0.0255	0.0255	0.0280	1.61	5.97	8.15
Treatment F-day7_3L	2.00	0.00450			0.0255			15.4		
Treatment F-day14_1L	2.00	0.00450			0.0128			0.926		
Treatment F-day14_2L	2.00	0.00450	0.00450	0.00400	0.0255	0.0191	0.0073	0.926	0.926	0.120
Treatment F-day14_3L	2.00	0.00450			0.0255			0.926		
Treatment F-day28_1L	2.00	0.00450			0.0255			0.926		
Treatment F-day28_2L	2.00	0.00450	0.00450	0.00400	0.0255	0.0255	0.0280	0.926	1.11	0.31
Treatment F-day28_3L	2.00	0.00450			0.0255			1.46		
Treatment F-day42_1L	2.00	0.00450			0.0255			1.04		
Treatment F-day42_2L	2.00	0.00450	0.00450	0.00400	0.0255	0.0255	0.0280	1.19	1.11	0.08
Treatment F-day42_3L	2.00	0.00450			0.0255			1.06		
Treatment F-day56_1L	2.00	0.00450			0.0255			0.698		
Treatment F-day56_2L	2.00	0.00450	0.00450	0.00400	0.0255	0.0255	0.0280	1.90	1.30	0.64
Treatment F-day56_3L	2.00	0.00450			0.0255			0.926		

Appendix D-8 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water in treatment A

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment A-day0_1D	2.00	2.10	2.05	0.05	No sediment			No plants		
Treatment A-day0_2D	2.00	2.06								
Treatment A-day0_3D	2.00	2.00								
Treatment A-day28_1D	2.00	2.10	2.08	0.04						
Treatment A-day28_2D	2.00	2.11								
Treatment A-day28_3D	2.00	2.03								
Treatment A-day56_1D	2.00	1.83	1.80	0.03						
Treatment A-day56_2D	2.00	1.80								
Treatment A-day56_3D	2.00	1.77								

Appendix D-9 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water in treatment B

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment B-day0_1L	2.00	1.95	2.06	0.09	No sediment			No plants		
Treatment B-day0_2L	2.00	2.09								
Treatment B-day0_3L	2.00	2.13								
Treatment B-day28_1L	2.00	2.02	2.04	0.02						
Treatment B-day28_2L	2.00	2.03								
Treatment B-day28_3L	2.00	2.07								
Treatment B-day56_1L	2.00	1.65	1.71	0.08						
Treatment B-day56_2L	2.00	1.80								
Treatment B-day56_3L	2.00	1.67								

Appendix D-10 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water, sediment and plants in treatment C

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment C-day0_1D	2.00	2.04	2.35	0.32	0.0275	0.0275	0.002	No plants		
Treatment C-day0_2D	2.00	2.69			0.0275					
Treatment C-day0_3D	2.00	2.31			0.0275					
Treatment C-day28_1D	2.00	1.06	1.06	0.03	1.48	1.39	0.39			
Treatment C-day28_2D	2.00	1.02			1.74					
Treatment C-day28_3D	2.00	1.09			0.962					
Treatment C-day56_1D	2.00	0.652	0.693	0.045	0.909	1.02	0.12			
Treatment C-day56_2D	2.00	0.686			1.14					
Treatment C-day56_3D	2.00	0.742			1.02					

Appendix D-11 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water and sediment in treatment D

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment D-day0_1L	2.00	1.24	1.71	0.55	0.0275	0.0275	0.002	No plants		
Treatment D-day0_2L	2.00	1.58			0.0275					
Treatment D-day0_3L	2.00	2.32			0.0275					
Treatment D-day3_1L	2.00	1.98	1.88	0.09	0.00683	0.00781	0.00132			
Treatment D-day3_2L	2.00	1.82			0.00931					
Treatment D-day3_3L	2.00	1.84			0.00729					
Treatment D-day7_1L	2.00	1.26	1.28	0.03	0.912	0.904	0.177			
Treatment D-day7_2L	2.00	1.28			1.08					
Treatment D-day7_3L	2.00	1.32			0.723					
Treatment D-day14_1L	2.00	1.40	1.33	0.07	0.0357	0.0363	0.0029			
Treatment D-day14_2L	2.00	1.30			0.0394					
Treatment D-day14_3L	2.00	1.28			0.0338					
Treatment D-day28_1L	2.00	1.02	1.07	0.05	0.0257	0.0271	0.0013			
Treatment D-day28_2L	2.00	1.08			0.0273					
Treatment D-day28_3L	2.00	1.11			0.0283					
Treatment D-day42_1L	2.00	0.893	0.922	0.025	0.0268	0.0305	0.0032			
Treatment D-day42_2L	2.00	0.937			0.0321					
Treatment D-day42_3L	2.00	0.935			0.0326					
Treatment D-day56_1L	2.00	0.746	0.754	0.038	0.0381	0.0470	0.0084			
Treatment D-day56_2L	2.00	0.722			0.0482					
Treatment D-day56_3L	2.00	0.796			0.0548					

Appendix D-12 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water and plants in treatment E

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment E-day0_1L	2.00	1.00	1.03	0.03	No sediment			0.926	0.773	0.264
Treatment E-day0_2L	2.00	1.03						0.468		
Treatment E-day0_3L	2.00	1.06						0.926		
Treatment E-day28_1L	2.00	0.833	0.925	0.113				14.8	25.1	15.3
Treatment E-day28_2L	2.00	1.05						17.8		
Treatment E-day28_3L	2.00	0.891						42.7		
Treatment E-day56_1L	2.00	0.208	0.464	0.224				9.58	18.5	7.7
Treatment E-day56_2L	2.00	0.558						22.8		
Treatment E-day56_3L	2.00	0.626						23.0		

Appendix D-13 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water, sediment and plants in treatment F

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment F-day0_1L	2.00	2.04	2.31	0.29	0.0275	0.0275	0.002	0.505	0.608	0.096
Treatment F-day0_2L	2.00	2.62			0.0275			0.697		
Treatment F-day0_3L	2.00	2.28			0.0275			0.622		
Treatment F-day3_1L	2.00	1.87	1.84	0.11	0.269	0.205	0.065	8.14	8.42	0.66
Treatment F-day3_2L	2.00	1.72			0.208			7.95		
Treatment F-day3_3L	2.00	1.92			0.139			9.18		
Treatment F-day7_1L)	2.00	0.989	1.08	0.11	0.601	0.597	0.021	9.05	6.35	4.70
Treatment F-day7_2L	2.00	1.04			0.615			9.07		
Treatment F-day7_3L	2.00	1.20			0.574			0.926		
Treatment F-day14_1L	2.00	1.12	1.07	0.05	1.55	1.39	0.29	14.7	15.7	2.7
Treatment F-day14_2L	2.00	1.07			1.57			18.8		
Treatment F-day14_3L	2.00	1.01			1.06			13.6		
Treatment F-day28_1L	2.00	0.778	0.720	0.053	1.04	0.951	0.106	15.1	14.1	2.2
Treatment F-day28_2L	2.00	0.672			0.833			11.5		
Treatment F-day28_3L	2.00	0.712			0.981			15.6		
Treatment F-day42_1L	2.00	0.372	0.355	0.027	0.049	0.041	0.012	3.23	7.40	7.68
Treatment F-day42_2L	2.00	0.324			0.0275			2.70		
Treatment F-day42_3L	2.00	0.367			0.0458			16.3		
Treatment F-day56_1L	2.00	0.0045	0.004	0.004	0.0286	0.0284	0.0008	11.9	12.2	7.7
Treatment F-day56_2L	2.00	0.0045			0.0290			20.1		

Treatment F-day56_3L	2.00	0.0045			0.0275			4.74		

Appendix D-14 Analysis of variance for pH of the water phase varying with treatment and time

Source of Variation	Degree of freedom	Sum of square	Mean of square	F	P
Treatments	7	10.1	1.44	6.15	<0.001
Time (days)	2	4.07	2.04	8.71	<0.001
Residual	56	13.1	0.234		
Total	65	27.3	0.42		

Appendix D-15 Multiple comparison (Tukey test) for pH of the water phase in each treatment to isolate the groups that differ from the others based on treatment

Comparison	Difference of Means	p	q	P	P<0.05
E vs. D	1.307	8	8.106	<0.001	Yes
E vs. C	1.161	8	7.203	<0.001	Yes
E vs. F	0.868	8	5.383	0.008	Yes
E vs. H	0.843	8	4.603	0.038	Yes
E vs. G	0.838	8	4.576	0.040	Yes
E vs. A	0.657	8	4.073	0.096	No
E vs. B	0.531	8	3.295	0.297	Do Not Test
B vs. D	0.776	8	4.811	0.026	Yes
B vs. C	0.630	8	3.908	0.126	No
B vs. F	0.337	8	2.088	0.816	Do Not Test
B vs. H	0.312	8	1.704	0.927	Do Not Test
B vs. G	0.307	8	1.677	0.933	Do Not Test

Note: A, B, C, D, E, F, G and H are name of treatments as described in Table 6-2.

Appendix D-15 (Continued) Multiple comparisons (Tukey test) for pH of the water phase in each treatment to isolate the groups that differ from the others based on treatment

Comparison	Difference of Means	p	q	P	P<0.05
B vs. A	0.126	8	0.779	0.999	Do Not Test
A vs. D	0.650	8	4.032	0.103	No
A vs. C	0.504	8	3.129	0.360	Do Not Test
A vs. F	0.211	8	1.310	0.982	Do Not Test
A vs. H	0.187	8	1.019	0.996	Do Not Test
A vs. G	0.182	8	0.992	0.997	Do Not Test
G vs. D	0.468	8	2.556	0.618	Do Not Test
G vs. C	0.323	8	1.762	0.914	Do Not Test
G vs. F	0.0294	8	0.161	1.000	Do Not Test
G vs. H	0.00500	8	0.0246	1.000	Do Not Test
H vs. D	0.463	8	2.529	0.630	Do Not Test
H vs. C	0.318	8	1.734	0.921	Do Not Test
H vs. F	0.0244	8	0.133	1.000	Do Not Test
F vs. D	0.439	8	2.723	0.540	Do Not Test
F vs. C	0.293	8	1.820	0.900	Do Not Test
C vs. D	0.146	8	0.903	0.998	Do Not Test

Appendix D-16 Multiple comparison (Tukey test) for pH in the water phase in each treatment to isolate the groups that differ from the others base on time

Comparison	Difference of means	p	q	P	P<0.05
0.000 vs. 28.000	0.598	3	5.419	0.001	Yes
0.000 vs. 56.000	0.0329	3	0.333	0.970	No
56.000 vs. 28.000	0.565	3	5.121	0.002	Yes

Appendices E: Pesticides residues in each compartment (water, sediment and plants) in the outdoor experiment, weather data during the experiment and statistical tests. (Chapter 7)

Appendix E-1 Daily weather data (mean from every hour for 24 hours); wind speed, air temperature, soil temperature, relative humidity and solar radiation during experiment from 9th August 2011 to 6th September 2011

Day	Wind speed (m/s)			Air temperature (^oC)			Soil temperature - 10 cm (^oC)			Relative humidity (%)			Solar radiation (kW/m^2)
	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Total
0	0.03	1.83	0.73	8.87	19.53	13.66	15.84	17.02	16.50	73.22	103.58	95.70	12.08
1	0.08	2.24	1.06	9.04	18.59	13.61	16.05	17.32	16.68	57.60	103.53	81.98	15.58
2	0.03	1.13	0.50	8.84	16.23	13.30	15.99	16.82	16.36	103.48	103.58	103.55	3.99
3	0.11	0.98	0.54	13.86	18.62	16.22	16.38	17.37	16.81	103.53	103.63	103.59	7.03
4	0.08	2.71	1.35	13.03	18.99	15.70	16.81	17.32	17.07	83.97	103.58	97.70	7.39
5	0.00	1.60	0.75	13.03	20.07	17.18	16.95	18.00	17.42	75.57	103.63	93.48	10.09
6	0.00	1.11	0.41	10.06	18.99	14.98	16.83	17.61	17.26	58.37	103.58	88.92	9.32
7	0.00	1.09	0.45	7.07	19.42	13.76	15.92	17.20	16.64	56.78	103.53	85.87	14.03
8	0.03	1.83	0.98	11.01	20.59	14.92	16.46	17.36	16.86	78.54	103.58	96.40	9.16
9	0.05	1.14	0.49	7.10	18.49	13.03	15.77	16.90	16.41	59.34	103.53	84.24	12.54
10	0.00	1.95	0.64	7.26	17.52	12.73	15.38	16.48	16.00	67.23	103.58	90.66	11.00
11	0.00	1.03	0.41	7.62	20.31	14.85	15.42	16.99	16.23	60.57	103.53	83.69	14.24
12	0.08	0.78	0.51	12.13	23.23	18.13	16.17	17.71	16.91	59.14	103.58	83.10	12.99
13	0.01	1.43	0.53	11.30	21.00	16.69	16.93	17.85	17.39	68.76	103.58	89.43	12.11

Note; Rainfall did not shown because the value was 0.00 mm during the experiment.

Appendix E-1 (Continued) Daily weather data (mean from every hour for 24 hours); wind speed, air temperature, soil temperature, relative humidity and solar radiation during experiment from 9th August 2011 to 6th September 2011

Day	Wind speed (m/s)			Air temperature (°C)			Soil temperature - 10 cm (°C)			Relative humidity (%)			Solar radiation (kW/m²)
	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Total
14	0.00	1.89	0.62	7.87	20.87	14.51	16.08	17.47	16.83	52.43	103.53	81.99	16.11
15	0.20	0.98	0.55	10.85	16.75	13.89	16.42	17.00	16.71	74.96	103.58	96.71	6.05
16	0.00	0.93	0.37	9.15	22.12	14.82	16.04	17.25	16.65	59.08	103.58	89.27	10.03
17	0.00	1.26	0.45	10.82	18.92	13.97	15.89	16.92	16.47	63.49	103.58	91.28	10.94
18	0.02	1.18	0.45	10.17	14.00	12.14	15.84	16.48	16.02	103.48	103.58	103.53	2.65
19	0.00	0.85	0.26	7.92	15.24	11.73	15.09	15.79	15.53	91.49	103.58	102.13	7.17
20	0.03	1.79	0.93	8.06	17.16	12.77	14.78	15.85	15.36	63.08	103.53	86.30	14.12
21	0.08	2.32	0.95	9.01	15.60	12.28	14.96	15.50	15.25	61.18	103.53	84.06	9.99
22	0.02	1.61	0.44	7.50	15.69	11.54	14.53	15.25	14.91	76.13	103.58	98.35	5.75
23	0.62	2.23	1.48	14.83	24.70	19.79	17.38	18.94	18.20	62.36	92.47	79.01	12.18
24	0.00	2.04	0.61	13.05	24.75	18.52	17.47	19.03	18.24	66.92	103.63	90.46	10.97
25	0.04	2.34	0.70	13.15	25.43	18.09	17.47	19.46	18.60	64.26	103.63	95.65	15.18
26	0.03	2.13	0.63	11.82	19.06	15.94	17.27	18.62	18.17	98.36	103.63	102.90	6.02
27	0.00	1.38	0.60	9.94	21.32	16.16	17.08	18.82	17.92	56.47	103.58	83.26	16.31
28	0.01	2.05	0.52	9.96	17.24	13.17	16.41	17.38	17.03	103.53	103.58	103.56	5.11
	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Total
	0.05	1.58	0.65	10.15	19.33	14.76	16.19	17.30	16.77	72.53	103.19	91.96	300.12

Note; Rainfall is not shown because the value was 0.00 mm during the experiment.

Appendix E-2 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water in treatment A

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment A-day0_1D	2.00	1.42	1.41	0.0105	No sediment			No plants		
Treatment A-day0_2D	2.00	1.42								
Treatment A-day0_3D	2.00	1.40								
Treatment A-day14_1D	2.00	1.14	1.12	0.0647						
Treatment A-day14_2D	2.00	1.18								
Treatment A-day14_3D	2.00	1.05								
Treatment A-day28_1D	2.00	1.01	1.00	0.0376						
Treatment A-day28_2D	2.00	1.04								
Treatment A-day28_3D	2.00	0.963								

Appendix E-3 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water in treatment B

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment B-day0_1L	2.00	1.35	1.37	0.0339	No sediment			No plants		
Treatment B-day0_2L	2.00	1.41								
Treatment B-day0_3L	2.00	1.35								
Treatment B-day14_1L	2.00	0.0700	0.143	0.0635						
Treatment B-day14_2L	2.00	0.180								
Treatment B-day14_3L	2.00	0.180								
Treatment B-day28_1L	2.00	0.0136	0.00752	0.00524						
Treatment B-day28_2L	2.00	0.00450								
Treatment B-day28_3L	2.00	0.00450								

Appendix E-4 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water, sediment in treatment C

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment C-day0_1L	2.00	1.35	1.39	0.0635	0.0150	0.0136	0.00363	No plants		
Treatment C-day0_2L	2.00	1.36			0.0163					
Treatment C-day0_3L	2.00	1.46			0.00946					
Treatment C-day14_1L	2.00	0.572	0.582	0.0236	0.228	0.155	0.0982			
Treatment C-day14_2L	2.00	0.609			0.195					
Treatment C-day14_3L	2.00	0.565			0.0436					
Treatment C-day28_1L	2.00	0.209	0.214	0.0140	0.0163	0.0212	0.00425			
Treatment C-day28_2L	2.00	0.230			0.0237					
Treatment C-day28_3L	2.00	0.203			0.0236					

Appendix E-5 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water and sediment in treatment D

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment D-day0_1L	2.00	1.36	1.38	0.0192	0.00313	0.00261	0.000694	No plants		
Treatment D-day0_2L	2.00	1.39			0.00183					
Treatment D-day0_3L	2.00	1.39			0.00289					
Treatment D-day7_1L	2.00	0.179	0.215	0.127	0.00828	0.0106	0.00374			
Treatment D-day7_2L	2.00	0.356			0.0149					
Treatment D-day7_3L	2.00	0.109			0.00863					
Treatment D-day14_1L	2.00	0.0045	0.00450	0.00400	0.00101	0.00191	0.000846			
Treatment D-day14_2L	2.00	0.0045			0.00270					
Treatment D-day14_3L	2.00	0.0045			0.00201					
Treatment D-day28_1L	2.00	0.0045	0.00450	0.00400	0.0255	0.0182	0.0126			
Treatment D-day28_2L	2.00	0.0045			0.0255					
Treatment D-day28_3L	2.00	0.00450			0.00371					

Appendix E-6 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water and plants in treatment E

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment E-day0_1L	2.00	0.599	0.299	0.297	No sediment			0.926	0.926	0.120
Treatment E-day0_2L	2.00	0.294						0.926		
Treatment E-day0_3L	2.00	0.0045						0.926		
Treatment E-day1_1L	2.00	0.203	0.0706	0.115				0.00206	0.00177	0.000979
Treatment E-day1_2L	2.00	0.00450						0.00258		
Treatment E-day1_3L	2.00	0.00450						0.000682		
Treatment E-day3_1D	2.00	0.00450	0.00450	0.00400				0.926	0.926	0.120
Treatment E-day3_2D	2.00	0.00450						0.926		
Treatment E-day3_3D	2.00	0.00450						0.926		
Treatment E-day5_1D	2.00	0.00450	0.00450	0.00400				0.00250	0.310	0.534
Treatment E-day5_2D	2.00	0.00450						0.000593		
Treatment E-day5_3D	2.00	0.00450						0.926		
Treatment E-day7_1L	2.00	0.00450	0.00450	0.00400				0.926	0.926	0.120
Treatment E-day7_2L	2.00	0.00450						0.926		
Treatment E-day7_3L	2.00	0.00450						0.926		

Appendix E-7 Summary mean and standard deviation (STDEV) of thiamethoxam (TMX) residues in water, sediment and plants in treatment F

Sample ID	Added TMX (mg L^{-1})	TMX in water (mg L^{-1})	Mean	STDEV	TMX in sediment (mg kg^{-1})	Mean	STDEV	TMX in plants (mg kg^{-1})	Mean	STDEV
Treatment F-day0_1L	2.00	0.395	0.331	0.0766	0.0019	0.00360	0.00377	0.926	0.618	0.534
Treatment F-day0_2L	2.00	0.246			0.0079			0.00125		
Treatment F-day0_3L	2.00	0.352			0.0010			0.926		
Treatment F-day1_1L	2.00	0.165	0.361	0.186	0.0072	0.0231	0.0219	0.00116	0.309	0.534
Treatment F-day1_2L	2.00	0.534			0.0481			0.00105		
Treatment F-day1_3L	2.00	0.383			0.0141			0.926		
Treatment F-day3_1L)	2.00	0.201	0.110	0.095	0.0164	0.0119	0.00695	0.000841	0.000617	0.000325
Treatment F-day3_2L	2.00	0.119			0.0153			0.000766		
Treatment F-day3_3L	2.00	0.0111			0.0039			0.000244		
Treatment F-day5_1L	2.00	0.00450	0.00450	0.00400	0.0009	0.00155	0.00102	0.926	0.617	0.535
Treatment F-day5_2L	2.00	0.00450			0.0027			0.000100		
Treatment F-day5_3L	2.00	0.00450			0.0010			0.926		
Treatment F-day7_1L	2.00	0.00450	0.00450	0.00400	0.0023	0.0177	0.0280	5.47E-05	0.309	0.535
Treatment F-day7_2L	2.00	0.00450			0.0008			7.61E-05		
Treatment F-day7_3L	2.00	0.00450			0.0500			0.926		

Appendix E-8 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water in treatment A

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment A-day0_1D	2.00	1.56	1.52	0.04	No sediment			No plants		
Treatment A-day0_2D	2.00	1.50								
Treatment A-day0_3D	2.00	1.49								
Treatment A-day14_1D	2.00	1.43	1.41	0.05						
Treatment A-day14_2D	2.00	1.45								
Treatment A-day14_3D	2.00	1.35								
Treatment A-day28_1D	2.00	1.46	1.44	0.08						
Treatment A-day28_2D	2.00	1.52								
Treatment A-day28_3D	2.00	1.35								

Appendix E-9 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water in treatment B

Sample ID	Added TMX (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment B-day0_1L	2.00	1.44	1.46	0.03	No sediment			No plants		
Treatment B-day0_2L	2.00	1.50								
Treatment B-day0_3L	2.00	1.46								
Treatment B-day14_1L	2.00	1.06	1.15	0.09						
Treatment B-day14_2L	2.00	1.14								
Treatment B-day14_3L	2.00	1.24								
Treatment B-day28_1L	2.00	1.07	1.12	0.09						
Treatment B-day28_2L	2.00	1.06								
Treatment B-day28_3L	2.00	1.22								

Appendix E-10 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water and sediment in treatment C

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment C-day0_1L	2.00	1.40	1.45	0.08	0.0106	0.0164	0.010	No plants		
Treatment C-day0_2L	2.00	1.41			0.0112					
Treatment C-day0_3L	2.00	1.55			0.0275					
Treatment C-day14_1L	2.00	0.745	0.74	0.03	0.365	0.405	0.054			
Treatment C-day14_2L	2.00	0.764			0.385					
Treatment C-day14_3L	2.00	0.698			0.466					
Treatment C-day28_1L	2.00	0.299	0.32	0.03	0.250	0.228	0.028			
Treatment C-day28_2L	2.00	0.350			0.238					
Treatment C-day28_3L	2.00	0.297			0.196					

Appendix E-11 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water and sediment in treatment D

Sample ID	Added MET ($mg\ L^{-1}$)	MET in water ($mg\ L^{-1}$)	Mean	STDEV	MET in sediment ($mg\ kg^{-1}$)	Mean	STDEV	MET in plants ($mg\ kg^{-1}$)	Mean	STDEV
Treatment D-day0_1L	2.00	1.51	1.54	0.03	0.0436	0.0338	0.009	No plants		
Treatment D-day0_2L	2.00	1.56			0.0275					
Treatment D-day0_3L	2.00	1.56			0.0303					
Treatment D-day7_1L	2.00	0.857	0.831	0.03	0.212	0.186	0.090			
Treatment D-day7_2L	2.00	0.834			0.259					
Treatment D-day7_3L	2.00	0.801			0.0857					
Treatment D-day14_1L	2.00	0.476	0.508	0.04	0.171	0.201	0.047			
Treatment D-day14_2L	2.00	0.492			0.255					
Treatment D-day14_3L	2.00	0.556			0.176					
Treatment D-day28_1L	2.00	0.125	0.130	0.01	0.0719	0.0688	0.004			
Treatment D-day28_2L	2.00	0.128			0.0647					
Treatment D-day28_3L	2.00	0.137			0.0698					

Appendix E-12 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water and plants in treatment E

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment E-day0_1L	2.00	1.61	1.47	0.12	No sediment			46.1	43.2	2.7
Treatment E-day0_2L	2.00	1.42						40.8		
Treatment E-day0_3L	2.00	1.38						42.8		
Treatment E-day1_1L	2.00	1.40	0.47	0.81				43.9	47.6	8.0
Treatment E-day1_2L	2.00	0.00650						56.8		
Treatment E-day1_3L	2.00	0.00650						42.0		
Treatment E-day3_1D	2.00	0.00650	0.532	0.456				0.926	3.17	3.88
Treatment E-day3_2D	2.00	0.782						0.926		
Treatment E-day3_3D	2.00	0.809						7.65		
Treatment E-day5_1D	2.00	0.627	0.657	0.042				33.1	16.3	16.1
Treatment E-day5_2D	2.00	0.706						14.8		
Treatment E-day5_3D	2.00	0.640						0.926		
Treatment E-day7_1L	2.00	0.578	0.558	0.059				0.926	3.9	5.1
Treatment E-day7_2L	2.00	0.492						0.926		
Treatment E-day7_3L	2.00	0.605						9.8		

Appendix E-13 Summary mean and standard deviation (STDEV) of metalaxyl-M (MET) residues in water, sediment and plants in treatment F

Sample ID	Added MET (mg L^{-1})	MET in water (mg L^{-1})	Mean	STDEV	MET in sediment (mg kg^{-1})	Mean	STDEV	MET in plants (mg kg^{-1})	Mean	STDEV
Treatment F-day0_1L	2.00	1.46	1.46	0.05	0.0400	0.0316	0.0079	16.8	21.6	9.6
Treatment F-day0_2L	2.00	1.50			0.0245			32.7		
Treatment F-day0_3L	2.00	1.41			0.0302			15.3		
Treatment F-day1_1L	2.00	1.14	1.20	0.05	0.0302	0.056	0.040	21.2	22.6	3.8
Treatment F-day1_2L	2.00	1.22			0.0351			26.8		
Treatment F-day1_3L	2.00	1.22			0.102			19.6		
Treatment F-day3_1L)	2.00	1.02	1.00	0.05	0.1024	0.0666	0.0328	20.9	26.3	4.8
Treatment F-day3_2L	2.00	1.04			0.0380			30.3		
Treatment F-day3_3L	2.00	0.941			0.0595			27.6		
Treatment F-day5_1L	2.00	0.593	0.641	0.091	0.0595	0.137	0.088	20.8	17.7	4.5
Treatment F-day5_2L	2.00	0.745			0.118			19.7		
Treatment F-day5_3L	2.00	0.584			0.233			12.5		
Treatment F-day7_1L	2.00	0.513	0.512	0.036	0.233	0.120	0.098	8.02	10.5	3.9
Treatment F-day7_2L	2.00	0.548			0.0627			15.0		
Treatment F-day7_3L	2.00	0.476			0.0634			8.50		

Appendix E-14 Analysis of variance of pH in water phase varying treatments and time

Source of Variation	Degree of freedom	Sum of squares	Mean square	F	P
Treatment	7	29.29	4.18	91.2	<0.001
Time (days)	6	4.77	0.795	17.3	<0.001
Residual	67	3.07	0.0459		
Total	80	65.3	0.816		

Appendix E-15 Multiple comparison (Tukey test) pH of water phase in each treatment to isolate the group to groups that differ from the others for factor: treatment

Comparison	Difference of means	p	q	P	P<0.05
E vs. G	2.38	8	28.4	<0.001	Yes
E vs. C	2.23	8	29.6	<0.001	Yes
E vs. B	2.15	8	28.5	<0.001	Yes
E vs. A	2.09	8	27.8	<0.001	Yes
E vs. D	1.06	8	15.9	<0.001	Yes
E vs. H	0.892	8	10.6	<0.001	Yes
E vs. F	0.541	8	8.93	<0.001	Yes
F vs. G	1.84	8	21.9	<0.001	Yes
F vs. C	1.69	8	22.5	<0.001	Yes
F vs. B	1.61	8	21.4	<0.001	Yes

Note: A, B, C, D, E, F, G and H are name of treatments as described in Table 7-2.

Appendix E-15 (Continued) Multiple comparisons (Tukey test) pH in water phase in each treatment to isolate the group to groups that differ from the others for factor: treatment

Comparison	Difference of means	p	q	P	P<0.05
F vs. A	1.55	8	20.6	<0.001	Yes
F vs. D	0.523	8	7.840	<0.001	Yes
F vs. H	0.351	8	4.19	0.076	No
H vs. G	1.48	8	14.6	<0.001	Yes
H vs. C	1.34	8	14.1	<0.001	Yes
H vs. B	1.26	8	13.3	<0.001	Yes
H vs. A	1.20	8	12.6	<0.001	Yes
H vs. D	0.172	8	1.95	0.865	No
D vs. G	1.31	8	14.9	<0.001	Yes
D vs. C	1.17	8	14.5	<0.001	Yes
D vs. B	1.09	8	13.5	<0.001	Yes
D vs. A	1.03	8	12.8	<0.001	Yes
A vs. G	0.283	8	2.98	0.421	No
A vs. C	0.141	8	1.61	0.946	Do Not Test
A vs. B	0.0589	8	0.671	1.000	Do Not Test
B vs. G	0.224	8	2.36	0.707	Do Not Test
B vs. C	0.0822	8	0.937	0.998	Do Not Test
C vs. G	0.142	8	1.50	0.963	Do Not Test

Note: A, B, C, D, E, F, G and H are name of treatments as described in Table 7-2.

Appendix E-16 Multiple comparison (Tukey test) pH in water phase in each treatment to isolate the group to groups that differ from the others for factor: time

Comparison	Difference of means	p	q	P	P<0.05
0.000 vs. 28.000	0.598	3	5.419	0.001	Yes
0.000 vs. 56.000	0.0329	3	0.333	0.970	No
56.000 vs. 28.000	0.565	3	5.121	0.002	Yes

Appendix E-17 Input parameters for pesticide characteristics for the TOXSWA model

Data category	parameter	units	Values for thiamethoxam	Source of data	Value for metalaxyl-M	Source of data
General	Molar mass	g mol^{-1}	291.71	Pesticide database	279.33	Pesticide database
	Saturated vapour pressure	Pa	$6.60x10^{-9}$	Pesticide database	0.0033	Pesticide database
	Molar enthalpy of vaporization	J mol^{-1}	95000	Model user's manual	95000	Model user's manual
	Solubility in water	mg L^{-1}	4100	Pesticide database	26000	Pesticide database
	Molar enthalpy of dissolution	J mol^{-1}	27000	Model user's manual	27000	Model user's manual
	Diffusion coefficient in water	M^2 d^{-1}	40	Model user's manual	40	Model user's manual
Transformation	- Half-life in water	Days	0.73	Corrected with hydrolysis and photolysis	10.7	Corrected with hydrolysis and photolysis
	- Half-life in sediment at 20^oC	Days	27.7	Laboratory data (Chapter 4)	8.20	Laboratory data (Chapter 4)
	-Activation energy	J mol^{-1}	54000	Model's user manual	54000	Model's user manual

Appendix E-17 (Continued) Input parameter for pesticide characteristics for the TOXSWA model

Data category	parameter	units	Values for thiamethoxam	Source of data	Value for metalaxyl -M	Source of data
Sorption	**Suspended solids**					
	-Organic matter sorption coefficient (K_{om})	L kg^{-1}	0	Give value 0 becasue no suspended solid	0	Give value 0 because no suspended solid
	- Freundlich exponent	No unit	0.93	Laboratory data (Section 3.2)	0.74	Laboratory data (Section 3.2)
	- Reference concentration in liquid phase	mg L^{-1}	2	Applied concentration	2	Applied concentration
	Sediment					
	- K_{om}	L kg^{-1}	18.95	Calculate from K_{oc} (Section 3.2))	21.3	Calculate from K_{oc} (Section 3.2))
	- Freundlich exponent	No unit	0.93	Laboratory data (Section 3.2)	0.74	Laboratory data (Section 3.2)
	- Reference concentration in liquid phase	mg L^{-1}	2.0	Added concentration	2.0	Added concentration
	Macrophyte					
	- Sorption coefficient	L kg^{-1}	3.49	Calculated from laboratory data	12.4	Calculated from laboratory data

Appendix E-18 Input parameters governing water and sediment characteristics and hydrology for the TOXSWA model

Data category	Parameters	Units	Values for thiamethoxam	Source of data	Value for metalaxyl-M	Source of data
Water-sediment systems	**Water layer**					
	-Water depth	m	0.06	Laboratory data	0.06	Laboratory data
	-Length of water layer	m	0.06	Laboratory data	0.06	Laboratory data
	-Bottom width	m	0.10	Laboratory data	0.10	Laboratory data
	Side slope	m	0.00001	Set minimum	0.00001	Set minimum
	Macrophyte					
	-dry weight	(g m^{-2})	44.3	Laboratory data (Chapter 5)	44.3	Laboratory data (Chapter 5)
	-Depth def. Perimeter	(hor/ver)	0.06	Laboratory data	0.06	Laboratory data
Water-sediment systems	**Suspended solids**					
	-Concentration suspended solids	mg L^{-1}	1	Set minimum	1	Set minimum
	-Mass ratio organic matter	No unit	0.086	Calculated form % organic carbon	0.086	Calculated from % organic carbon

Appendix E-18 (Continued) Input parameters governing water and sediment characteristics and hydrology for the TOXSWA model

Data category	Parameters	Units	Values for thiamethoxam	Source of data	Value for metalaxyl-M	Source of data
Water-sediment systems	**Sediment segment** -Thickness	m	0.03	Laboratory data	0.03	Laboratory data
	-Segment	No unit	10	Selected by user	10.0	selected by user
Hydrology	-Flow velocity	$m\ d^{-1}$	0	Estimated from laboratory data	0	Estimated from laboratory data
	-Water depth water body	m	0.06	Laboratory data	0.06	Laboratory data
	Temperature in water and sediment	^{o}C	14.9	Average air temperature under field condition for treatment F	14.9	Average air temperature under field condition for treatment F
	-Dispersion coefficient in water	$M^2\ d^{-1}$	20	Model's user manual	20	Model's user manual
	-Dispersion length in sediment	m	0.1	Model's user manual	0.1	Model's user manual

Appendix E-18 (Continued) Input parameters governing water and sediment characteristics and hydrology for the TOXSWA model

Data category	Parameters	Units	Values for thiamethoxam	Source of data	Value for metalaxyl-M	Source of data
Hydrology	**Upward seepage and concentration pesticide in incoming water**					
	-Seepage	mm d^{-1}	0	Laboratory data	0	Laboratory data
Simulation	-Concentration	mg L^{-1}	0	Laboratory data	0	Laboratory data
	-calculation time step	s	600	Default value	600	Default value
	Output time					
	-time interval of output	days	0.5	Default value	0.5	Default value