CRANFIELD UNIVERSITY

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Evaluating the Potential of Constructed Wetlands to Mitigate Pesticide Runoff from Agricultural Land to Surface Waters

School of Water, Energy and Environment

PhD

Academic Year: 2016 - 2017

Supervisor: Dr Mick Whelan, Dr Raffaella Villa and Prof Bruce Jefferson

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This thesis is submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Abstract

Pesticides make important contributions to modern agriculture. However, diffuse transfers of pesticide from agricultural land to surface water can lead to significant compliance failures in drinking water supplies under the EU Drinking Water Directive. Article 7 of the Water Framework Directive promotes a prevention-led approach in drinking water supply catchments which is based on a range of catchment management solutions to mitigate diffuse pollution. This includes non-structural interventions, such as modifying crop rotations and changing the timing and amount of pesticide applied and structural measures, such designating buffer and no-spray zones and the construction of attenuation ponds and wetlands. Although the performance of constructed wetlands for diffuse-source nutrients is now well understood, there is currently little in the literature on the behaviour of pesticides in these systems – particularly under transient conditions typical of storm events. One of the simplest and cheapest constructed wetland designs has a free-water-surface. Understanding the performance of these systems is particularly important because they are most likely to be implemented. The primary aim of this project was, therefore, to improve understanding of the processes affecting pesticide fate and transport in free-surface constructed wetlands in order to assess their utility as attenuation features.

The study focused on six pesticides: metaldehyde, quinmerac, carbetamide, metazachlor, propyzamide and pendimethalin. Metaldehyde has been reported as the biggest pesticide challenge currently facing the UK water industry.

Two free-surface constructed wetland systems (the South and North Wetlands) situated at Hope Farm in Knapwell (Cambridgeshire, UK) were monitored over two winter field seasons. Discharge was measured at control structures (v-notch weirs and Venturi flumes) installed at the inflow and outflow of each feature (using a combination of pressure transducers and ultrasonic sensors) and pesticide concentrations were determined in water samples collected typically every eight hours using automatic water samplers. Concentrations were measured using direct injection liquid chromatography coupled with tandem quadrupole mass spectrometry (LC-MS-MS). A multi-component method was developed to allow

high rates of sample throughput with minimal preparation. The LOQs obtained ranged from 0.2 to 1.0 µg L^{-1}, which is acceptable for detecting concentrations in natural water samples in this project. After autumn wet-up, discharge response to rainfall was flashy in both wetland catchments. Pesticide concentrations typically increased rapidly in the first significant post-application storm event and then decreased during hydrograph recession. Concentrations measured in the inflow and outflow of both wetland systems were often very similar, suggesting little attenuation for the pesticides monitored – particularly during storm events when both concentrations and loads increased but when retention times decreased. The main explanation for poor performance was the very short hydraulic residence time of these systems (determined using pulse-injection dye tracing exercises employing rhodamine WT). The solute residence time estimated during hydrographs was typically ~32 minutes, giving little time for pesticide sorption to sediment or vegetation, degradation or plant uptake. In the North Wetland, which is bunded at the outflow, discharge is intermittent in the autumn, immediately following post-harvest pesticide applications. This means that static periods exist with no inlet and outlet flows, during which some pesticide losses were observed (approximately 12% for metaldehyde and 20% for metazachlor). This suggests that these systems may be of some value in reducing fluxes and concentration for limited periods. During the subsequent winter period, however, when water levels in the wetland over-topped the outflow pipe, residence times were short and fluxes in the outflow were similar to those in the inflow (i.e. negligible removal was observed).

A set of degradation and sorption experiments were conducted in the laboratory to investigate potential mechanisms of pesticide attenuation. The sorption experiments were based on the OECD test 106 guidelines. Results showed a linear isotherm for sorption and desorption for all individual pesticides ($R^2 > 0.97$). They suggested that the apparent affinity of the pesticides evaluated for organic matter in the Hope Farm wetlands was significantly lower than that reported previously in soils for metaldehyde and carbetamide, was similar for quinmerac and propyzamide and slightly higher for metazachlor. Sorption experiments conducted using a mixture of pesticides in wetland sediment showed that the

presence of other compounds can influence the sorption capacity of the sediment.

The degradation studies looked at water-sediment systems, following the OECD 308 test guidelines. A short “pseudo lag phase” of approximately seven days was apparent in many of the experiments, in which the rate of concentration change was lower than the rate observed thereafter. This is a commonly reported phenomenon in laboratory degradation studies which can be caused by slow adaptation of degrading microorganisms. Interestingly, this phenomenon does not appear to have been apparent in the North Wetland under static conditions. This may be due to the development of a competent microbial community in this system as a consequence of repeated exposure. Rate constants were explicitly hypothesised to be inversely proportional to water depth because the majority of the degrading microbes are assumed to inhabit the sediment in fixed biofilms (i.e. freely suspended cells and cells associated with suspended solids are relatively unimportant as degraders). The water volume to sediment surface area (i.e. the water depth) is, therefore, expected to control the concentration change in the water column. In the outdoor mesocosms, fitted rate constants were higher in treatments with 20cm water depth than when water depth was 40cm, suggesting that the depth control hypothesis may have some validity. When the depth was 10cm, factors such as sediment-water exchanges (owing to the particularly low water volume to sediment mass ratio) may have confounded the depth effect.

Overall, the field and laboratory data reported here suggest that small free-surface wetland features may be relatively ineffective at reducing pesticide concentrations and loads, unless the catchment size is small relative to the wetland dimensions. This means that a large number of such features would need to be constructed to make an appreciable difference at the catchment scale.

Keywords:

Pesticide pollution; free-water surface constructed wetlands; sorption; monitoring; degradation;

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List of Abbreviations

DAI	Direct Aqueous Injection
DEFRA	Department for Environment, Food and Rural Affairs
DEM	Digital Elevation Model
DrWPA	Drinking Water Protected Area
DWD	Drinking Water Directive
DWI	Drinking Water Inspectorate
DT_{50}	Degradation half-life
EA	Environment Agency
EFSA	European Food Safety Authority
EPA	Environmental Protected Agency
EU	European Union
FAO	Food and Agriculture Organization Mobility
FOCUS	Forum of the Co-ordination of Pesticide Fate Models and their Use
FWS CW	Free-Water Surface Constructed Wetland
HRT	Hydraulic Residence Time
K_d	Adsorption-desorption distribution coefficient
K_{oc}	Organic carbon-water partition coefficient
K_{ow}	Octanol-water partition coefficient
LC-MS/MS	Liquid chromatography mass spectrometry
LOD	

LOQ	Limit of Detection
OECD	Limit of Quantification
PPDB	Organisation for Economic Co-operation and Development
RSPB	Pesticide Properties Database
SPE	Royal Society for the Protection of Birds
WFD	Solid phase Extraction
VFS	Water Framework Directive
	Vegetated Filter Strips

List of Publications and Presentations

Publications

Ramos, A.M., Whelan, M.J., Cosgrove, S., Villa, R., Jefferson, B., Campo, P., Jarvis, P., Guymer, I. (2017). A multi-component method to determine pesticides in surface water by liquid-chromatography tandem quadrupole mass spectrometry. *Water and Environment Journal v3*. 1-8 Published

Presentations

- Ramos, A.M. *Evaluation of free-water surface constructed wetlands for mitigating pesticide transfers from agricultural land to surface waters.* **WETPOL 2015 International Symposium on Wetland Pollutant Dynamics and Control and the Annual Conference of the Constructed Wetland Association, York, 13-18th September, 2015;**

  Oral presentation;

  Poster presentation (runner up);

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  Oral presentation;

  Poster presentation;

1 . Introduction

1.1 The context of the thesis

A wide range of pesticides is used in modern agriculture to enhance yield and quality. Most pesticides are synthetic organic compounds which have specific activity against a pest (weed, insect, fungus or mollusc). Despite their obvious agricultural utility, many pesticides can be transferred from land to ground and surface waters where they can create problems for the ecology of the receiving water body or for compliance with drinking water quality regulations if the water is abstracted for public supply. Such legal compliance challenges may or may not be associated with risks to human health.

1.1.1 Routes of pesticide transfer from land to water

Pesticides can contaminate surface waters *via* point sources at specific locations such as accidental spills, farmyard runoff or sewage treatment plants (herbicides are widely employed in urban areas for weed control and these can be washed off hard surfaces and into surface water drains which are directed to sewage treatment plants in areas with combined sewers). They can also enter surface waters *via* diffuse-sources - generated by a variety of different activities across the landscape with no specific point of discharge (Destandau *et al.,* 2013). Diffuse-source pollution of pesticides used in agriculture can occur to surface and ground waters *via* a range of pathways. For surface waters the main pathways are overland flow (Brown and Hollis, 1996; Williams *et al.,* 1996), leaching to field drains or lateral through flow, drain flow in artificial field drains (Tediosi *et al.,* 2012) and spray drift (Felsot *et al.,* 2011).

Surface Runoff

Surface runoff or overland flow occurs either when the rainfall intensity is greater than the infiltration rate of the soil (Rainfall > Soil Infiltration Rate) or when the soil is saturated (saturation excess overland flow) (Ward and Robinson, 2001). If the overland flow is initiated and pesticides are present in the pore water close to the soil surface or sorbed to particles at the surface, there is the potential for them to be transported downslope towards surface waters (Gregoire *et al.,* 2009; Pullan *et al.,* 2016). The higher the soil water content, the higher is the likelihood of surface runoff (Boithias *et al.*, 2014).

Brown and Hollis (1996) measured significant concentrations (22, 28 and 2.5 µg L^{-1}, respectively) of alachlor, atrazine and pendimethalin concentrations in surface runoff samples during in the first event after application in a study in Warwickshire (UK). Williams *et al.,* (1996) also reported high pesticide (trifluralin) concentrations in surface runoff (at 15, 20 and 86 µg L^{-1} at different locations in the first runoff event which occurred 3 days after application) in the Rosemaund catchment in Herefordshire.

Pesticide losses in the dissolved form via runoff water often tend to be higher than those occurring sorbed to soil particles, since the runoff water volume is always higher than the number of eroded particles (Muller *et al.,* 2002). Pesticides with an organic-carbon partition coefficient (K_{oc}) higher than 1000 L kg^{-1} (*e.g.* pendimethalin) tend to be more strongly sorbed to soil particles and here, particle-associated losses can be the most important loss pathway (Reichenberger *et al.,* 2007). Pesticides with intermediate sorption have a higher tendency to be lost with surface runoff than weakly sorbing compounds because the latter tend to be more easily leached away from the soil surface by infiltration (Gevao *et al.,* 2000).

Leaching and Artificial field drains

Leaching is the movement of water downwards through the soil. If pesticides are present in the soil, as the water percolates downward through the soil profile, pesticides in the soil can dissolve in the water and move downward with the percolating water (Jarvis, 2016). The main factors affecting the transfer of pesticides into surface waters via artificial drain flows are: soil (texture and structure), drainage system (drain depth and spacing), pesticide properties (sorption, degradation and volatility), weather (temperature, rainfall), application rate and season (spring, summer or autumn) (Gregoire *et al.,* 2009; Stuart *et al.,* 2012b).

In the UK, approximately 70% of arable land is drained. The purpose of installing artificial field drains is to prevent topsoil saturation by removing the water excess from the soil (Pullan *et al.,* 2016; Reichenberger *et al.,* 2007). The downward movement of the water with pesticides can reach artificial field drains, which have been shown to be a major pathway for pesticide transfer from land to surface water in the UK. Tediosi *et al.,* (2012) measured drain flow concentrations from a heavy clay soil in Upper Cherwell catchment in the UK and reported peak propyzamide concentrations of 56 µg L^{-1} and peak carbetamide concentrations of 694 µg L^{-1}. Both herbicides were transported rapidly to the drain outlet in the first storm event after application, with peak concentrations occurring approximately coincidentally with the hydrograph peak (the graph of discharge over time), where carbetamide (K_{oc} = 89 L kg^{-1}) leached more rapidly than propyzamide (K_{oc} = 840 L kg^{-1}). Brown and van Beinum (2009) reviewed 23 field drainage experiments across Europe. The authors showed the maximum concentration of pesticide in drain flow and a seasonal loss of pesticide to drains were significantly related to the strength of pesticide sorption to the soil, the half-life of the pesticide in soil, the interval between applications, the first drain flow and the clay content of the soil. Pesticide concentration was found to be higher in the first drain flow peak after pesticide application. (Brown and van Beinum, 2009; Evans, 2009; Sinclair *et al.,* 2010; Tediosi *et al.,* 2012).

1.1.2 Pesticide pollution and drinking water resources

In the European Union (EU), the quality of surface and ground waters is regulated mainly by the Water Framework Directive (WFD: EC, 2000) which aims to achieve “good ecological status” (Dolan *et al.,* 2012; Dolan *et al.,* 2013). The quality of drinking water at the point of supply is regulated by the European Drinking Water Directive (DWD) (Figure 1.1). The objective of the DWD is to protect the health of all citizens in the EU by making sure drinking water is clean and safe to consume. This is achieved by requiring water to meet standards for a total of 48 parameters that must be monitored and tested regularly (Dolan *et al.,* 2012; Dolan *et al.,* 2013). These include bacteria, nitrates, metals and pesticides. The DWD sets a maximum admissible concentration in drinking water at the point of supply for any individual pesticide (including metabolites) of 0.1 µg L^{-1} (except for 0.03 µg L^{-1} for aldrin, dieldrin, heptachlor and heptachlor epoxide). In addition, the total concentration of all pesticides should not exceed 0.5 µg L^{-1}. Both of these standards (0.1 and 0,5 µg L^{-1}) were based on a philosophy adopted in the 1980's that pesticides should not be present in drinking water regardless of the actual risks posed. This was due to uncertainties about the toxicological impacts of pesticides on human health at the time the regulations were first drawn up. The 0.1 µg L^{-1} limit was, therefore, set as a surrogate zero because it was the limit of detection of most instruments during that period (Dolan *et al.,* 2012; Dolan *et al.,* 2013). This approach can be thought of as "hazard based" rather than "risk based". In hazard based regulation, exposure (e.g. the amount of chemical ingested) is not compared with an effect threshold (the level of chemical ingestion which results in an adverse effect). Adverse effect thresholds are usually derived from standard tests on metabolism, toxicity, carcinogenicity, genotoxicity, and also irritancy trials – often using rats as a model mammal (Magnusson *et al.,* 2013; Wohlfahrt *et al.,* 2010). In risk based schemes, there is always an assessment of the level of exposure required to cause harm. Hazard based schemes are often considered to be conservative relative to those using risk (i.e. they offer a higher level of protection to the target organism – in this case, people). However, risk assessment of pesticide impact on human health can be challenging due to variability and uncertainty in the duration and level of exposure, pesticide chemistry and modes of action and the large range of compounds used on crops (and hence the potential for mixtures to be present). In addition, it is complicated by the combined exposure to humans from both food and water. In general, pesticide ingestion via the consumption of food containing residues greatly exceeds that from drinking contaminated water at concentrations around 0.1 µg L^{-1} (Li *et al.,* 2018).

In addition to their potential negative effects on human health, pesticides can pose risks to the environment by contamination of water, sediment and air. Pesticide residues can have toxic effects on non-target organisms. The adverse effects of pesticide on the environment depend on interactions between their physicochemical properties (e.g. vapour pressure, stability, solubility, pKa of the pesticide, partition coefficients and soil persistence), soil factors (e.g. pH, organic components, inorganic surfaces, moisture content and the composition of the soil microflora and fauna), and the plant species present and meteorological variations. Soil properties and weather conditions can be highly variable from site to site and from year to year, so the results from field studies on the fate and behaviour of pesticides are specific for one particular location and season. Although the agricultural areas/fields are the primary recipient of pesticides, water bodies that are adjacent to agricultural areas are usually the ultimate recipient for pesticide residues (Warren *et al.,* 2003; Stuart *et al.,* 2011)

Water treatment companies are responsible for supplying potable water in compliance with the DWD. In the UK (England and Wales), compliance is regulated by the Drinking Water Inspectorate (DWI) (Dolan *et al.,* 2012; Dolan *et al.,* 2013). The DWD and the WFD intersect in river catchments used for water supply. Article 7 of the WFD deals specifically with water bodies used for the abstraction of drinking waters, which are designated as Drinking Water Protected Areas (DrWPAs) (Figure 1.1). Diffuse pollution of pesticides (mainly from agriculture) is a major problem for the raw water quality in many DrWPAs (Reichenberger *et al.,* 2007; Moore *et al.,* 2001). A principle of Article 7 is that catchment management to control contamination at source ("Prevention-led approach"), rather than investment in existing or new treatment, should be used to remediate diffuse-source water quality issues in DrWPAs. Since 2000, the strategy has been to increase awareness of diffuse pesticide pollution and develop management strategies to prevent it (Stuart *et al.,* 2012a). In the UK, the Environment Agency and the Department for Environment, Food and Rural Affairs (DEFRA) are responsible for regulating the WFD (Stuart *et al.,* 2012a).

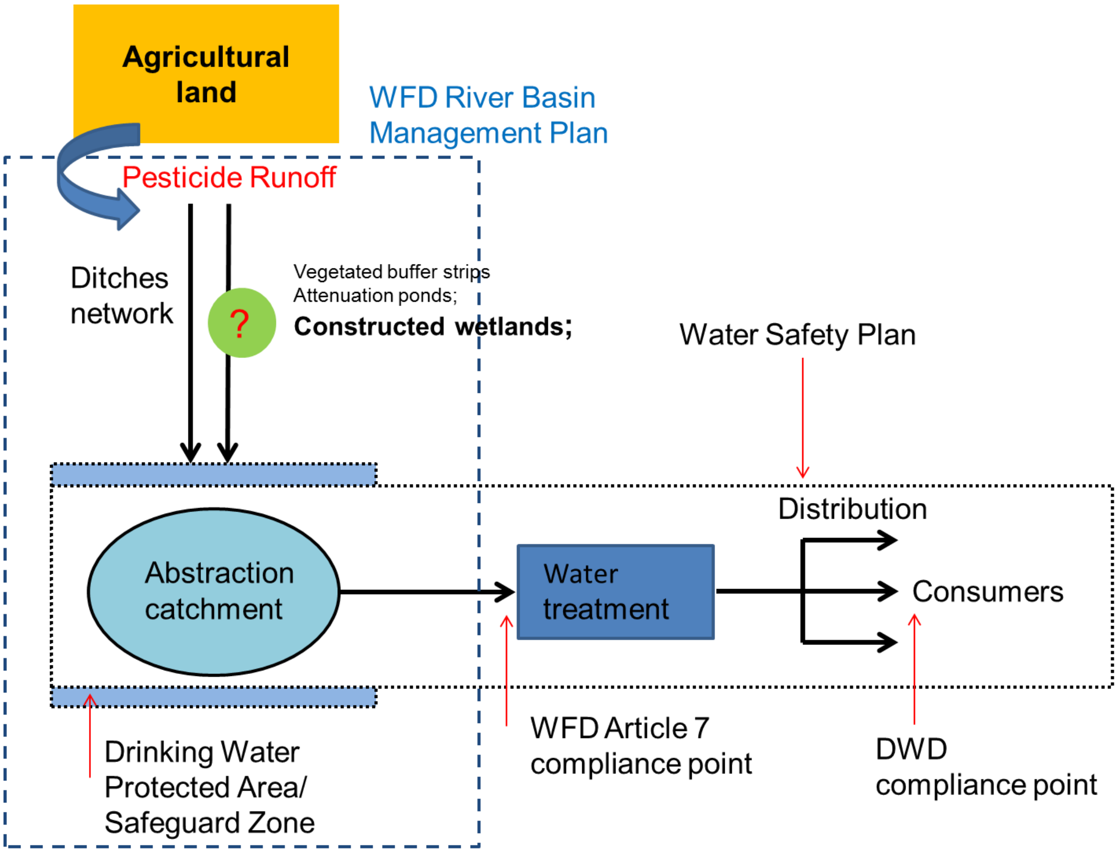

Figure 1.1. Schematic overview of WFD and DWD policies (elaborated by the author)

A number of pesticides periodically present DWD compliance challenges to water companies – most commonly in surface waters. Of the 486 DrWPAs in England, almost 25% (122) are at risk of failure to meet WFD requirements for pesticides. The risk of pesticide contamination of drinking water supplies in England tends to be higher in eastern and southern areas (with some issues in the southwest too) due to the prevalence of arable agriculture and associated use of a greater range of pesticides in these regions (Garthwaite *et al.,* 2014). Problem pesticides include propyzamide and carbetamide (commonly used herbicides in the UK) (e.g. Tediosi *et al.,* 2012) and metaldehyde. Metaldehyde is a pesticide widely used to control slugs and snails on arable land. It is regularly detected at high concentrations (>> 0.1 mg L^{-1}) in abstracted water in many water supply catchments around the UK (Lu *et al.,* 2017) and it currently represents the biggest pesticide-related challenge faced by UK water companies because it cannot be removed by current water treatment technologies without significant expense (Tao and Fletcher, 2013).

1.1.3 Limitations of a “Prevention-led approach”

Article 7 promotes a “Prevention-led approach” to achieving DWD compliance in water bodies used for drinking water supply (Dolan *et al.,* 2012; Dolan *et al.,* 2013). This is based on a range of catchment management solutions to mitigate diffuse pollution (Dolan *et al.,* 2012; Dolan *et al.,* 2013; Reichenberger *et al.,* 2007). This includes (i) structural measures such as the use of buffer zones near to water courses to intercept and reduce overland flow (thereby encouraging infiltration and sorption of pesticides) or the use of biological filters (biobeds) to treat farm yard runoff (pesticide losses from hard standings in farm yards have been blamed for high local exposure in surface waters receiving farm yard runoff) and (ii) non-structural approaches such as changes in pesticide application rates, the timing of application to avoid wet periods wherever possible or crop rotations to reduce the area of land receiving problem pesticides in any one year or to change the operational procedures for filling-up and washing-down spray equipment where these operations can lead to spills and associated contamination of nearby water bodies.

These measures are all believed to work at certain times and in certain contexts but are probably not going to be effective everywhere all the time. Buffer zones, for example, will be relatively ineffective at the catchment scale if the main runoff pathway is *via* artificial field drains. Similarly, biobeds and best practices in sprayer filling and wash-down will have relatively little effect at the catchment scale if the majority of pesticides are being transferred to the catchment outlet from diffuse-sources in the fields (*e.g.*, again, *via* field drains). The idea of constructing specific attenuation features in the landscape (e.g. ponds or wetlands) either in-field or on ditch networks has, therefore, been suggested as an additional measure which could be taken to reduce pesticide transfers to water abstraction points. Simple free-water surface constructed wetlands (FWS CWs) can be constructed relatively cheaply and could be deployed across wide areas. However, relatively little is known about the effectiveness of such features –

which is likely to vary temporally (*e.g*. with rainfall and runoff patterns) and spatially (e.g. with the size and composition of the wetland with respect to the size and composition of the contribution catchment). A review from 180 studies (Reichenberger *et al.,* 2007) on the effectiveness and feasibility of mitigation strategies to reduce pesticide inputs to ground and surface water reported a particular lack of knowledge on the efficiency and major removal mechanisms of structural features. There is, therefore, a need to understand if such features can make an effective contribution to catchment management from the perspective of decreasing contamination at water abstraction points.

1.1.4 Non-structural approaches for managing diffuse-source pesticide transfers

Several non-structural mitigation measures have been developed to reduce pesticide transfers to surface waters (Gregoire *et al.,* 2009; Reichenberger *et al.,* 2007). The first and most obvious approach is to reduce the total application of pesticides to the catchment. Since the efficacy of most pesticides is threshold-dependent (i.e. there is a minimum application rate to a particular crop which will be effective against the particular target pest or disease) this cannot be achieved by simply reducing the application rate. Rather, a change in the fraction of the treated area is required in the catchment under consideration. This can be done, for example, by changing the frequency which a particular crop (receiving the pesticide under consideration) appears in the arable rotation. For instance, oilseed rape is often grown in a one to three rotation in the UK with winter wheat. If this was reduced to a one in four, the total area of oilseed rape grown in any one year would (statistically, at least) decrease. Another way to reduce inputs would be to impose restrictions on the crops on which particular pesticides can be used or on where in a particular catchment certain pesticides can be applied. For example, restrictions could be imposed on the use of certain products on certain soil types or certain field based on their vulnerability to runoff. Such measures would be difficult to enforce and would, thus, rely on voluntary action.

Another non-structural approach to reducing pesticide exposure to water is to try and minimise spray drift. Spray drift is the unintentional transfer of pesticide to water bodies close to the sprayed area as a consequence of transport of liquid droplets by the wind. Drift to water transfer is affected by *inter alia* droplet size distribution, boom height, vehicle forward speed, wind velocity and distance from the water body (Felsot *et al.,* 2011). Typically exposure from drift decreases with distance so leaving an area adjacent to the edge of the water body which does not receive spray (a non-spray zone) can reduce drift significantly. Other measures to reduce drift include using special low drift nozzles on boom sprayers and restricting spraying when wind velocities are too high.

Finally, bans (*e.g. via* the withdrawal of registration or via the refusal to re-register a particular active ingredient) are also an option and have been employed in the UK for chemicals such as isoproturon (Stuart *et al.,* 2012a). The second non-structural approach to pesticide management involves shifting application dates so as to minimise the potential losses post-application. This could be achieved by only applying under certain soil moisture conditions (*e.g.* when the soil is relatively dry or when field drains are not running freely). It could also involve the use of weather forecasting – for example, only applying when rainfall is not expected for a few days. Whilst such measures could potentially help to reduce pesticide transfers overall, they too are difficult to enforce and come with risks to the farmer who needs to make the treatment or risk a decrease in yield or quality as a consequence of a pest outbreak.

1.1.5 Structural approaches to the control of diffuse-source pesticide transfers

A number of structural approaches have been proposed to the control of diffuse-source pesticides transfers including the use of buffer zones (also known as vegetated filter strips), detention ponds and construction of wetland features – either in the field or on the ditch or stream network.

Vegetated Filter Strips

Vegetated Filter Strips (VFS) is a mitigation feature which is known to attenuate pesticides transfers to surface waters via overland flow (Carluer *et al.,* 2011). VFS is usually implemented along field edges to water bodies. Their main aim is to increase infiltration and hence increase the sorption of pesticides during runoff events. Reichenberger *et al.,* (2007) showed that VFS can reduce pesticide transfers. However, their efficacy is dependent on the characteristics of the storm event (e.g. precipitation rate, soil moisture) and the site (e.g. width of VFS, slope, upslope contributing area, soil type and vegetation) (Passeport *et al.,* 2013). A review from Arora *et al.,* (2007) showed the overall retention of pesticides in VFS for a wide range of conditions (e.g. weather, rainfall, soil type and widths) was as high as 62% for weakly adsorbing pesticides (K_{oc} < 100 L kg^{-1}), 63% for moderately sorbing pesticides (100 L kg^{-1} < K_{oc} > 1000 L kg^{-1}) and 76% for strongly sorbing pesticides (K_{oc} > 1000 L kg^{-1}). However, both reviews concluded that it is practically impossible to assure very high removal efficiency for all pesticides in all events due to the variability of hydrological factors and pesticide properties. Once runoff discharge is high and flow velocities are fast many VFS features eventually fail and pesticide mitigation potential becomes very ineffective (Reichenberger *et al.,* 2007).

Retention Ponds and Constructed Wetlands

Another structural approach to the control of diffuse pollution transfers involves constructed wetlands and/or retention ponds. Such systems are commonly used as secondary or tertiary treatment units in waste water treatment. They often have high rates of biological activity and they can transform many common pollutants into harmless by-products. In general, constructed wetlands require little operation and maintenance when compared with technical treatment units (Carluer *et al.,* 2011; Reichenberger *et al.,* 2007; Vymazal, 2010).

Constructed wetlands can be divided into surface flow and subsurface flow systems. Depending on the direction of the water flow, subsurface flow systems can be subdivided into Horizontal Flow (HF) and Vertical Flow (VF) wetlands (Dotro *et al.,* 2017). Subsurface flow constructed wetlands are a separate type of feature in which water and associated pollutants are passed (vertically or horizontally) through a solid matrix (e.g. gravel). This encourages contact between the water and the solid surfaces which are often inhabited by fixed microbial biofilms (Vymazal, 2010). Such films are known to be very effective at removing organic contaminants because the microbes in the film use the contaminants as a carbon source – breaking them down. Trickling filter beds used in sewage treatment operate along the same principles. Although potentially very effective at removing pesticides from water (Carluer *et al.,* 2011) one major problem with subsurface flow wetlands is that they have limited maximum flow rates. At very high flows they quickly become inundated and flood – significantly reducing their effectiveness (Reichenberger *et al.,* 2007). They are also more costly and more difficult to construct than free-surface wetlands which are often simply excavations.

Ponds and free-water surface wetlands (FWS CWs) are open areas of shallow water which can be used for temporary storage of excess water during storm events. If the storage period is long enough relative to the removal rates operating within them (*e.g.* degradation by microbes, volatilisation, sorption to sediment or uptake by vegetation), such features can be effective for removing pollution from surface water runoff (Gregoire *et al.,* 2009).

Retention ponds can be classified as open water systems (which can be both aerobic and anaerobic) with depths over 1m and (distinctively from FWS CWS) they do not have vegetation. Retention ponds have been successfully deployed in the USA and Europe to intercept macronutrients in surface runoff. Retention ponds have shown specifically effective in removing Biochemical Oxygen Demand (BOD), Total Suspended Solids (TSS), Coliform Bacteria and Nutrients (e.g. 10-25% of ammonia nitrogen can be removed) (Schulz, 2004; Vymazal and Brezinova, 2015). Retention ponds slow down water movement, allowing a longer period for sorption and/or degradation of pesticides in the water column as well as for settlement of suspending sediment associated with pesticides.

A DEFRA report (PS2247, 2014) about the use of detention ponds to mitigate transfer of pesticides to surface waters via drain flow showed that pesticide removal in ponds were generally low (0.02% for pendimethalin and 1.9% for metaldehyde). Two pesticides with higher values for the organic carbon to water partition coefficient (K_{oc}) (propyzamide, K_{oc} = 840 L kg^{-1} and pendimethalin K_{oc} = 15,700 L kg^{-1}) were also monitored and were expected to have a more substantial removal (either via sorption to the bed sediment or to via deposition of suspended sediment). However, results also showed little attenuation (<1 %) for these compounds due to the high volume of water passing through the pond systems, which resulted in short residence time.

Figure 1.2 shows a schematic overview of an FWS CW. The system is composed of sediment which includes plant litter and a surface water layer (the water column) which often contains emerging plants. FWS CWs are relatively cheap to install using diggers and loaders and require low operation costs and no energy inputs. In terms of pollutant removal, FWS CW has been reported to be effective for attenuating nitrogen via nitrification in the water column and subsequent denitrification in the litter layer (Figure 1.2) (Vyzamal, 2010).

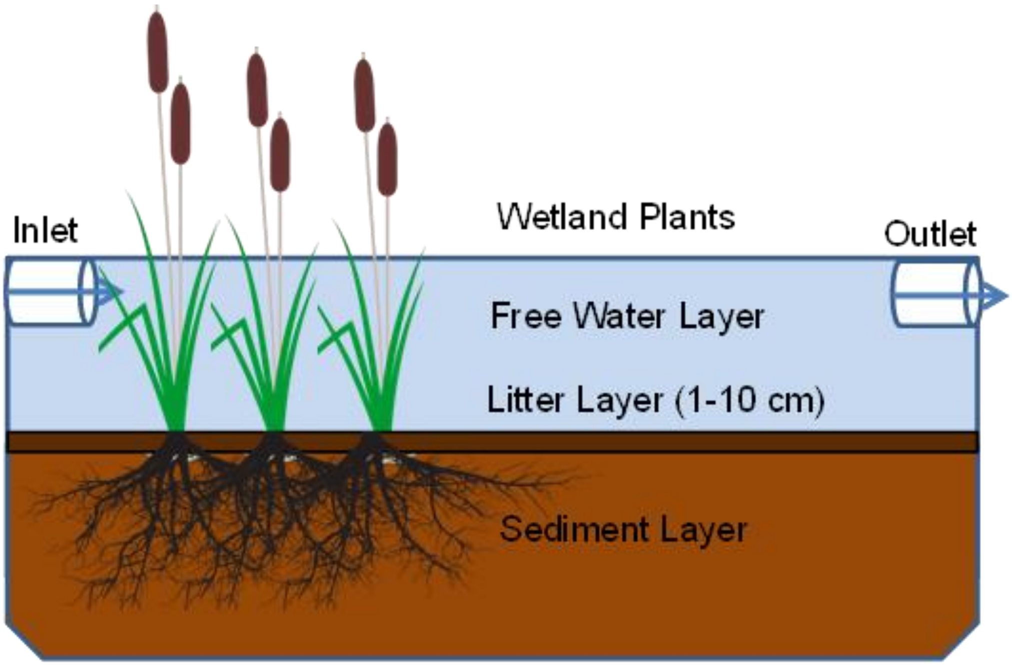

Figure 1.2. Schematic diagram of an FWS CW illustrating the different compartments (water-sediment-plants) (elaborated by the author)

A number of mesocosm studies have indicated that constructed wetland systems do have the potential to dissipate a range of soluble pesticides (Sherrard *et al.,* 2004), and there is some evidence that such systems may also perform effectively at the field scale using FWS CWs (Passeport *et al.,* 2013). However, although field scale studies have been performed using both high surface areas (Passeport *et al.,* 2013; Budd *et al.,* 2009; Tournebize *et al.,* 2016) and small surface areas (Braskerud and Haarstad 2003; Maillard *et al.,* 2011) the studies generally had relatively long retention times (in order of days).

Passeport *et al.,* (2013) reported load reductions between 45 and 96% for 11 herbicides and 5 fungicides in an FWS CW serving a tile-drained catchment of 46 ha. The size of this wetland was 1280 m^2 with an average hydraulic retention time (HRT) of about 8 hours. Results showed greater removal efficiency for pesticides with higher K_{oc} values and low application rates, and sorption was described as the dominant process responsible for the pesticide removal. It should be noted that sorption is unlikely to be a significant net loss process in low retention time systems or when the ratio of pesticide concentrations in sediment and water is close to the equilibrium ratio (*i.e.* adsorption-desorption distribution coefficient K_d). However, if the sediment is relatively “clean” – as might be the case in the first loss event of the season, net sorption could be important. Furthermore, it should be pointed out that sediment can also be a source for the pesticide to the overlying water if the concentration in sediment is high and the water is relatively “clean”.

Braskerud and Haarstad (2003) reported pesticide removal in the range from 3 to 67% in an FWS CW with a surface area of 840 m^2 covering 0.4% of a 21 ha catchment area. The HRT in this system was just one day, suggesting that retention times may not need to be very high for some removal to take place. They suggest that pesticide loss from water could have been due to several possible processes including sorption to sediment particles and organic matter, biodegradation and redox reactions.

The residence time of an FWS CW is critical for removal of pesticides. The HRT is defined as the ratio between the wetland volume and the flow rate at the outlet (Zahraeifard and Deng, 2011). However, this theoretical value is often quite different from the real solute residence time determined using tracer tests with dyes like rhodamine WT (*e.g.* Whelan *et al.,* 2007). Low values for the real HRT could be caused by poor solute mixing sometimes known as short-circuiting, which will ultimately have an impact and most likely a reduction on the removal efficiency (Vallee *et al.,* 2015).

Vallee *et al.,* (2015) studied the relationship between water residence time and pesticide removal in a pilot-scale FWS CW. The study looked at the mitigation of six pesticides (3 fungicides and 3 herbicides) at HRTs of 7, 14, 21, 28, 33 and 75 hours and under static conditions. As expected, FWS CWs were generally less effective during short HRTs (15.2 to 100%) compared to long HRT (17.8 to 100%). During the static period (no flow) the degradation half-life (DT_{50}) values of all the pesticide in the water phase were less than 4 days. Again, like in the study of Braskerud and Haarstad (2003), these findings suggest that the HRT does not actually have to be that long (as little as seven hours in this case) for some removal to be observed.

The HRT depends on the inflow (and outflow) discharge which, in turn, depends on the catchment area (i.e. runoff will be approximately proportional to catchment area). Therefore, the catchment area to wetland volume ratio will be critical for the removal efficiency, where higher removal is expected for low catchment area to volume ratio) (Jayaratne *et al.,* 2010). However, relatively large FWS CWs with hydraulic residence times of the order of days are not easy or cheap to build due to land availability and not easy to maintain. Therefore, it is important to monitor and verify the capability of small constructed wetlands situated on the farm ditch network in order to assess their efficiency in terms of pesticide removal.

1.1.6 Pesticide removal mechanisms in FWS CWs

Pesticide distribution between different environmental compartments (water, sediment and plants) is dependent on physicochemical properties such as aqueous solubility, organic carbon partition coefficient (K_{oc}), the octanol-water partition coefficient (K_{ow}), the Henry's Law constant and the pesticide half-life in water and sediment (DT_{50s}). The processes responsible for pesticide removal in FWS CWs include hydrolysis, sorption, microbial degradation, volatilisation and plant uptake. These are represented schematically in Figure 1.3. The extent to which each of these processes is involved in pesticide removal in FWS CWs depends on factors such as the organic matter content, and the clay content of the sediment, the system pH, redox conditions, vegetation distribution and state (many wetland species die back in winter) and residence time. Of these processes, net sorption and biodegradation are often considered to be the most important removal mechanisms for most pesticides in FWS CWs (Rae *et al.*, 1998; Katagi, 2016).

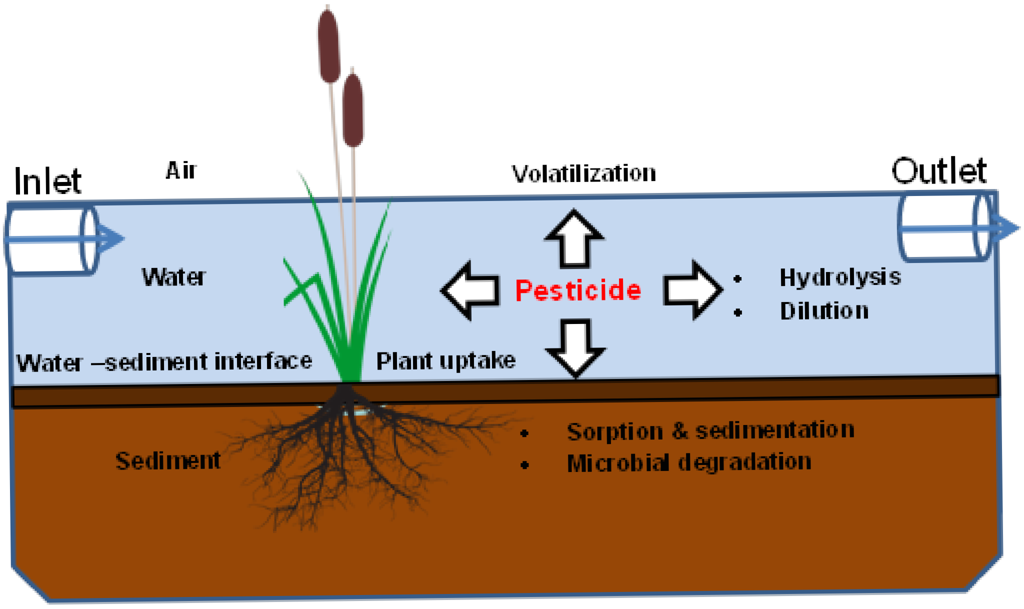

Figure 1.3. Schematic illustration of pesticide removal mechanisms in FWS CWs (elaborated by the author)

Sorption

Sorption (which includes adsorption to particle surfaces and absorption within the bulk organic matter matrix) can affect chemical mobility and availability for biodegradation (Rae *et al.*, 1998; Wauchope *et al.*, 2002; Warren *et al.*, 2003). The adsorption-desorption of pesticides in wetland sediment is expected to play an important role in the fate of these compounds in FWS CWs. Most pesticides are non-polar and hydrophobic, meaning that they are not very soluble in water. Therefore, non-polar pesticides tend to move out of the water and onto sediment/soil which contains non-polar carbon material. The amount of organic carbon content present in sediment (or soil) is what determines the amount of pesticide adsorbed. The sorption partition coefficient (K_d) indicates the relative mass of pesticide sorbed into sediment (or soil) compared with the mass dissolved in water. The variability of K_d is huge, in part, because of the variability in organic carbon concentration in soil and sediments, due to the fact that organic carbon is the principal sorbent for many pesticides. Usually, the organic to carbon partition coefficient (K_{oc}) is preferred for determining the ability of sediment to sorb a pesticide. The K_{oc} is obtained by dividing the K_d value by the organic carbon concentration of the sediment (g C g^{-1} dry sediment). The K_{oc} is the pesticide-specific parameter that indicates the propensity of a pesticide to sorb to organic matter (high K_{oc} indicates a high affinity for organic carbon) (Deshauer and Knaber, 1990; Rae *et al.,* 1998; Wauchope *et al.,* 2002; Warren *et al.,* 2003).

Polarity has a significant impact on whether a pesticide will partition into the sediment. If the pesticide is polar, it will tend to remain in the water phase and not be sorbed by the sediment. If a pesticide is non-polar, on the other hand, it will tend to partition from the water phase into the sediment. Once the sorption occurs, non-polar pesticides will strongly bind to the sediment matrix. However, irreversible desorption or slowly reversible desorption might occur resulting in hysteresis (Wauchope *et al.,* 2002; Warren *et al.,* 2003).

The pH also has an important effect on pesticide sorption, in particular for ionisable pesticides such weak acids and bases. For example, quinmerac is in a predominantly non-ionic form at pH less than 4.3 but at pH higher than 7 it is anionic (negative). If the pH of the soil or sediment is acidic, quinmerac will thus not be sorbed as much because the sediment particles tend to carry a net negative charge which repels the anion (Wauchope *et al.,* 2002; Warren *et al.,* 2003). Other factors that have an influence on pesticide sorption to sediment are the amount of salts present in the water (salinity) and the organic matter in solution.

The Organisation for Economic Co-operation and Development (OECD) describes standardized guidelines for testing of chemicals. The OECD test 106 aims to estimate the adsorption/desorption behaviour of a chemical on different soil types. The method is suitable to be modified and used to test pesticides in different media (e.g. wetland sediment). The goal is to obtain a sorption value which can be used to predict partitioning under a variety of environmental conditions. At equilibrium, sorption coefficients for pesticides in various sediments are determined as a function of sediment characteristics (organic carbon, clay content, texture and pH). The test comprises three different steps. Step 1 is based on a preliminary study to assess the water to sediment ratio, equilibration time for adsorption and the amount of test substance adsorbed at equilibrium. The adsorption of the test substance on the surfaces of the test vessels and the stability of the test substance during the test period will be also be assessed as blanks and control experiments. In Step 2 sorption is studied in five different types of sediment and the sorption kinetics at a single concentration and determination of distribution coefficient (K_d) and (K_{oc}) can be calculated. In Step 3 sorption isotherms are fitted to the data to determine the influence of concentration on the extent of adsorption (desorption isotherms can be also be calculated after immediately the sorption step).

It should be noted that the determination of desorption (net movement from sediment to water) coefficients (K_d^{des}) is rarely reported but is potentially very important to better understand the mobility and availability of pesticides in water-sediment systems. Similarly, sorption is usually determined for individual pesticides in isolation of other organic pollutants. However, in reality, wetland sediment is often exposed simultaneously to contamination by several pesticides which are applied together or in the same period. This could result in competition for sorption – depending on the nature of the dominant sorption mechanisms operating for the pesticides under consideration. The effect of such mixtures on sorption has rarely been reported. It is, therefore, important to evaluate if the presence of other pesticides can alter the sorption parameters (Chefetz *et al.,* 2004). The third objective is to understand the contribution of sorption in attenuating pesticides in FWS CWs by studying the sorption capacity of wetland sediment for pesticide in individual and mixture solutions

Degradation

Degradation of a pesticide in an FWS CW can occur chemically and/or microbially (Sing, 2008). Examples of chemical degradation include hydrolysis and oxidation-reduction. Hydrolysis is a reaction of a pesticide with water, resulting in a cleavage of the molecule into smaller and more water-soluble compounds. Oxidation-reduction reactions can be biologically-mediated, chemical or photochemical involving the transfer of electrons. The process involves two chemical species, one losing one or more electrons – oxidation – and the other accepting one or more electrons – reduction (Singh, 2008).

Microbial degradation or biodegradation is the natural process in which microorganisms decompose organic compounds like pesticides (Singh, 2008). This process involves enzymes which can act either within the microbial cell or extracellularly. Every biodegradation step is catalysed by a specific enzyme. If the enzyme is not present then biodegradation will not occur. This is the reason why some pesticides are persistent in the environment. The abundance and activity of degradative enzymes depend on environmental factors which drive microbial growth (*e.g.* pH, temperature, salinity, organic matter content and quality and the availability and quantity, of surface area to promote microbial binding) and the history of microbial contact with the pesticides concerned. Biodegradation also depends on the properties of the pesticide and the initial concentrations of pesticide in water (Aislabie and Lloyd-Jones 1995; Lu *et al.,* 2006).

To study the biodegradation rate of pesticides in soil, sediment and water, standardised laboratory degradation studies are normally performed where water and/or soil samples are spiked with a known amount of the pesticide and incubated under certain environmental conditions (temperature, soil water content, soil or sediment type) and the pesticide concentration is measured over a period of time in order to understand the kinetics of dissipation. If degradation takes place according to first order kinetics (exponential decrease in concentration over time) then a half-life can be derived. For understanding the expected behaviour of pesticides in wetlands, the OECD 308 (OECD, 2002) test is the most appropriate of the standard laboratory methods available. This can be used to determine the aerobic and anaerobic transformation of organic compounds in dark aquatic systems containing water and sediment (OECD, 2002). The test is often conducted under standardised conditions.

Complete biodegradation of a pesticide involves the transformation of the compound into carbon dioxide and water, in which is sometimes referred as ultimate biodegradation. Then can be determined using radio-labelled test material by monitoring the evolution of radio-active CO_2. During this process, carbon and energy are used for microbial growth. Primary biodegradation, in contrast simply involves the transformation of a parent compound into a metabolite with different chemical properties. This can be tracked by specific analysis (*i.e.* disappearance of a parent compound) which may or may not determine the fate of metabolites (OECD, 2002).

In all cases, it is common to observe a lag phase in the loss of a chemical due to biodegradation. This is often due to the “acclimation” or “adaptation” of the microorganism to exposure with the pesticide under consideration (Passeport *et al.,* 2011; Pesce *et al.,* 2010). As an example, Pesce *et al.,* (2010) showed evidence for adaptation of microbial communities in riverine sediment to diuron mineralization. The experiment was set up in an aquarium filled with riverine sediment and water. One contained diuron in water, to simulate surface water runoff and the second contained diuron-treated soil to simulate erosion followed by a strong rainfall event. Results showed a higher removal potential and a shorter lag phase for the system with treated soil than with riverine sediment. Boivin *et al.,* (2005) studied the sorption and degradation dynamics of 2,4-dichlorophenoxyacetic acid (2,4-D) in three agricultural soils. A lag phase of 6 to 10 days was noticed in the different soils, but after this period rapid degradation was observed.

The third objective is understand the contribution of degradation in attenuating pesticides in FWS CWs.by studying the degradation of the studied pesticides in several mesocosms experiments including microbial activity inhibition, initial concentrations of pesticides and the influence of the water depth.

1.1.7 Review of current methods for pesticide analysis

Exposure in different environmental compartments, including soil, food, water and air may be harmful to the health of not only humans but also other organisms. Thus, the concentration levels of pesticides (and metabolites) present in the different environmental compartments should be continuously monitored (Dalton and Frick, 2008; Dolan *et al.,* 2012; Stuart *et al.,* 2012).

In this context, to properly monitor the environmental fate of pesticides in different environmental samples, effective and robust analytical methods for the determination of these compounds at low concentrations (e.g. ngL^{-1}) are necessary. Pesticides residues in different environmental samples have been analysed using different chromatographic methods such gas chromatography (GC) and high-performance liquid chromatography (HPLC). Because most pesticides exhibit low volatility and thermal stability, mass spectrometry is frequently used for their determination. Pesticide concentrations in the environment are usually low (< 10 $\mu g\ L^{-1}$) and therefore several samples preparation steps are often required, such as solid phase extraction (SPE), solid phase micro-extraction or liquid-liquid extraction. Most of these sample preparation steps present several disadvantages, such as using expensive cartridges units, long procession times per sample, low recoveries and difficult extraction when dealing with pesticides with different polarities (Wan *et al.,* 2005; Hao *et al.,* 2015). Direct aqueous injection (DAI) methods have been extensively reported for the analysis of a wide range of pesticides in different environmental samples, such food, water and soil. The main advantages of these methods are easy sample preparation and the capability of processing high numbers of samples with reduced time of analysis (Crescenzi *et al.,* 1997; Quintana *et al.,* 2001, Irace-Guigand *et al.,* 2004).

Due to the large number of pesticides used in agriculture, the development of simultaneous determination methods capable of analysing several pesticides in one single run has significant advantages for environmental monitoring. The first objective of this study was to develop an analytical method for the simultaneous determination of concentrations for several pesticides in surface water. Theses pesticides are metaldehyde, quinmerac, carbetamide, metazachlor, propyzamide and pendimethalin.

1.2 Aim and objectives of the thesis

The primary aim of this thesis was to improve understanding of the processes affecting pesticide fate and transport in FWS CWs in order to assess their utility as potential attenuation features.

The thesis has three general objectives:

- To develop a rapid and easy method for the determination of pesticides in environmental waters;
- To determine the effectiveness of existing FWS CWs to retain and degrade pesticides transferred from land to surface waters;
- To understand the relative contribution of different removal mechanisms (sorption and degradation) for pesticide attenuation in FWS CWs;

1.3 Thesis Structure

This thesis is divided into six chapters. The main chapters are formatted as papers for publication in journals. All papers were written by André Ramos and edited by the supervisory team (Dr Mick Whelan, Dr Raffaella Villa and Prof Bruce Jefferson). Additional inputs were made by Dr Pablo Moreno Campo from Cranfield University on the analytical method which was developed and by Prof Ian Guymer from the University of Warwick who helped to set up the flow monitoring structures and conduct dye tracing. All field work was carried out at Hope Farm (Knapwell, Cambridgeshire, UK) which is owned and operated by the Royal Society for the Protection of Birds (RSPB). All experimental work was undertaken at Cranfield University by André Ramos.

The first chapter provides an overview of the pesticide pollution problem for drinking water resources, the “prevention-led approach” offered by catchment management and the limitations which exist in the knowledge of their effectiveness and the principal mechanisms operating.

Chapter 2 describes a multi-component method to determine, simultaneously, several different pesticides in water by liquid-chromatography tandem quadrupole mass spectrometry. The target pesticides selected were metaldehyde and five herbicides (quinmerac, metazachlor, carbetamide, propyzamide and pendimethalin).

Chapter 3 outlines a monitoring study which was conducted on two FWS CWs at Hope Farm. Inlet and outlet concentrations were measured and compared to assess any reduction in concentration under a range of dynamic conditions, including storm events and base flow. Chapter 3 also includes data collected during a static period (with no flow) in one of the systems.

Chapter 4 presents a study of pesticide sorption in wetland sediment. This chapter provides an insight into the sorption and desorption capacity of the wetland sediment to retain pesticides present in water either single or as mixtures.

Chapter 5 describes the fate of pesticides in laboratory micro and mesocosm of water-sediment systems. This chapter focuses on mimicking static conditions which occur periodically in one of the wetlands at Hope Farm during which pesticide concentrations were observed to decrease over time. The laboratory experiments were conducted to (i) understand if decreases in pesticide concentration were due to microbial activity or other processes; (ii) to assess the effect of initial pesticide concentration on degradation rate and (iii) test the hypothesis that the overall degradation rate in water is inversely proportional to the water depth.

Chapter 6 provides a general discussion of the project including a summary of the new knowledge gained on the potential of free-water surface constructed wetlands for pesticide attenuation, together with some insights on expected mitigation mechanism (*i.e* sorption, degradation and, potentially, volatilisation). This chapter also provides an overview of study limitations and makes some recommendations for further research and for the potential contribution of these features to catchment management.

1.4 Pesticides Used

Throughout the thesis six different pesticide active ingredients were investigated: metaldehyde, quinmerac, carbetamide, metazachlor, propyzamide and pendimethalin. The main use and relevant physiochemical properties are listed in Table 1.1. With the exception of pendimethalin, all the compounds examined have organic carbon-water partition coefficients (K_{oc}) less than 840 L kg^{-1}, which suggests that they will be moderately mobile in soil and, hence, prone to leaching losses. All six pesticides are widely used in arable agriculture in Europe and have been previously detected at concentrations of concern in UK water bodies Tediosi *et al.,* 2012).

Table 1-1. Main use and physicochemical properties for the studied pesticides

Pesticide	Type	*Koc* (L kg^{-1})[2]	Log K_{ow}[3]	Aqueous Solubility (mgL^{-1})[4]	Typical Application Rate (g ha^{-1})
Metaldehyde	Molluscicide	240	0.12	188	0.18
Metazachlor	Herbicide	54	0.03	450	0.75
Propyzamide		840	0.002	9	1.05
Quinmerac		86	0.039	10700	0.25
Carbetamide		89	1.78	3270	1.79
Pendimethalin		17581	5.2	0.33	1.09

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2 . A multi-component method to determine pesticides in surface water by liquid-chromatography tandem quadrupole mass spectrometry

A.M.Ramos[1]; M.J.Whelan[2]; S.Cosgrove[1]; R.Villa[1]; B.Jefferson[1]; P.Campo[1]; P.Jarvis[1]; I.Guymer[3];*

[1]Water Science Institute, School of Energy, Environment and Agrifood, Cranfield University, Bedford, MK43 0AL, UK

[2]Department of Geography, University of Leicester, Leicester, LE1 7RH, UK

[3]School of Engineering, University of Warwick, UK

2.1 Abstract

Pesticide pollution of surface water is a major concern in many agricultural catchments. The development of rapid and accurate methods for determining pesticide concentrations in water samples is, therefore, important. Here we describe a method for the simultaneous analysis of six pesticides (metaldehyde, quinmerac, carbetamide, metazachlor, propyzamide and pendimethalin) in natural waters by direct aqueous injection with liquid chromatography-tandem mass spectrometry. The method validation showed good linearity from 0.2 to 50.0 µg L^{-1} with correlation coefficients between 0.995 to 0.999. Method accuracy ranged from 84 to 100% and precision (RSD) from 4 to 15%. The limits of detection for the targeted pesticides ranged from 0.03 to 0.36 µg L^{-1}. No significant matrix effects on quantification were observed (*t* test). The method was tested on water samples from a small arable catchment in eastern England. Peak concentrations for the determinants ranged from 1 to 10 µg L^{-1}.

Keywords

Direct injection; LC-MS/MS; pesticide pollution; surface water

2.2 Introduction

Agriculture is generally considered to be the greatest contributor to pesticide pollution in many ground and surface waters, although in some catchments runoff from hard surfaces may be locally important (Tournebize *et al.,* 2013). Pesticide monitoring is a challenging task because a high number of active ingredients are typically used in agricultural catchments with mixed land use (presenting a wide range of physiochemical properties) which is applied at different times of year and at different rates. This means that several different analytical methods may need to be employed on a single sample in order to detect the compounds of interest. The challenges of detecting target compounds can also be exacerbated by the episodic nature of pesticide transport from land to water (which tend to occur predominantly during storm events) (Tediosi *et al.,* 2012). Hence, high sampling frequencies may be required to capture representative temporal patterns, which results in significant analytical costs. Most methods for pesticide analysis at the low concentrations generally encountered in natural water bodies require a sample pre-concentration step such as solid phase extraction (SPE), solid phase micro-extraction, or liquid-liquid extraction. Of these techniques, SPE is most commonly employed because it often provides good sample extraction, concentration and clean up (Whelan *et al.,* 2007; Li *et al.,* 2010). However, there are several disadvantages with this technique including potential for low recoveries, long processing times per sample, the high cost of SPE cartridges and differing extraction procedures for different classes of pesticide owing to their polarities.

As an alternative, direct aqueous injection (DAI) methods have been developed for the analysis of a wide range of pesticides in various sample matrices. Applications include analysis of polar organophosphorus pesticides in fruit and vegetables (Fenol *et al.,* 2007; Stachniuk and Fornal, 2013) and analysis of pesticides in potable water (Wan *et al.,* 2005; Hao *et al.,* 2015). The main advantages of DAI are easy sample preparation/ manipulation, low consumable costs and reduced analysis time allowing high sample throughput as well as low limits of detection.

In this paper, we describe a DAI multi-component method for the determination of six pesticides by LC-MS/MS in environmental waters. The specific requirements of the method were to be accurate and rapid so as to allow the efficient processing of a large number of samples. The pesticides analysed were metaldehyde, quinmerac, metazachlor, carbetamide, propyzamide and pendimethalin. Molecular structures and relevant physiochemical properties are listed in Table 2.1. With the exception of pendimethalin, all the compounds examined have organic carbon-water partition coefficient (K_{oc}) values less than 840 L kg^{-1}, which suggests that they will be moderately mobile in soil and, hence, prone to leaching losses. All six pesticides are widely used in arable agriculture in Europe and have been previously detected at concentrations of concern in UK water bodies (Tediosi *et al.,* 2012; Kay and Grayson, 2014). Metaldehyde is a particular problem for the UK water industry and has been responsible for the highest number of compliance failures in recent years (Environmental Agency, 2009; Kay and Grayson, 2014). It is a selective molluscicide which is widely used to control slugs and snails in several crops. It is only moderately mobile (K_{oc} = 240 L kg^{-1}) and has been observed to degrade in water-sediment interface with a median dissipation time (DT_{50}) of 12.2 days (Table 2.1) which should, in principle reduce the risk of leaching loss from soil.

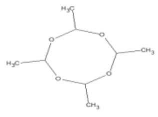
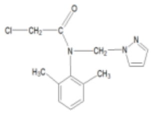
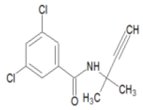
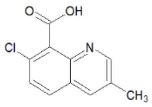
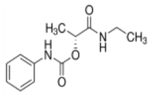
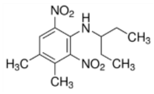
Quinmerac is used to control *Galium aparine*, *Veronica* spp. and other broad leaved weeds in cereals, oil seed rape and sugar beet. Carbetamide and propyzamide are herbicides used to control black grass infestations predominantly in oil seed rape (Mamy *et al.,* 2005). Metazachlor and pendimethalin are also herbicides used to control grass and broad-leaved weeds in a range of crops including oil seed rape and Brussel sprouts (Mamy *et al.,* 2005). Pendimethalin is not expected to be particularly mobile and was included to provide a contrast to the other more mobile compounds.

There are few published papers that report on the analysis of more than one of our target pesticides. In general, these protocols only included 2 or 3 pesticides at the most with fruits and vegetables being the studied matrices (Romero-Gonzalez *et al.,* 2008). Analysis in food stuffs requires an extraction step before any determination can take place. A popular method is QuEChERS which includes SPE followed by LC-MS/MS. Pesticides detected by this method include metazachlor, pendimethalin and quinmerac (Crescenzi *et al.,* 1997; Quintana *et al.,* 2001, Irace-Guigand et al., 2004). Others used homogenisation followed by evaporation or supercritical fluid extraction as the extraction step followed by GC-MS or GC-NPD (Nitrogen, Phosphorus Detection). Pesticides detected following these methods included carbetamide, propyzamide and pendimethalin (Irace-Guigand *et al.,* 2004) Tournebize *et al.,* 2013). Other protocols dealt with several of our target pesticides in water samples, namely carbetamide, metazachlor, propyzamide (Quintana *et al.,* 2001) metazachlor and pendimethalin (Irace-Guigand *et al.,* 2004). These protocols involved SPE followed by LC-MS and GC-MS respectively, although the method by Irace-Guigand et al., (2004) required additional UV-DAD detection.

Of the six target pesticides, metaldehyde appears to be one of the more difficult compounds to detect in complex samples containing several analytes. To the best of our knowledge, no method has been previously reported for the combined rapid determination of these particular six pesticides with minimal sample preparation approach in environmental water samples.

The method improves upon existing knowledge in order to produce a robust value analytical tool in which minimal sample preparation is needed to monitor pesticide concentrations from agricultural runoff.

Table 2-1. Physicochemical properties for the pesticides considered in this method.

Pesticide	Type	Molecular mass (gmol^{-1})	Chemical structure	Chemical formula	DT_{50} (days)^1			Koc (L kg^{-1})^2	Log K_{ow}^{3}	Solubility (mgL^{-1})^4	pKa
					Soil	Water-sediment	Water				
Metaldehyde	Molluscicide	176.21		$C_8H_{16}O_4$	5.1	12.2	11.5	240	0.12	188	n/a
Metazachlor	Herbicide	277.75		$C_{14}H_{16}ClN_3O$	8.6	20.6	216	54	0.03	450	n/a
Propyzamide		256.13		$C_{12}H_8Cl_2NO$	47	94	21	840	0.002	9	n/a
Quinmerac		221.6		$C_{11}H_8ClNO_2$	30	179.4	88.7	86	0.039	10700	4.31
Carbetamide		236.27		$C_{12}H_{16}N_2O_3$	12.4	55.5	9.1	89	1.78	3270	11.3
Pendimethalin		281.21		$C_{13}H_{19}N_3O_4$	90	16	4	17581	5.2	0.33	2.8

$^1DT_{50}$ – Median dissipation time in different test systems; $^2K_{OC}$ – organic carbon-water partition coefficient (L kg^{-1}); ^{3}Log K_{ow} – octanol-water partition coefficient; ^{4}Solubility in water (mg L^{-1}) (Lewis *et al.,* 2016)

2.2 Experimental

2.2.1 Chemicals and Reagents

Pesticide standards were purchased from QMX laboratories (Essex, United Kingdom), methanol (HPLC grade) and acetic acid (HPLC grade) were obtained from Sigma-Aldrich (United Kingdom). Ultrapure water was produced by PURELAB® ultra, Elga.

2.2.2 Standards and stock solutions

Pesticide stock solutions (100 µg L^{-1}) were prepared by dissolving the neat pesticides in methanol. Working standards were prepared by diluting with ultrapure water with concentrations of 0.2, 0.5, 1.0, 2.0, 5.0, 8.0 and 10.0 µg L^{-1} for each pesticide. All standards were stored at 4°C for a maximum of one month.

2.2.3 Instrumentation

All analyses were performed with a Waters Alliance 2695 liquid-chromatography system coupled to a Quattro premier XE tandem quadrupole. A Kinetex C18 column (5µm 150 × 2.1 mm, Phenomenex, UK) thermostated at 60 °C was used for chromatographic separation. The flow rate was 0.3 mL min^{-1} and the injection volume was 50 µL. The mobile phase consisted of ultra-pure water with 0.1% acetic acid (A) and methanol with 0.1% acetic acid (B). The elution started at 10% B and was linearly increased to 98% over 12 min, then maintained for 3 min before returning to the initial composition. The total time of analysis per sample was 18 min.

Operating conditions of the mass spectrometer were optimized by infusion of each individual pesticide at a concentration of 1 mg L^{-1} in a solution of 70% A and 30% B. Electrospray ionization (ESI) was performed in positive mode. The mass spectrometer was operated under multiple reaction monitoring (MRM) with two reactions monitored for each analyte (Table 2.2), with the exception of metaldehyde, which forms a Na^+ adduct and its fragmentation $[M+Na]^+$ showed a reaction whose precursor and fragment ions were *m/z* 198.9 and *m/z* 66.9, respectively. The UK Environment Agency recommends this reaction for quantitative purposes (EA, 2009).

Table 2-2. SRM transitions used for the target compounds.

Analytes	**1st transition – quantification**				**2nd transition – confirmation**				**Retention Time (min)**
	Percursor ion *(m/z)*	**Product ion *(m/z)***	**cone**	**collision**	**Percursor ion *(m/z)***	**Product ion *(m/z)***	**cone**	**collision**	
Metaldehyde	198.9	66.9	25	12	-	-	-	-	5.69
Quinmerac	222.3	204.3	30	25	222.3	176.3	30	25	6.57
Carbetamide	237.1	191.9	15	10	237.1	117.9	15	8	7.85
Metazachlor	278.1	133.8	15	15	278.1	209.9	15	15	9.43
Propyzamide	256.0	189.9	15	15	256.0	172.8	15	15	10.37
Pendimethalin	282.1	212.0	25	10	282.1	193.9	25	25	12.59

2.2.4 Sample collection and Analysis

The method was tested on samples collected from a monitoring study in a small headwater stream at Hope farm in Knapwell, Cambridgeshire, UK (Figure 2.1). The stream drains a low relief catchment (elevation range 41-78 m above mean sea level) of approximately 3.9 km^2, which is dominated by arable land.

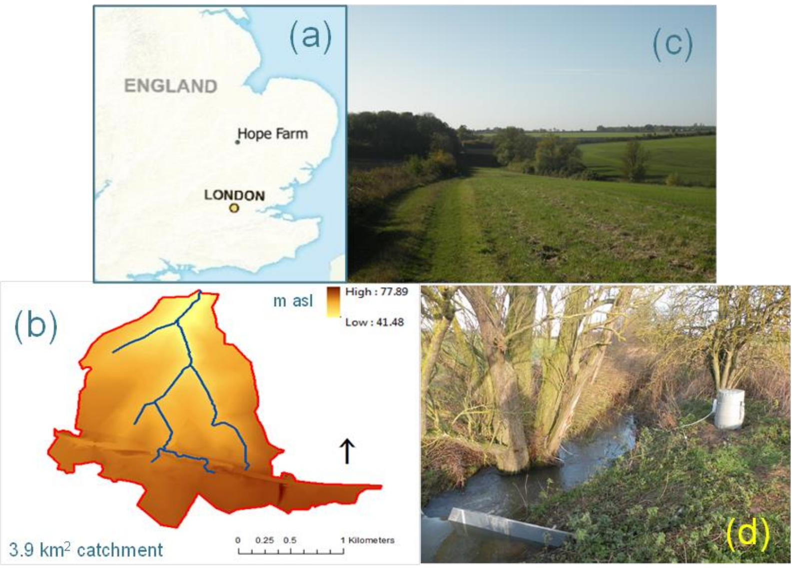


Figure 2.1. a) Location of study catchment b) Catchment boundary, stream network and digital elevation model; c) Catchment relief looking upstream; d) Automatic water sampler and v-notch weir installed at the catchment outlet.

The predominant crop rotation is wheat-oil seed rape and most of the soils belong to the Hanslope Soil Association, which is a typically under-drained. Stream discharge is low (but usually perennial) in summer, which suggests minimal baseflow contributions and is flashy in winter with flows often exceeding 150 L s^{-1} during storm events. The stream was monitored for five months between August and December 2014. Discharge was measured with a 90° v-notch weir, equipped with an ISCO AV2150 water level and a velocity sensor. Samples were collected with an ISCO 6712 automatic water sampler at constant sampling intervals of 8 h, with a sample volume of 250 mL.

Sample bottles were changed approximately every 7 days and replaced with fresh bottles which had been thoroughly pre-cleaned before each change-over using water and methanol. Pesticide concentrations in field bottle blanks, prepared with ultrapure water, were always less than the limits of detection (LOD) and often not detectable. Samples were refrigerated immediately upon arrival to the laboratory (typically less than 2 h after sample collection) and filtered through 0.2 µm syringe-mounted disc filters (Millipore Millex^{TM}, Fisher Scientific, UK) within 24 h of collection.

2.2.5 Sample injection and data processing

Sample runs consisted of eight working standards, followed by five unknown samples with solvent blanks and continuing calibration checks (5 µg L^{-1}) in between. Runs never exceeded 80 determinations including analytical standards, blanks, calibration checks and samples. Peak areas of target pesticides were obtained with Quantlynx v.4.1. Weighted (1/x) linear least-squares regression curves were fitted to the observations and not forced through the origin.

2.3 Results and Discussion

Figure 2.2 shows an example total ion chromatogram for the six pesticides in positive ion mode analysed over 18 min from a 10 µg L^{-1} standard of each pesticide in ultra-pure water.

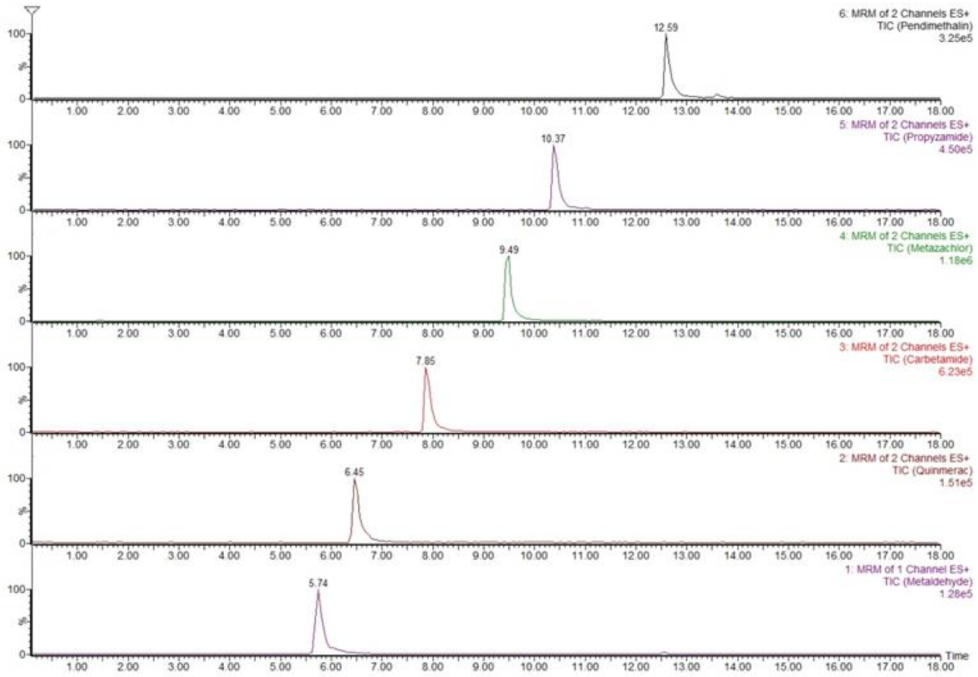


Figure 2.2.Example chromatograms of six pesticides at 10 µg L^{-1} in ultra-pure water by direct aqueous injection

2.3.1 Optimisation of the MS/MS parameters

For the MS operation, only ESI in positive mode was evaluated for the determination of the six pesticides. The optimum cone voltage and collision energies are reported in Table 2.3 Good peak shape and suitable signal-to-noise ratios were obtained with a dwell time of 0.25 s.

2.3.2 Optimisation of the LC conditions

Optimisation of mobile phase composition and elution gradient was very important to achieve good separation, high sensitivity, good ionization and resolution, particularly for trace analysis. Results (see example in Figure 2.2) showed that higher sensitivity and good peak shape could be achieved with 0.1% acetic acid in both eluents. The gradient was optimised to obtain improved resolution and shorter analysis time.

2.3.3 Validation procedures

The analytical method was validated according to the performance criteria established by ICH guidelines (ICH, Harmonised Tripartite Guideline 2005). The validation parameters evaluated were linearity, accuracy, precision, LODs, limits of quantification (LOQs) and matrix effect.

Linearity

Method linearity was evaluated by analysing the response for the seven concentration levels prepared from the working standard solution described in Section 2.2 (0.2, 0.5, 1.0, 2.0, 5.0, 8.0 and 10 µg L^{-1}). Linear regression analysis of calibration data was performed by plotting the peak areas of the quantitative ion versus the corresponding standard concentrations. Good linearity was achieved with coefficients of determination between 0.994 to 0.999 (Table 2.3).The method provided acceptable precision, accuracy and linearity over the range of 0.2 to 10.0 µg L^{-1}.

Accuracy and Precision

Inter-day and intra-day accuracy and precision (RSD) were assessed. Inter-day comparisons express within laboratory across-day variations while intra-day comparisons express within laboratory within-day variations. The intra-day test consisted of five consecutive analyses, while the inter-day variations were assessed on different days for a 5 µg L^{-1} standard. Intra-day precision (RSD) varied from 17.4% (pendimethalin) to 3.1% (metaldehyde), while the inter-day precision varied from 11.4% to 24.3% (pendimethalin). Intra and inter-day accuracy values were close to 100%..

Detection and Quantification limits

Limits of detection (Equation 2.1) and quantification (Equation 2.2) were calculated using the standard deviation of the response and the slope, as described by ICH validation of analytical procedures (ICH, Harmonised Tripartite Guideline 2005):

$$LOD = 3.3 \times \frac{\sigma_R}{m} \tag{2.1}$$

$$LOQ = 10 \times \frac{\sigma_R}{m} \tag{2.2}$$

where σ_R is the standard deviation of the response and m is the slope of the calibration curve.

The standard deviation of the response was calculated from the standard deviation of y-intercepts in the regression lines fitted to the data. Limits of detection and quantification ranged from 0.05 to 0.3 µg L^{-1} and 0.2 to 1.0 µg L^{-1}, respectively (Table 2.3).

Table 2-3. Calibration curves, coefficient of determination (R^2), limit of detection (µg L^{-1}) and limit of quantification (µg L^{-1}).

Analyte	Calibration curve		R^2	*LOD* (µg L^{-1})	*LOQ* (µg L^{-1})
	Slope	Intercept			
Metaldehyde	2219.7 ± 15.3	168.9	0.9998	0.09	0.3
Quinmerac	2489.1 ± 17.3	45.9	0.9998	0.08	0.3
Carbetamide	5524.8 ± 33.9	289.9	0.9998	0.09	0.3
Metazachlor	11302 ± 47.1	584.1	0.9999	0.09	0.3
Propyzamide	4544.5 ± 72.9	628.3	0.9987	0.05	0.2
Pendimethalin	4636.1 ±154.8	223.7	0.9944	0.30	1.0

Matrix effects

To assess the matrix effect the slopes of the calibration curves for ultra-pure water (1) and stream water (2) were compared using a Student's *t* test (95%). The calculated value of *t*, t_{cal}, is defined by:

$$t_{cal} = \frac{|b_1 - b_2|}{\sqrt{S_{b1}^2 - S_{b2}^2}} \tag{3}$$

where b is the slope of the calibration line and S_b is the deviation of the slope.

The null hypothesis (there is no significant difference between the two calibration lines) was rejected when t_{cal} was greater than the theoretical value t_{theo} 2.306 ($p = 0.05$). Values of t_{cal} ranged from 0.5 to 1.3 for the different pesticides so that no significant matrix effect was found. After approximately 80 samples, the mass spectrometer sensitivity was observed to gradually decrease over time, probably because of deposition and accumulation of salts on the cone surface. Analytical controls were used to identify when this problem occurred. When sensitivity reduced by 15%, the run was interrupted and maintenance was carried out.

Blanks

Ultra-pure water and methanol were used as solvent blanks during method validation and field sample analysis. No carryover or system peaks were found. Additionally, target analytes were undetected in field blanks.

2.4 Applications of the method

Data for stream discharge and stream water concentrations of the six pesticides analysed in water samples collected from the study stream are shown in Figure 2.3, between August and December 2014. Daily rainfall data are also displayed. Pesticide concentrations tended to increase sharply during rainfall events with the highest concentrations typically occurring in the first storm event after application. This is consistent with observations reported elsewhere from catchments with under-drained heavy clay soils (Tediosi *et al.,* 2012).The highest concentrations were observed for metaldehyde over an event in late August which triggered a relatively low hydrograph peak. For quinmerac, which is applied later than metaldehyde, the first peak concentrations occur in an event around the 13th of October. Metaldehyde concentrations also increase in this event but with lower peaks. Other notable increases in concentration occur for carbetamide in a series of hydrographs starting on the 14th of November and for propyzamide in the event of the 11th of December, which also resulted in increases in pendimethalin concentrations. Both propyzamide and carbetamide tend to be applied a little later than some of the other herbicides due to the specific requirements of weed control timing for blackgrass on oilseed rape. Concentrations of metazachlor were consistently low, peaking at 0.37 µg L^{-1} on the 29th of October. The magnitude of peak concentrations will reflect a combination of factors including usage rate and the physio-chemical properties of the compound. Compounds with high values of K_{OC} (such as pendimethalin) will tend to bind to soil solids and hence have a lower propensity to leach than compounds which are more hydrophilic (such as metazachlor, quinmerac and carbetamide). For most compounds, peak concentrations were observed at the same time as the hydrograph peak or slightly after the peak flow (*i.e.* on the falling limb of the hydrograph), although apparent delays in the appearance of peak pesticide concentration may be artefacts of the relatively low sampling frequency adopted (8 h).

Concentrations for all the pesticide compounds examined tended to decrease in hydrograph recession periods in parallel with falling flow. Again, this is consistent with previous observations of pesticide behaviour during storm events (Tediosi *et al.,* 2012). Clearly, peak concentrations of all six pesticides were periodically greater than the maximum admissible concentration for drinking water. Although this stream is not directly abstracted for water supply, it does feed into the River Great Ouse system, which is used for municipal abstraction downstream. The important point to note for the purposes of this paper is that the temporal pattern and magnitude of observed concentrations is consistent with expectations under the environmental conditions experienced over the study period.

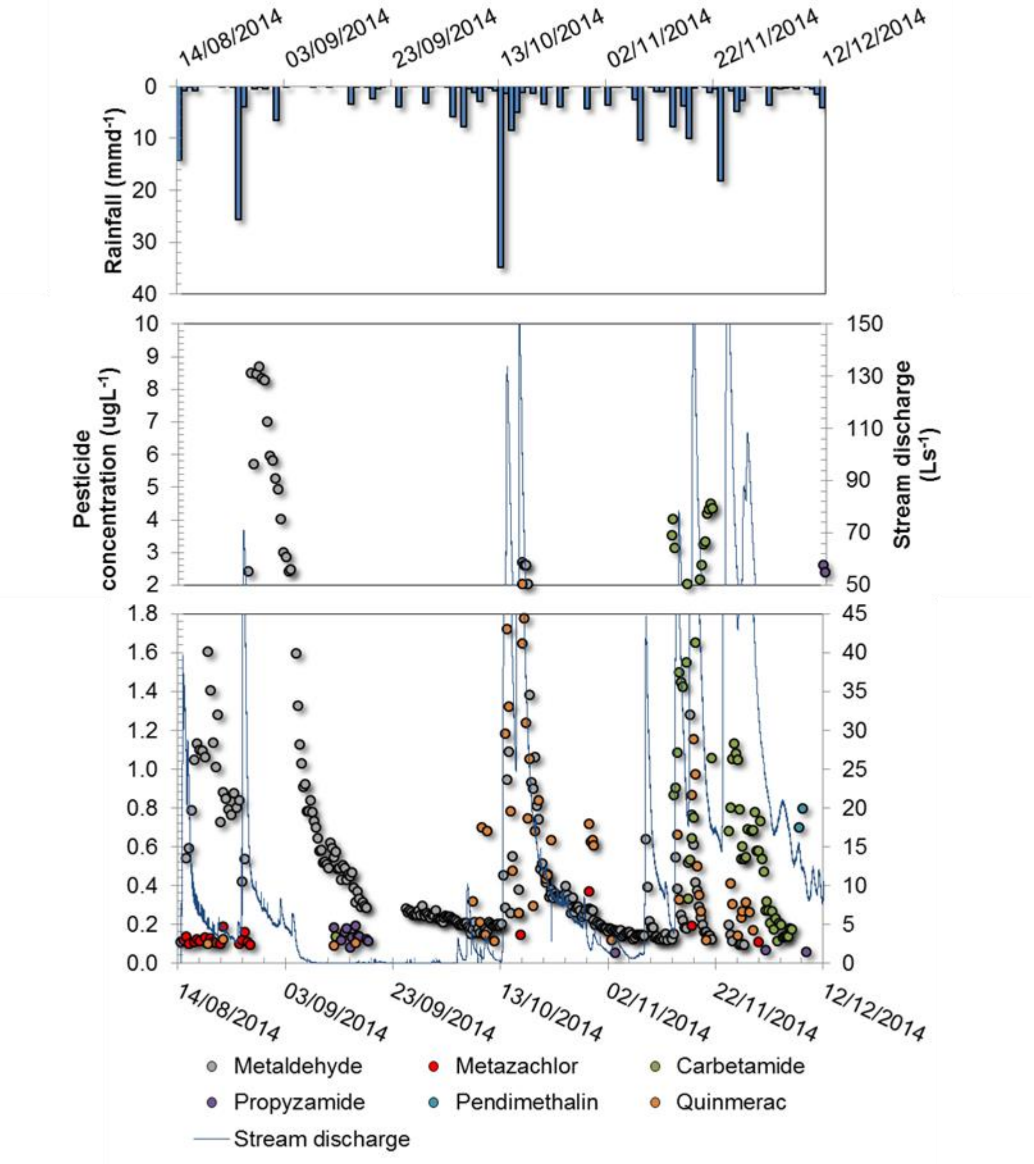


Figure 2.3. Rainfall (top panel), stream discharge (right axis) and pesticide concentrations (left axis) in the Hope Farm stream from August to December 2014.

2.5 Conclusions

An LC-MS/MS method for the simultaneous multi-residue analysis of six pesticide active ingredients in natural waters is presented in this paper. This DAI method is rapid and accurate and can be used for quantification and confirmation of metaldehyde, quinmerac, carbetamide, metazachlor, propyzamide and pendimethalin in water samples from ground and surface waters. The omission of a concentration and clean-up step means that sample processing is fast and straightforward. The method showed a good range of linearity (R^2 ranged from

0.995 to 0.999), accuracy (84 to 100%) and RSD precision (4 to 15%) and there was negligible apparent matrix effect compared to the same pesticides in ultra-pure water.

The LOQs obtained ranged from 0.2 to 1.0 µg L^{-1}. This is acceptable for detecting concentrations in natural water samples from many agricultural catchments where pesticide concentrations are high (edge of field concentrations often exceed 100 µg L^{-1}) but would be of limited value in assessing DWD compliance. The use of a multi-residue method with rapid and simple sample preparation reduces analysis time and improves laboratory efficiency. The temporal pattern and magnitude of concentrations in samples from a headwater arable stream were consistent with expectations for the environmental conditions experienced over the study period, suggesting that the method can yield a realistic description of pesticide exposure in natural waters.

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3. Evaluation of free-water surface constructed wetlands for mitigating pesticide transfers from agricultural land to surface waters

A.M.Ramos[1]; M.J.Whelan[2]; R.Villa[1]; B.Jefferson[1]; I.Guymer[3];

[1]Water Science Institute, School of Water, Energy and Environment, Cranfield University, Bedford, MK43 0AL, UK

[2]Department of Geography, University of Leicester, Leicester, LE1 7RH, UK

[3]School of Engineering, University of Warwick, UK

3.1 Abstract

During August to December 2014, two free-water surface constructed wetlands (FWS CWs) (Cambridgeshire, Knapwell, UK) were monitored to understand the potential to mitigate pesticide transfers from land to surface waters. Two FWS CWs were referred to the position in the farm and henceforth as the south and north wetlands systems. The South Wetland (SW) has a large catchment of 3.9 km^2, whereas North Wetland (NW) has a smaller catchment of 0.66 km^2 which is entirely within the farm. Dye trace results showed an average hydraulic residence time (HRT) of 2 hours approximately for both systems. Peak pesticide concentrations were typically observed in the first storm hydrograph after application, triggered by rainfall events. At the SW, peak concentrations of metaldehyde (9.0 $\mu g\ L^{-1}$), carbetamide (4.0$\mu g\ L^{-1}$) and propyzamide (2.5 $\mu g\ L^{-1}$) were observed. Higher peak concentrations of metaldehyde (30 $\mu g\ L^{-1}$), quinmerac (130 $\mu g\ L^{-1}$) and metazachlor (150 $\mu g\ L^{-1}$) were observed at the NW.

There was no significant difference between inlet and outlet concentrations (i.e. there was no pesticide removal) in either wetland system ($p > 0.05$). Overall, both systems showed low potential to attenuate the studied pesticides, particularly during storm events, due to the short HRTs.

From 03/09/2014 to 13/10/2014, NW behaved as a static system and concentrations of the metaldehyde, quinmerac and metazachlor decreased quasi-exponential over time, suggesting that this attenuation might be due to biodegradation.

Keywords

Pesticide pollution, FWS CWs, Removal efficiency

3.2 Introduction

Pesticide pollution in surface waters can present major compliance challenges to water companies abstracting for domestic supply (Dolan *et al.,* 2013). In the European Union (EU), the Drinking Water Directive (DWD) stipulates that water supplies after treatment must have concentrations of individual pesticides which are less than 0.1 µg L^{-1} (Directive 80/778/EEC [EC, 1980] as amended by Directive 98/83/EC). Compliance challenges are especially acute when pesticides are difficult and or expensive to remove in conventional treatment trains (Dolan *et al.,* 2013; Dolan *et al.,* 2014). An important example is metaldehyde, which is a selective molluscicide widely used in slug pellets and applied to a range of arable crops. It currently exceeds the DWD limit in a number of drinking water supply catchments on a regular basis (Lu *et al.,* 2017). The standard treatment method for pesticide removal from raw water is sorption to activated carbon. In the case of metaldehyde, sorption is effective in the short term but removal efficiency rapidly decreases over time resulting in a low removal rate overall without frequent and expensive activated carbon regeneration (Tao and Fletcher, 2013).

The water industry is coming under increasing pressure from the Drinking Water Inspectorate (DWI) to find alternative solutions to supplement improvements in water treatment technologies and the focus has started to shift to source control options (Dolan *et al.,* 2012). Possible mitigation strategies include employing buffer zones to reduce overland flow and associated pesticide transport, taking more care during sprayer fill-up and washdown operations, treating farm yard runoff (*e.g.* using biobeds) (Vallée *et al.,* 2015), changing the mix of active ingredients used (where possible) and changing crop rotations to reduce overall catchment-scale usage (Gregoire *et al.,* 2009; Reichenberger *et al.,* 2007). Many of these options will involve costs to farming and should, therefore, be based on a sound understanding of the processes contributing to pesticide loss from the farm, as well as demonstrating efficacy. For example, establishing buffer zones will be of little use if, as shown in the Upper Cherwell catchment by Tediosi *et al.,* (2012) the main pathway for pesticide transfer from land to water is via field drains – which can effectively short circuit vegetative buffer zones. In cases where it is difficult or undesirable to effect land use change or reduce application rates, it may still be possible to reduce concentrations in the receiving surface water network by constructing attenuation features in fields (Maillard *et al.,* 2011) or in ditches (Tediosi *et al.,* 2012). Natural and man-made wetland habitats are well known to provide efficient removal of organic materials, nutrients, and metals via a combination of sorption and biodegradation before they are released into surface water (Gregoire *et al.,* 2009; Reichenberger *et al.,* 2007; Williams, 2002). A number of mesocosm studies have indicated that constructed wetland systems do have the potential to dissipate a range of soluble pesticides (Sherrard *et al.,* 2004), and there is some evidence that such systems may also perform effectively at the field scale using FWS CWs (Passeport *et al.,* 2013). Therefore, there is the need to investigate if FWS CWs can be used as a catchment solution for reducing pesticide pollution from agricultural runoff. A five month monitoring campaign was conducted in two FWS CWs situated in Hope Farm, Knapwell, Cambridgeshire. Stream discharge, rainfall and concentrations (Inlet and outlet) of pesticides metaldehyde, carbetamide, quinmerac, metazachlor, propyzamide and pendimethalin were monitored to assess the removal efficiency of FWS CWs for a range of pesticides with different physicochemical properties.

Many pesticides have some affinity for sediment and can sorb to sediment surfaces and be sorbed within the organic matter matrix (Wauchope *et al.,* 2002). In some situations (*i.e* where there is a fugacity gradient between the water column and the sediment) the sediment can act as a sink for pesticides in the water column. Similarly, pesticides can “bleed” (desorbed) into the water column if the fugacity gradient is the other way round (higher fugacity gradients, pesticides may also be exchanged between the two compartments in association with particulates). The direction of the exchanges will depend on the net particulate balance and the concentrations of pesticides on suspended particles in the water column and on settled particles in the sediment itself. Sediment resuspension often occurs in high flow regimes, which can release previously deposited or sorbed pesticides in the water column. This study presents findings of a field experiment where concentrations in sediment pore water and water column where compared, to assess if FWS CWs can behave as a sink for pesticides.

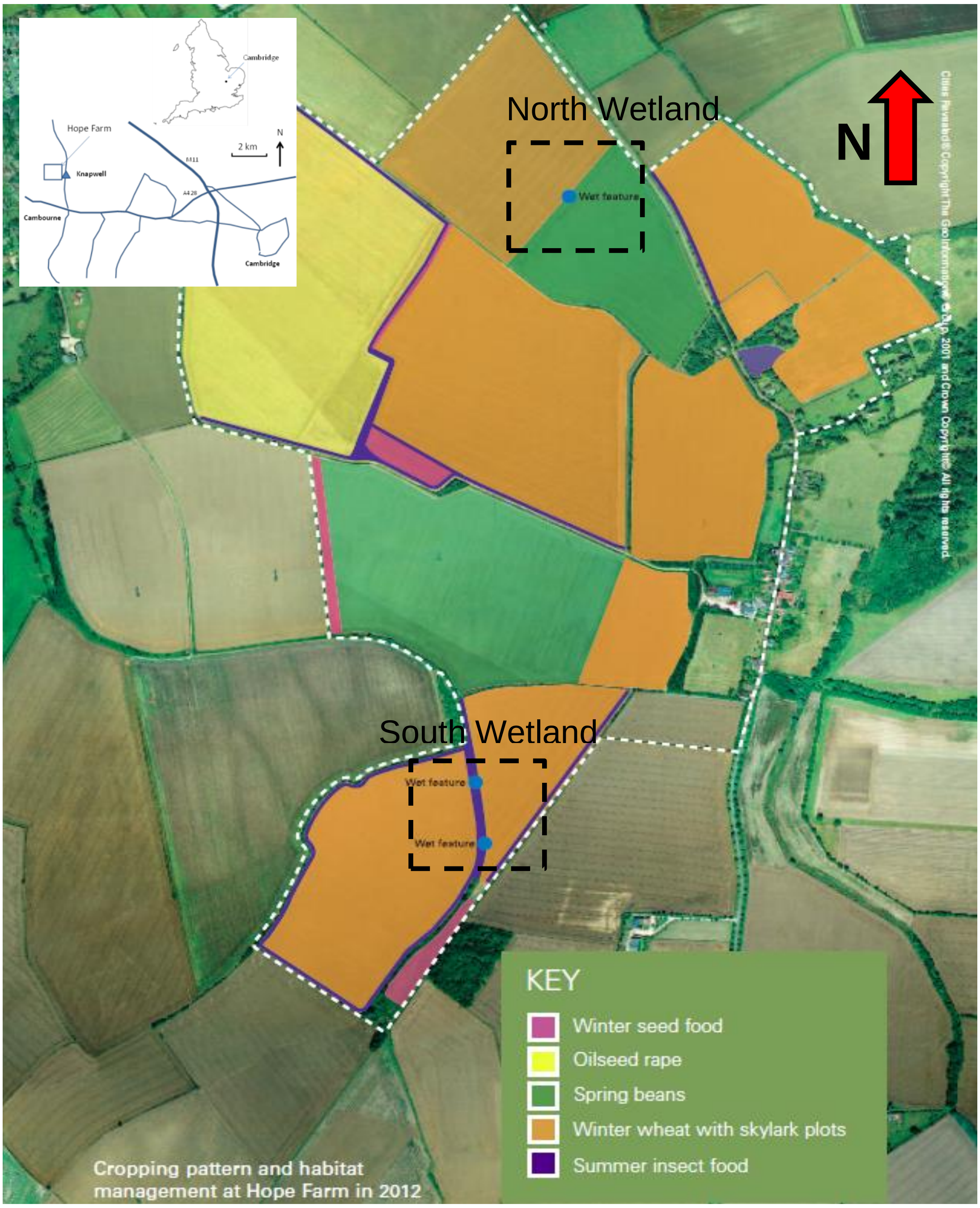
3.3 Methods

3.3.1 The study area

The study was conducted at Hope Farm, which is situated in Knapwell, Cambridgeshire (N 52°26’13’’, W 83°35’17’’) in eastern England (Figure 3.1). Over the last 12 years, the farm has been owned by the Royal Society for the Protection of Birds (RSPB) and operated on a commercial basis in order to demonstrate the feasibility of simultaneously generating reasonable economic margins and achieving a high level of wildlife protection. Key goals include maximising biodiversity, maintaining high profit, reducing greenhouse gas emissions and mitigating diffuse pollution.

Several small constructed wetlands have been built on the stream and ditch networks on the farm (Figure 3.2) – principally as water stores and to enhance the variety of habitats available on the farm for biodiversity – particularly bird populations. The farm occupies 1.81 km^2 although the stream which flows through it from the south has a much larger catchment area (3.9 km^2). The main soil type in the area is calcareous clay loam belonging to the Hanslope soil series.

All the monitored wetlands were a free water surface with emergent vegetation. Vegetation cover in all three systems was seasonal and was dominated by reeds (*Phragmites australis*) and bulrushes (*Typha latifolia*) which start growing in spring and die back in late autumn. The winter period was characterized by progressive stem decay which may progressively result in reduced flow resistance. Two FWS CWs were monitored, referred to henceforth as the north and south wetlands systems. It should be noted that the monitored wetlands were not constructed specifically for the purposes of mitigating diffuse-source pollution transfers. Ideally, their dimensions should be based on optimising residence time in order to allow for losses due to volatilisation and degradation (hydrolysis, photolysis and biodegradation) and for sorptive equilibration with the sediment. This should be achieved in the context of their upslope catchment area, where relative residence time can be approximated from the wetland volume to catchment area ratio, given that catchment area can be used as a surrogate for stream discharge.



Cropping pattern and habitat management at Hope Farm in 2012

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Figure 3.1. General location of the monitored wetlands at Hope Farm, Cambridgeshire, UK.

South Wetland system

At the south site, two wetlands have been placed in series (about 114 m apart) on a small stream: South Wetland 1 (SW1) and South Wetland 2 (SW2) (Figure 3.2).

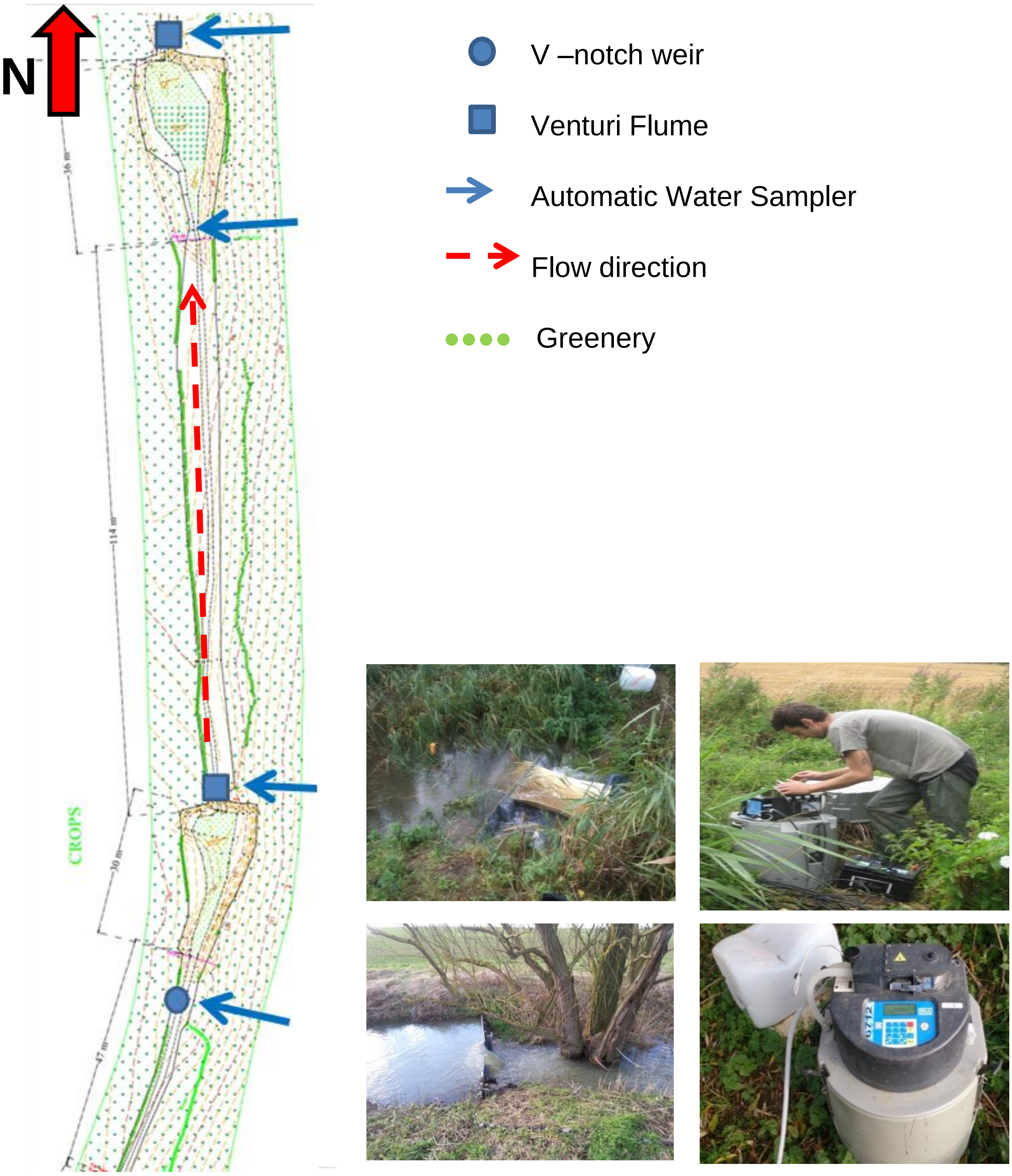

Figure 3.2. Detailed contour maps of the South Wetland system at Hope Farm, showing the locating of the flow control structures and automatic samplers Direction of flow is indicated with red dashed arrow.

The catchment area for this stream is approximately 3.9 km^2 (Figure 3.3) and water flow was continuous over the monitoring period (August to December 2014).

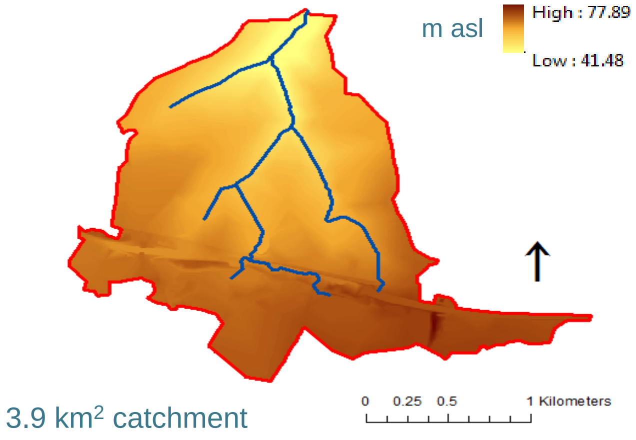

Figure 3.3. Catchment area and elevation map for the South Wetland system derived from UK Ordinance Survey Terrain 5 Data (5m gridded DEM)

North Wetland system

At the north site, a single constructed wetland (Figure 3.4) has been excavated on a drainage ditch.

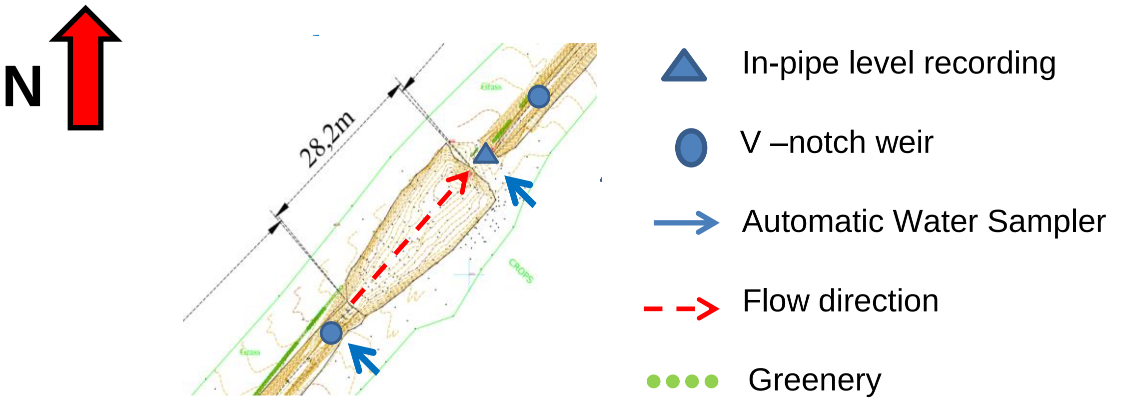

Figure 3.4. Detailed contour maps of The North Wetland system at Hope Farm showing the locations of the flow control structures and automatic samplers.

At the downstream end, a bund has been constructed which over flows via a 37 cm diameter pipe (Figure 3.5 b). This means that the flow regime on this system is intermittent (*i.e.* the wetland only flows when water levels exceed the level of the outflow pipe).

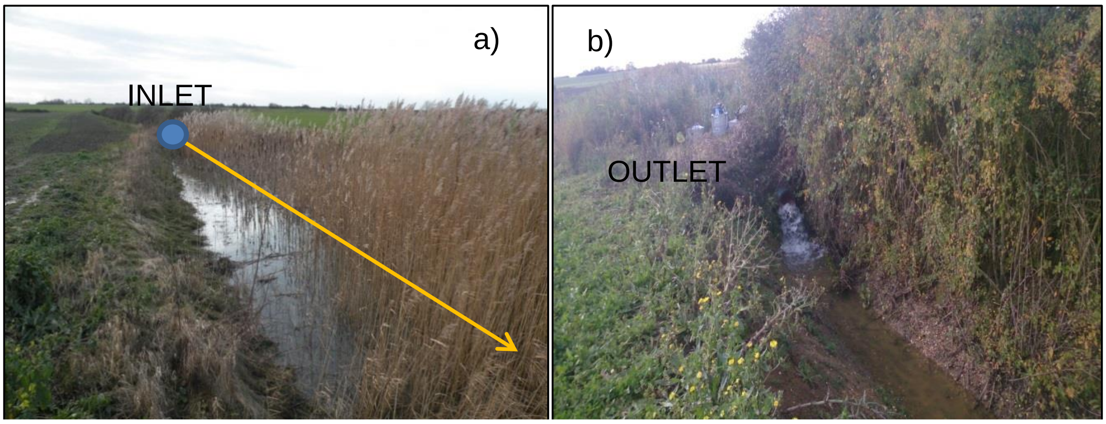

Figure 3.5. NW system – a) Inlet and overview of the wetland (the yellow line indicates flow direction) b) Outlet pipe

This feature drains a catchment of approximately 0.66 km^2 containing 4 different fields (Figure 3.6).

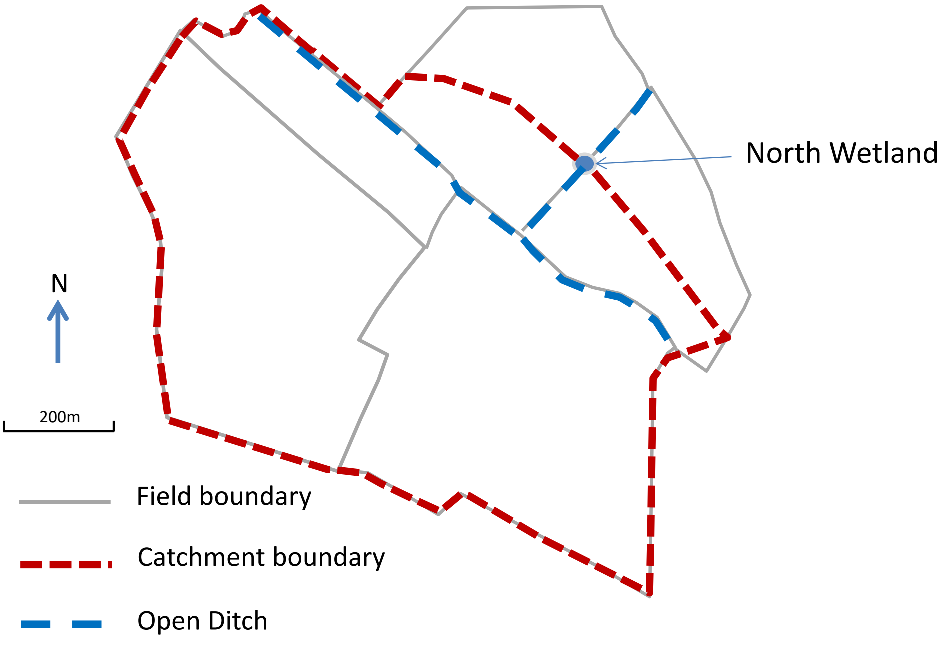

Figure 3.6. Catchment area and field boundaries for the NW

3.3.2 Monitoring Equipment

A tipping bucket rain-gauge was installed approximately 500 m east of the SW and was set to monitor rainfall every 1 min. Automatic water samplers (ISCO® 6712) were installed at the inlet and outlet of each wetland system and also used to log water depth, velocity and turbidity (frequency 1 minute) via attached probes (AV2150® submerged probe flow module, ISCO®) (Figure 3.3 c and 3.3f). Water samples were collected every 8 hours. Collection started in August 2014 and was more or less continuous through to mid-December 2014. Batteries and sampler bottles were changed once a week. All samples were kept in the dark at 4°C before analysis. Additional pressure transducers (Solinst® levelogger, UK) were installed at the outlet of SW1 and at the outlet of the NW to log water depth every 5 minutes (corrected for barometric pressure). V-notch weirs (Figure 3.3b) and venturi flumes (Figure 3.3g) were installed at three locations on the SW system to measure discharge from water depths using respective free-flow equations. Flows occasionally exceeded the maximum threshold for accurate discharge estimation in the flow control structures in the SW. Under these conditions, discharge was estimated from the cross-sectional area above the weir upper crests between the channel banks.

3.3.3 Dye Tracing

Dye tracing tests were conducted in collaboration with the School of Engineering at the University of Warwick. A pulse of Rhodamine WT (a red fluorescent dye: Hubbard *et al.,* 1982; Whelan *et al.,* 2007) was injected upstream of the inlet of the wetland under consideration and the concentrations of dye were monitored continuously at both the inlet and outlet using logging fluorometers (self-contained underwater fluorescence apparatus: SCUFA) fixed *in situ*. The hydraulic residence time is approximately given by the difference in the centroid arrival time at the inlet and outlet where the centroid is the centre of mass of the fitted breakthrough curve. In reality more sophisticated techniques of deconvolution or computation fluid dynamics can also be employed to yield the distribution of residence times (Ioannidou, 2018; Sonnenwald *et al.,* 2018).

3.3.4 Pesticide application

Six pesticide active ingredients with different organic carbon to water partition coefficients (K_{oc}), degradation half-lives (DT_{50}) and application rates (Table 3.1) were monitored: the molluscicide metaldehyde, and the herbicides quinmerac, carbetamide, metazachlor, propyzamide and pendimethalin. All pesticides were applied on the farm once a year between mid- August and mid-December 2014 with no reapplications in this period. It should be noted that in the case of the NW the catchment is small and entirely on the farm so applications are well known. In fact, only Field 5 (Figure 3.6) received pesticides in this catchment. However, in the case of the SW, the large catchment area includes several other farms and the application regime is unknown. Two fields operated by Hope Farm are in the SW catchment which received metaldehyde on 24/10/14 and 26/10/14 and pendimethalin on 28/10/14.

Table 3-1. K_{oc} and DT_{50} from Lewis *et al.,* (2016) and application rates for the six pesticides monitored in this study.

Chemical	K_{OC} (L kg^{-1})	DT_{50} (days)	Application Rate (kg ha^{-1})	Product name	Application date to Field 5
Metaldehyde	240	12.2	0.18	Tds Major®	19/08/2014
Quinmerac	86	179.4	0.25	Palometa®	21/08/2014
Carbetamide	89	55.5	1.79	Crawler®	4/12/14
Metazachlor	54	20.6	0.75	Palometa®	21/08/2014
Propyzamide	840	94	1.05	Artax Flo®	21/11/2014
Pendimethalin	17581	16	1.09	Crystal®	27/10/2014

3.3.4 Pesticide analysis

A multi-component analytical method was developed by Ramos *et al.,* (2017) to quantify pesticides concentrations in water samples. All analyses were performed with a Waters Alliance 2695 liquid chromatography system coupled to a Quattro Premier XE tandem quadrupole. A Kinetex C18 column (Phenomenex, UK) was used for chromatographic separation. Samples were filtered with 0.2 µm syringe filters (Milipore Millex^{TM,} Fisher Scientific, UK) and analysed in triplicate

3.3.5 Quality assurance

Possible losses of pesticides by sorption or degradation during sample storage were evaluated via a stability study. Pesticide standards were added to wetland water in polyethylene plastic bottles at nominal concentrations of 0.2 to 10 µg L^{-1} and incubated 4°C. Standards were analyzed over a period of 112 days using the method described by Ramos *et al.,* (2017). No significant sorption was observed in the filter membrane. Losses of all pesticides were below 3% over this period, suggesting that stored samples were stable.

3.3.6 Data analysis

For data analysis, only concentrations above the limit of detection (LOD) were considered. The inlet-outlet concentrations were plotted to compare performance in each wetland system. A slope of the regression line close to unity indicated concentrations at inlet and outlet were similar. A paired sample t-test was also performed to assess if there was a significant difference between inlet and outlet concentrations. The paired sample t-test for paired samples at 95% confidence interval was done with the null hypothesis being that the pesticide concentrations at the inlet and outlet were equal. The null hypothesis was rejected when the p-value was below 0.05.

3.4 Results and Discussion

3.4.1 South Wetland system

Figure 3.7 shows daily rainfall and stream discharge at SW inlet and outlet during the monitored period from 14/08/2014 to 24/12/2014. The average discharge on SW system was 19.3 L s^{-1}. Total rainfall during the monitored period was 341 mm (753 mm $year^{-1}$).

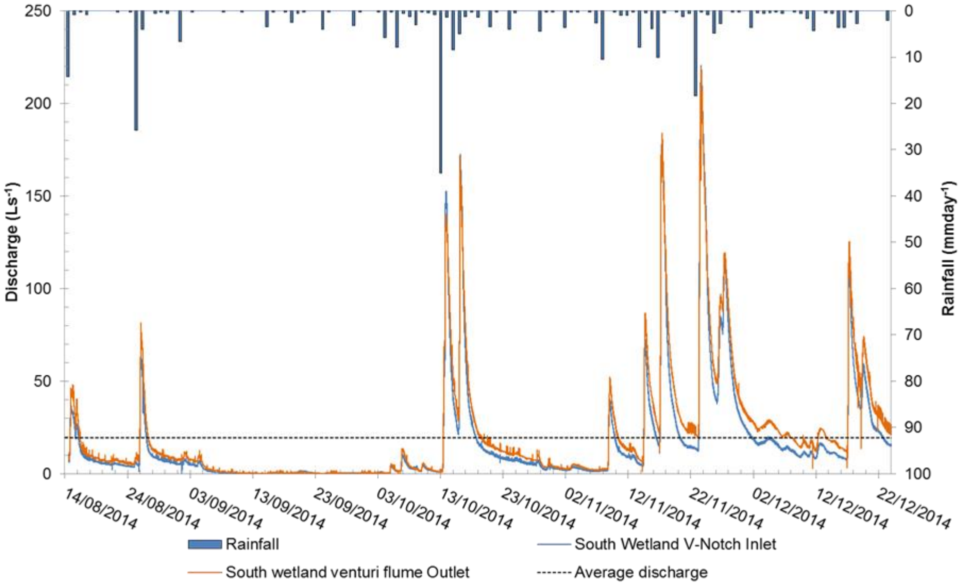

Figure 3.7. Discharge at inlet and outlet of SW system and rainfall during the monitored period (14/08/2014 to 24/12/2014)

Figure 3.7 shows the recorded discharge (L s^{-1}) was very similar at the inlet and outlet. Several peaks discharges were observed after rainfall events. Lag time to peak discharge was typically 24 hours and recession curves were approximately exponential in all cases. Two significant rainfall events occurred during August: (14 mm day^{-1} on 14/08/2014 which generated a discharge of 46 L s^{-1} and 26 mm day^{-1} on 25/08/2014 which generated 78 L s^{-1}). Base flow during summer dry periods (e.g. 3/09/2014 - 3/10/2014) was about 1.5 L s^{-1}, but higher in the winter. Maximum daily rainfall (35 mm day^{-1}) was recorded on 13/10/2014 which generated a discharge of 152 L s^{-1} the day after. The maximum observed discharge was 170 L s^{-1} (23/11/2014).

Several dye traces were conducted to estimate the residence time of the SW system. The HRT of the SW system (*i.e.* the two small wetlands in series) was an average of 1.9 hours. However, during high flow peaks (e.g.13/10/2014 and 22/11/2014) hydraulic residence time decreased to 32 minutes. During baseflow, the estimated HRT was around 4 hours. This HRT is short compared with other studies reported in the literature which are often in the order of days (Maillard *et al.,* 2011; Passeport *et al.,* 2013).

Pesticide concentrations

Metaldehyde

Rainfall, discharge and metaldehyde concentrations in the inlet and outlet of the South wetland system are shown in Figure 3.8. Metaldehyde concentrations were already elevated above the limit of detection (LOD) when monitoring started on the 14/08/14 – possibly responding to a storm even on the same day – and suggesting that metaldehyde had already been applied in some of the catchment. The highest concentrations of metaldehyde (9 µg L^{-1} at inlet SW1) were observed on the 28/08/14 about three days after the rainfall event and associated flow peak of 25/08/14. This delay in concentration response could have been due to the disintegration of the slug pellets on the soil surface and the transport of metaldehyde to field drains under the relatively dry soil conditions during this period. Soil moisture may also control the rate of pellet disintegration.

A second major increase in metaldehyde concentrations was observed during October (13/10/14), where levels rose from 0.5 to 4 µg L^{-1} during the rising limb of the hydrograph. Again, similar concentrations were observed in both the inlet and outlet of SW2. The third increase in metaldehyde concentrations was observed during November (17/11/14) in which concentrations increased from 0.1 to 1.3 µg L^{-1} at the inlet, with similar levels observed at the outlet. Metaldehyde concentrations in inlet and outlet samples (*i.e.* where the outlet sample was collected within 1 hour of the inlet sample time) were plotted against one another to assess removal efficiency. A slope close to unity indicates that metaldehyde inlet and outlet concentrations were similar (Appendix A1, Figure 7.1). These concentrations were also compared formally using a paired t-test to assess whether differences were statistically significant. For metaldehyde, 220 paired inlet and outlet samples were analysed. The paired sample t-test results showed no significant difference ($p = 0.98$) between inlet and outlet concentrations of metaldehyde.

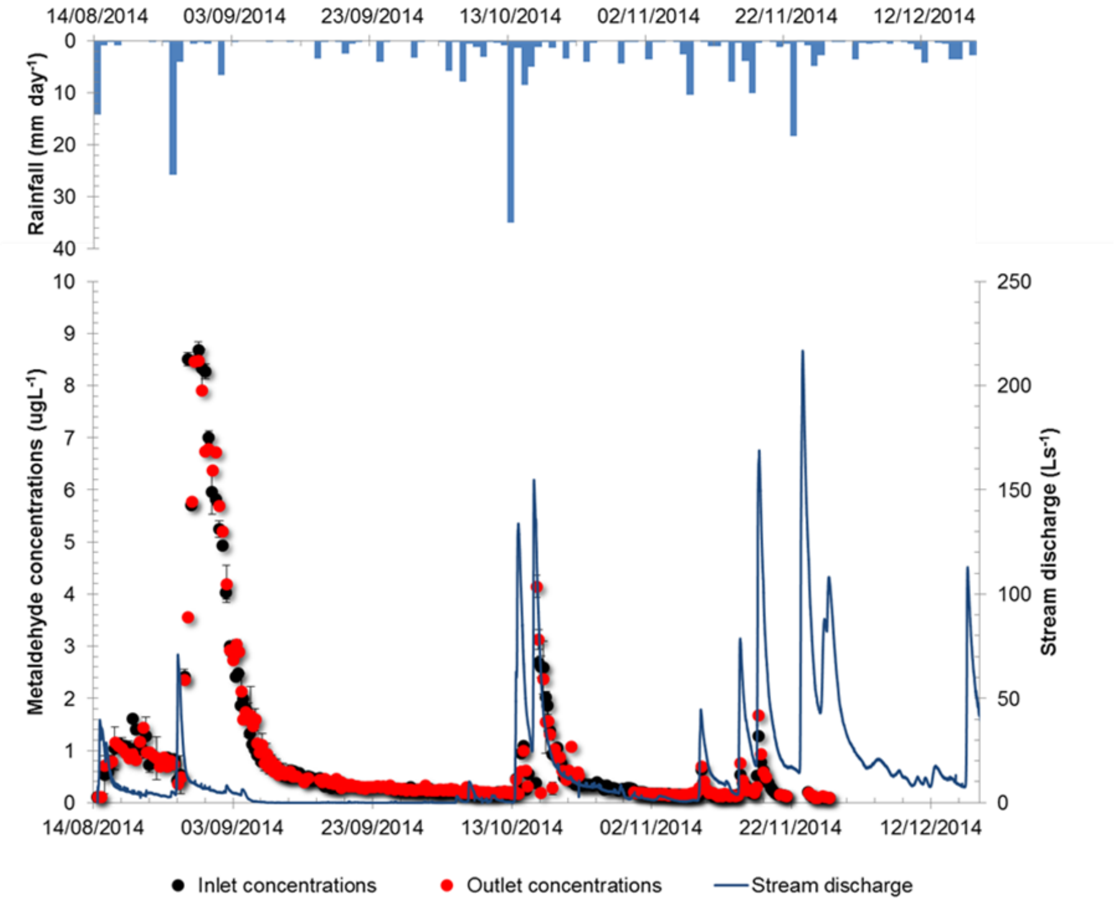

Figure 3.8. Metaldehyde concentrations (μg L^{-1}) inlet and outlet of SW system, daily rainfall (mm day^{-1}) and stream discharge (L s^{-1})

Carbetamide

Figure 3.9 shows discharge (L s^{-1}), rainfall (mm day^{-1}) and carbetamide concentrations (μg L^{-1}) observed on the inlet and outlet of SW system during the monitored period. Prior to mid-November, carbetamide concentrations were close to or below the LOD (0.09 μg L^{-1}). In the case of carbetamide the concentration pattern appears to be inconsistent with the hydrological data – at least for the first half of the data set shown (13/11/14 to 20/11/14) – with elevated concentrations during hydrograph recessions. Concentrations increased to 4.0 μg L^{-1} before the peak discharge on 15/11/14. Currently, there is not a physically feasible explanation for these data, but it was retained because they add information value regarding pesticide behaviour in the wetland system. Phillips and Bode, (2010) reported peak concentrations of diazinon during an initial peak discharge and suggested that could reflect the wash off of pesticides or spillage. However, in this case for carbetamide, concentrations should be higher and would be noticed at one particular moment and not in different days (13/11/2014 -16/11/2014).Due to the autosamplers failures, samples were not taken from 21/11/14 to 23/11/14. Carbetamide concentrations of 1.0 μg L^{-1} were noticed on 24/11/14 both inlet and outlet of SW and decreased over time to LOD limits during the falling limb of the hydrograph.

Carbetamide concentrations in the inlet and outlet samples were plotted (Appendix 7, Figure 7.2). The slope close to unit showed concentrations to be very similar. The paired sample t-test showed no significant difference ($p = 0.72$) between 47 samples collected in total (at the inlet and outlet).

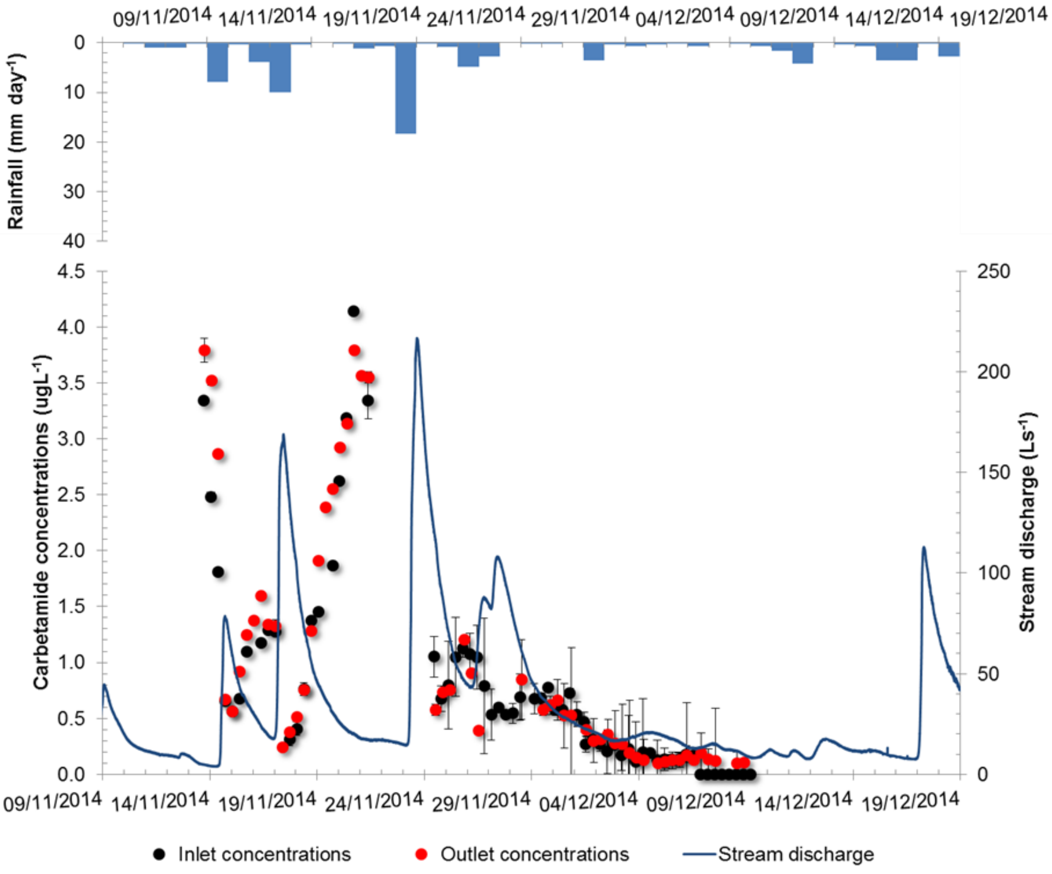

Figure 3.9. Carbetamide concentrations (μg L^{-1}) inlet and outlet of SW system, daily rainfall (mm day^{-1}) and stream discharge (L s^{-1})

Propyzamide

Figure 3.10 shows discharge (L s^{-1}), rainfall (mm day^{-1}) and propyzamide concentrations (µg L^{-1}) observed on the inlet and outlet of SW system during the monitored period. Propyzamide concentrations increased significantly between early and mid-December – presumably after application in the catchment and subsequent release in the rainfall event of the 11th-14th December which generated only a minor increase in stream discharge but a marked increase in concentrations. During this period, propyzamide concentrations of 2.6 µg L^{-1} were observed at the inlet and decreased to 1.3 µg L^{-1} over time until 14/12/2014. An early a peak discharge of 112 L s^{-1} on 17/12/2014 was observed and propyzamide concentrations increased to 2.1 µg L^{-1} after 7 hours.

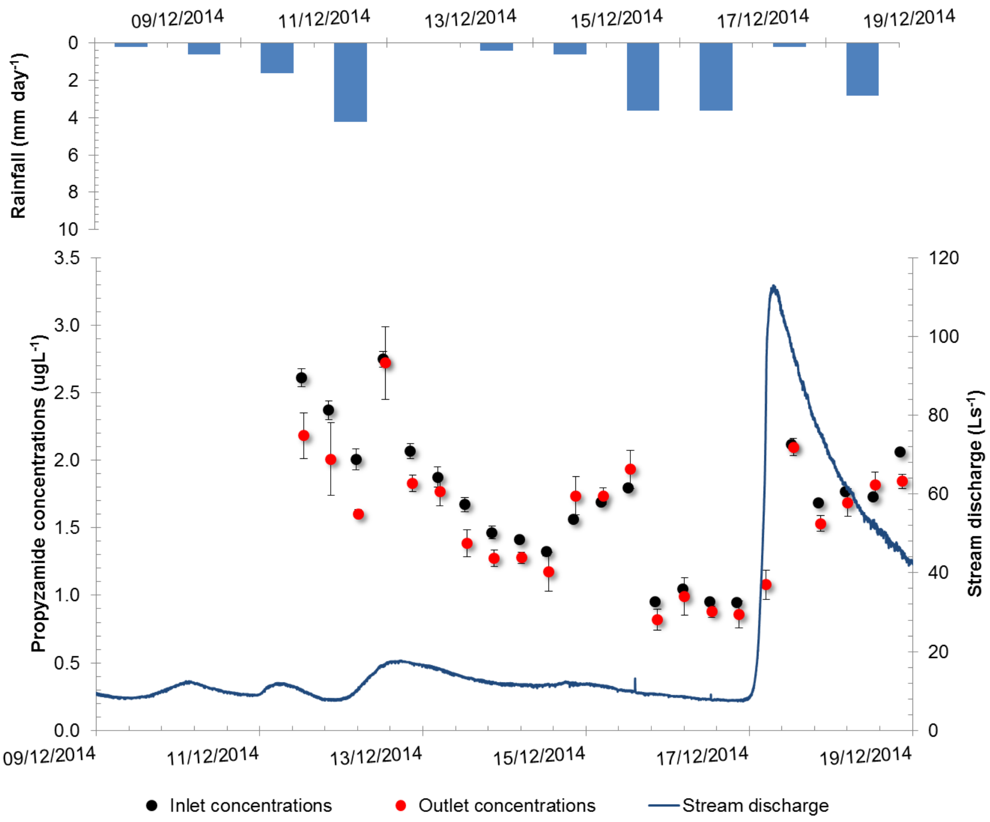

Figure 3.10. Propyzamide concentrations (µg L^{-1}) inlet and outlet of SW system, daily rainfall (mm day^{-1}) and stream discharge (L s^{-1})

Propyzamide concentrations in the inlet and outlet samples were plotted (Appendix 7, Figure 7.3). The slope close to unit showed that propyzamide inlet and outlet concentrations were similar. The paired sample t-test showed no significant difference ($p = 0.35$) between 23 samples collected in total.

Results suggested that SW system does not have any potential for mitigating pesticides with a range of chemical properties (e.g. K_{oc}, and DT_{50}). This is most easily explained by the short HRT of SW system. As shown in Figure 3.8 , 3.9 and 3.10, pesticides inputs in streams are generated after application triggered by rainfall events. The highest peak concentrations of metaldehyde, carbetamide and propyzamide were observed after peak discharges on 26/08/2014, 17/11/2014 and 17/12/2014, respectively. The HRT during the peak concentrations was 161, 94 and 135 minutes, respectively. Bendoricchio *et al.,* (2000) on guidelines for the design of FWS CWs, describes the HRT as an important parameter for controlling the removal efficiency of organic pollutants and suggested for effective attenuation, the detention time should be in between 5 and 14 days. Normally, HRT yields higher removal rates, because pesticides have time to interact with the sediment, microorganisms and plants responsible for removal via uptake, sorption and chemical reactions (e.g. hydrolysis, biodegradation) (Budd *et al.,* 2011; Maillard *et al.,* 2011; Passeport *et al.,* 2013).

Comparing concentrations in sediment pore water and the water column at SW1 outlet

Over some of the monitored period, concentrations of metaldehyde at the outlet of SW1 were higher than those observed at the other stations on the SW system (Figure 3.11)

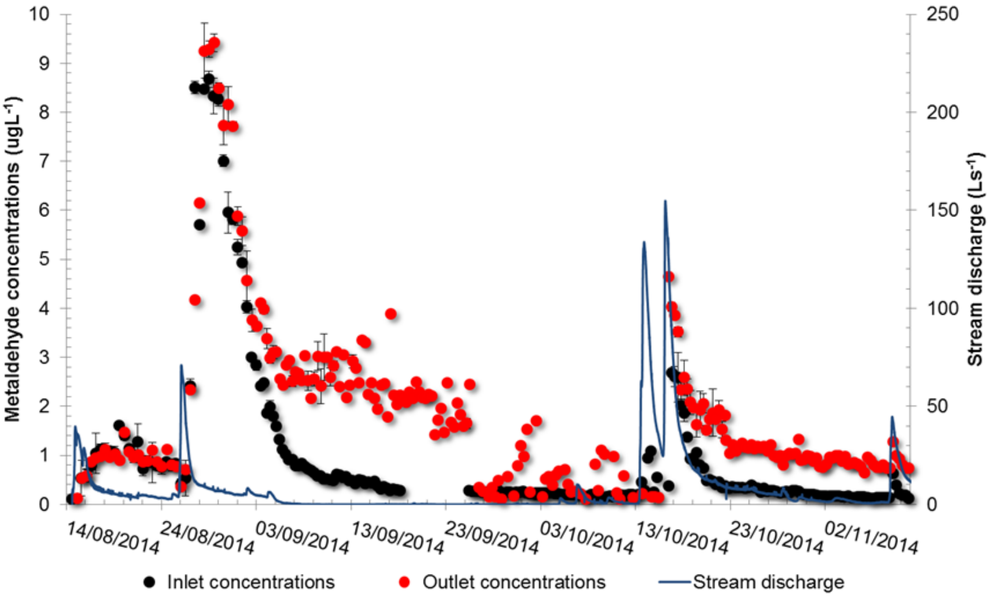

Figure 3.11. Metaldehyde concentrations (μg L^{-1}) inlet and outlet of SW1 and stream discharge (L s^{-1})

After the peak concentrations of 9.0 μg L^{-1} on the 30/08/2014, outlet concentrations stayed relatively higher than the inlet throughout several days. Similar observations were seen after the peak discharge on 13/10/2014, where outlet concentrations are higher than the inlet.

The elevated concentrations at South Wetland 1 outlet are due to an artefact of some sort. Inspection of the sampler tube during mid-November showed that it had been buried with sediment. This probably occurred during the recession period of the event hydrograph which occurred on the 25/08/2014. Therefore water samples may have been collected from the pore water than from the water column. To confirm this hypothetical explanation, a field experiment was performed in November 2015. On the 26/11/15, two automatic water samplers were set up such that one sampled from the water column and the other sampled from beneath the sediment surface. Samples were collected every 8 hours, with a sampling delay between the two samples of 5 minutes to avoid mixing the samples. Samples were collected for one week (*i.e.* a total of 24 samples were collected). Metaldehyde concentrations measured in samples collected from the sediment pore water and the water column are shown in Figure 3.12.

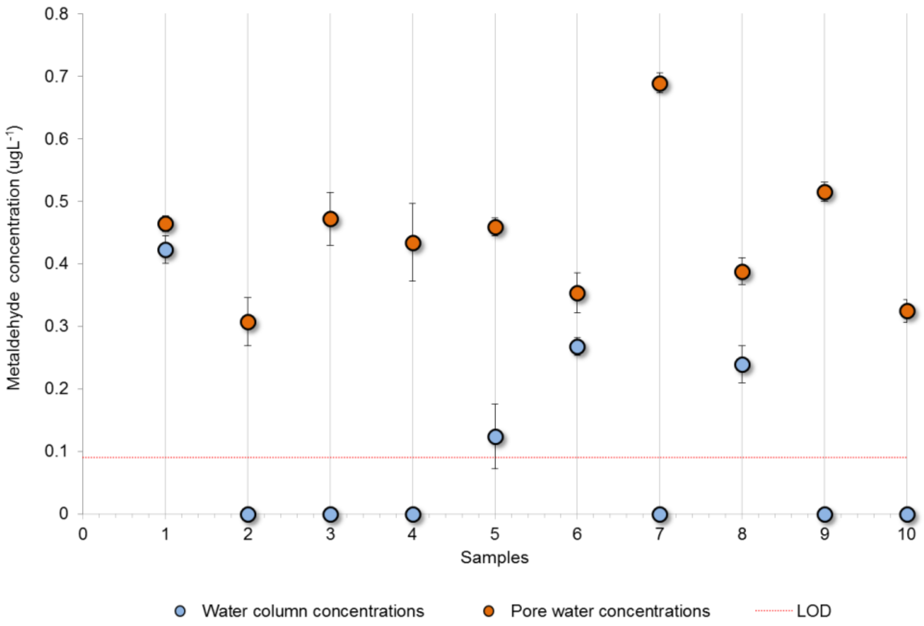

Figure 3.12. Metaldehyde concentrations in samples collected from beneath the pore water and from the water column in November 2015

Concentrations in samples collected from beneath the sediment surface (mainly interstitial water, but also some particulates were collected too) were higher than in samples collected from the water column. Although the magnitude of the difference between the concentrations collected using the two samplers was not as large as the difference between concentrations observed in autumn 2014, these data suggest that the hypothesis for explaining the concentration discrepancies at this station in 2014 is a reasonable one.

This phenomenon was also observed by Tournebize *et al.,* (2016) who reported higher concentrations of pesticides on free-water surface wetlands outlets and explained these observations via detachment of sediment and biofilm during storm events. This could be explain by understanding the adsorption-desorption kinetics of pesticides in wetland sediment. Usually, pesticides sorption in sediment will be faster reaching equilibrium in order of hours, followed by a slow sorption over a longer period. The initial fast sorption is a surface phenomenon, followed by a slow sorption and migration of the pesticide into the organic matter matrix and mineral structure of the sediment. Desorption process will be similar to sorption, but the equilibrium will be achieved at slower rate. However, once the concentrations the water phase decreases, the adsorbed pesticides will move from the sediment phase to the water phase to establish the equilibrium (Bowman and Sans, 1984). Results suggested sorption of pesticides in sediment-soil systems can be reversible and depending on the floods can mobilize the return to the water column, according to their dissipation dynamics in soil and sediments. Adsorption of pesticides to aquatic sediment data is of interest for understanding its fate in surface and groundwater. This would help on designing structural prevention approaches for pesticides attenuation, such vegetated ditches, ponds and constructed wetlands systems. Adsorption-desorption studies are usually design for determination of K_{oc} values in soils rather than aquatic sediments, in which, there is evidence to be different (Gao *et al.,* 1998)

3.4.2 North Wetland system

Rainfall, discharge and water depth

The following pesticides were applied to a limited fraction of the NW catchment (date and rate shown in parentheses): metaldehyde (19/8/14; 0.18 kg ha^{-1}); quinmerac (21/8/14; 0.25 kg ha^{-1}); carbetamide (4/12/14; 1.79 kg ha^{-1}); metazachlor (21/8/14; 0.75 kg ha^{-1}); propyzamide (21/11/14; 1.05 kg ha^{-1}) (Table 3.1). Figure 3.13 shows daily rainfall, outlet pipe discharge and the concentrations of quinmerac, metazachlor and metaldehyde in the NW between late August and late October 2014. The reliability of the flow control structures in the NW was poor overall and on several occasions, failures occurred on v-notch weirs installed upstream and downstream of the wetland. The outlet pipe discharge and the level logger data within the wetland were, therefore, considered to be most reliable (at least in the initial monitoring period in autumn 2014). Both the ditch and the wetland were relatively dry in early August. The NW is bunded at the outlet and the outlet pipe of the wetland was not observed to flow when the recorded level logger water level was below 43.5 cm. Unfortunately, no water level data were available prior to 3/9/2014 so it is not possible to correlate flow with water level for this event. Water depth decreased linearly over time between the 3/9/2014 and the 13/10/2014. During this period the NW essentially behaved as a static system with no outlet flows (and probably little if any inlet flows: a few minor rainfall events were recorded in this period). The point at which the water level in the wetland reduced to below the level of the overflow is indicated with a red dashed line (Figure 3.13).

According to the pesticide application information supplied by the farm manager, Palometa (12.5% quinmerac and 35.5% metazachlor) was applied to Field 5 (0.26 km^2) in the NW catchment (Figure 3.7) on 21/08/2014. The event of the 25/08/2014 triggered a significant peak in quinmerac concentrations of 150 µg L^{-1} recorded in inlet samples (data not shown) and 130 µg L^{-1} in samples collected at the outlet. Outlet discharge decreased sharply in the post-event period suggesting that rapid hydrological pathways such as overland flow may have played a significant part in the event. Hope farm soil was defined as clay loam soil, with an infiltration rate of 3 to 5 mm hour^{-1} (Gregoire *et al.,* 2010). Most of the rainfall event occurred on 25/09/2014, took place between 8 pm and 12 pm (17.1 mm), at an hourly rate of 4.27 mm hour^{-1}. Considering the previously amount of rainfall, that could have increased the soil moisture content and the influence of the slope of field 5 on the infiltration rate, it was assumed that the transfer of pesticides occurred via overland flow (*e.g.* surface runoff).

Concentrations in inlet and outlet samples decreased more gradually than the outflow discharge – particularly in samples collected from the outlet. No flow was detected after 4/9/2014 and it was assumed that samples from both the inlet and outlet were being collected from static water in this period. Inlet quinmerac concentrations (data not shown) decreased from 150 µg L^{-1} (26/08/2014) to 6.5 µg L^{-1} (06/09/2014). Some samples were missing from the sampler bottle tray during this period, due to lack of flow and, therefore, the data at the inlet over this period were difficult to interpret. Quinmerac concentrations at the outlet decreased to 50 µg L^{-1} on 2/09/2014. This decline was partly due to dilution caused by minor rainfall events in this period, as well as water turnover (high-concentration advective outflow replaced with lower concentration inflow). Subsequently, quinmerac concentrations decreased slightly during the rainless period (13/10/2014), in parallel with the linear decrease in water depth (from 30 cm to 12 cm). The concentration in the last sample taken from the outlet before the storm event on the 13/10/2014 (25 mm day^{-1}) was 35 µg L^{-1}. This event caused water levels to increase beyond the overflow and discharge to increase to 186 L s^{-1} (not shown in Figure 3.20). In parallel, quinmerac concentrations rapidly decreased to 5 µg L^{-1}. This was a clear dilution effect in which quinmerac appears to have been flushed out of the wetland by low concentration inflows. This is interesting because it suggests that either the hydrological pathways which were active during this event (e.g. overland flow) were not spatially coincident with significant amounts of residual quinmerac in the soil or that quinmerac concentrations in soil pore water were insignificant at this time.

Relative changes in metaldehyde concentration over the initial part of the period after the event of the 25/8/2014 were very similar to those observed for both quinmerac and (to a lesser extent) metazachlor. This reflects the dynamics of inflow and outflow discharge and concentrations as well as the temporal pattern of concentration change during the recession period of the event. Like for quinmerac, in the period after the 4/9/2014, metaldehyde concentrations also appeared to decrease more gradually. On 25/09/2014, metaldehyde concentration was 7.0 µg L^{-1} and decrease to 0.6 µg L^{-1} (data was removed from Figure 3.20.) just in 8 hours. This data was removed because this observation was not consistent with the other pesticides and probably was due to an analytical artefact. The current hypothesis is based on metaldehyde volatilisation from the water samples from bottles before analysis. Metaldehyde has a relatively high Henry's law constant (3.5 Pa m^3 mol^{-1}) (Lewis *et al.,* 2016) compared with other pesticides. This means that it is possible for some volatile loss to occur from the water samples, in particular if there is a significant headspace or if the bottles are improperly sealed (Kolk and Crum, 1993). However, further studies need to be conducted in order to confirm whether this is a valid hypothesis (e.g. measuring and modelling metaldehyde volatilisation under different temperatures).

The behaviour of metazachlor during the static period differed from quinmerac and metaldehyde. During the static period, metazachlor concentrations decreased quasi-exponentially from 54 µg L^{-1} to 2.6 µg L^{-1}. The mechanisms for this removal are still not completely understood but the shape of the concentration decay suggests that some biodegradation of metazachlor may have occurred within the wetland over this period.

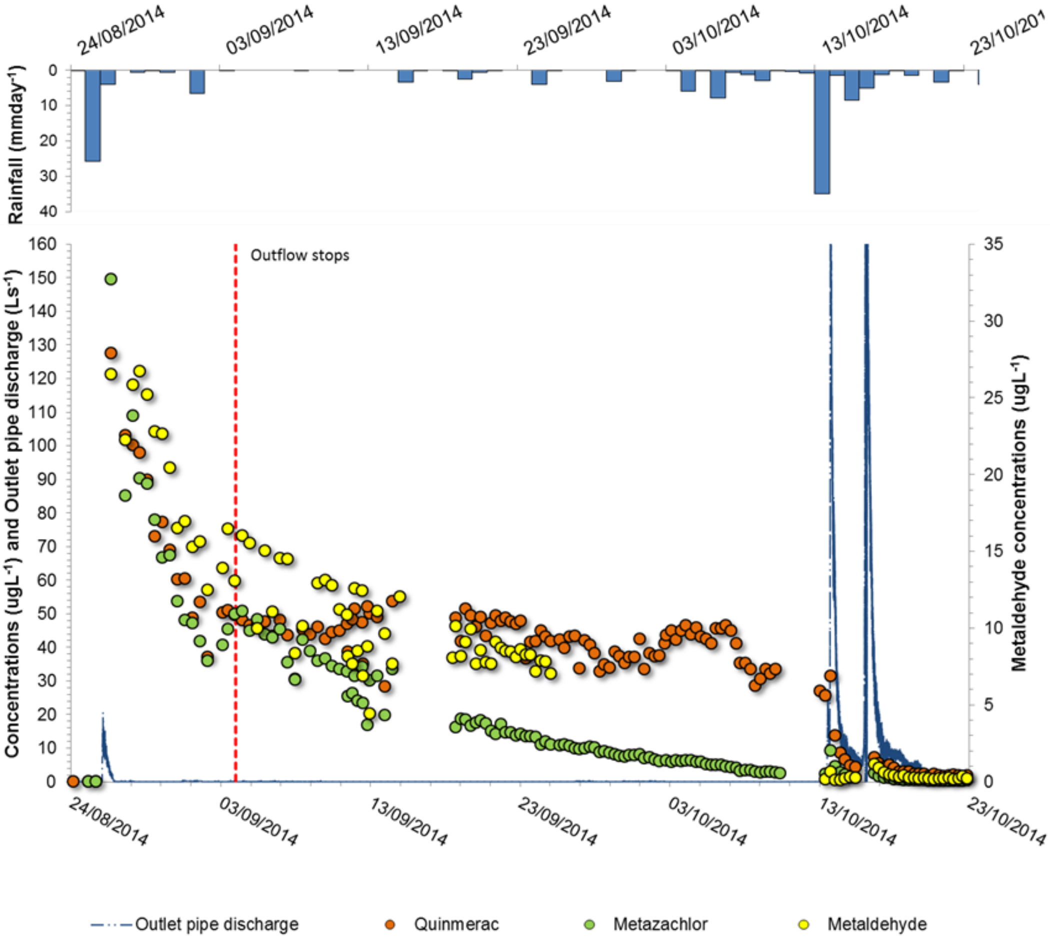

Figure 3.13. Outlet pipe discharge and the concentrations of quinmerac, metazachlor and metaldehyde in the NW between late August and late October 2014. The point at which the water level in the wetland reduced to below the level of the overflow is indicated with the red dashed line. Note different y-axis for metaldehyde.

The decrease in metazachlor and metaldehyde observed during the static period in the NW were the first real observations for these pesticides. The findings suggest that FWS CWs can mitigate these pesticides to some extent and the removal mechanism is likely to be microbially-mediated biodegradation. However, the HRTs required for these systems to obtain a 50% reduction in concentration for metaldehyde and metazachlor would need to be at least equivalent to their apparent *DT_{50}*s (i.e. 17.3 and 9.9 days, respectively).

Pesticides concentrations during outflow periods

Several peak concentrations of quinmerac, metazachlor, metaldehyde and propyzamide were recorded on the inlet and outlet of NW during the outflow period from 13/10/2014 to 19/12/2014.

Quinmerac

The rainfall event of 34 mm day^{-1} on the 13/10/2014 generated peak discharge of 187 L s^{-1}. Quinmerac concentrations decreased from 32 µg L^{-1} to 8.6 µg L^{-1} at the outlet (Figure 3.14). The increased water volume in the wetland promoted a dilution of quinmerac within the system. Concentrations were relatively constant throughout mid-November both at the inlet and outlet. Outlet flow was not recorded from 19/10/2014 to 8/11/2014, due to some technical failures. However, several visits to the farm and information from the farm manager confirmed that the wetland was flowing at this particular period. Several quinmerac peak concentrations were observed during the end of November and December. Concentrations decreased over time to a minimum of 0.9 µg L^{-1} on 16/12/2014. Quinmerac concentrations in paired inlet and outlet samples were plotted (Appendix A2, Figure 7.4). The slope close to the unit showed that quinmerac concentrations at the inlet and outlet. The paired sample t-*test showed no significance difference ($p = 0.73$) between 182 samples in total collected at the inlet and outlet.

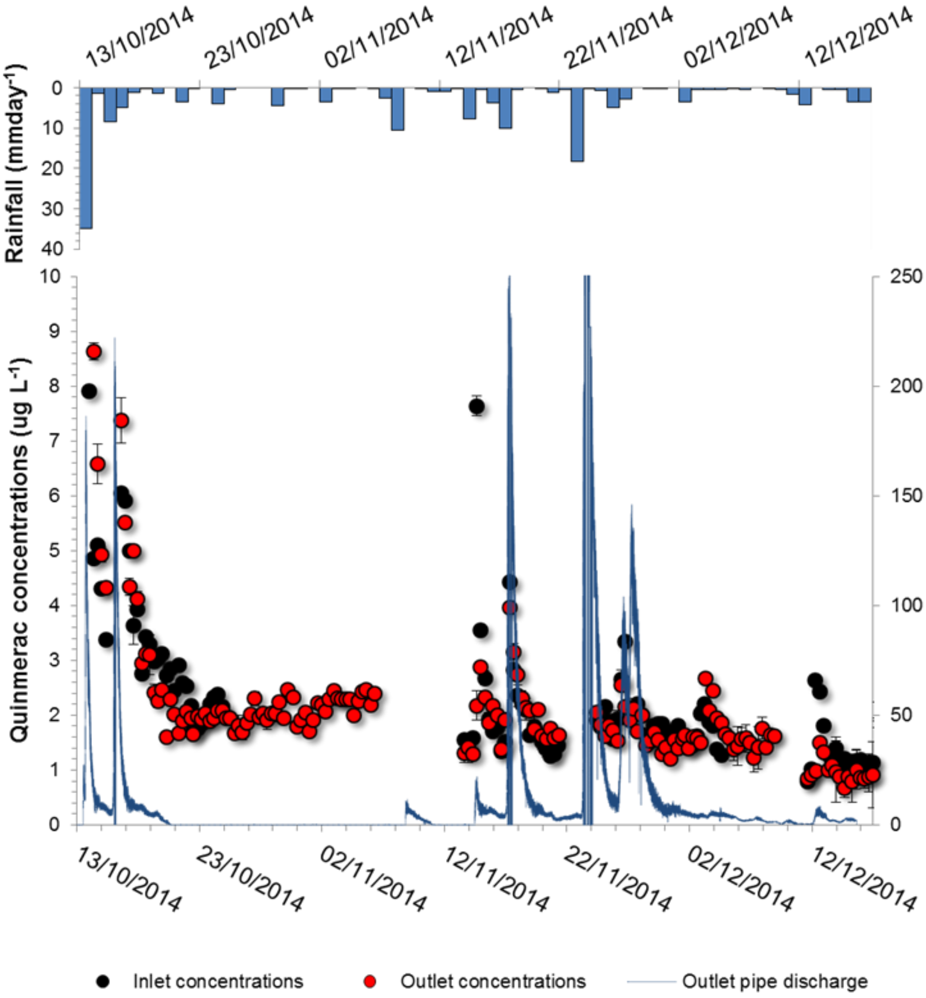

Figure 3.14. Quinmerac concentrations (µg L^{-1}) at the inlet and outlet of NW, daily rainfall (mm day^{-1}) and outlet discharge (L s^{-1})

Metazachlor

Peak concentrations of metazachlor of 4.5 and 2.5 µg L^{-1} were observed after the wetland started to flow. Concentrations rapidly decreased over the following days to 0.5 µg L^{-1} (Figure 3.15). Several peaks concentrations of metazachlor were observed during mid-November and December but concentrations did not exceed approximately 1.0 µg L^{-1} levels. Concentrations decreased to limit of detection limits on the end of December 2014. Metazachlor concentrations in paired inlet and outlet samples were plotted against one another. The slope was close to unity, suggesting that concentrations were very similar. The paired sample t-test showed no significant difference (p = 0.44) between the 110 samples in total collected at the inlet and outlet.

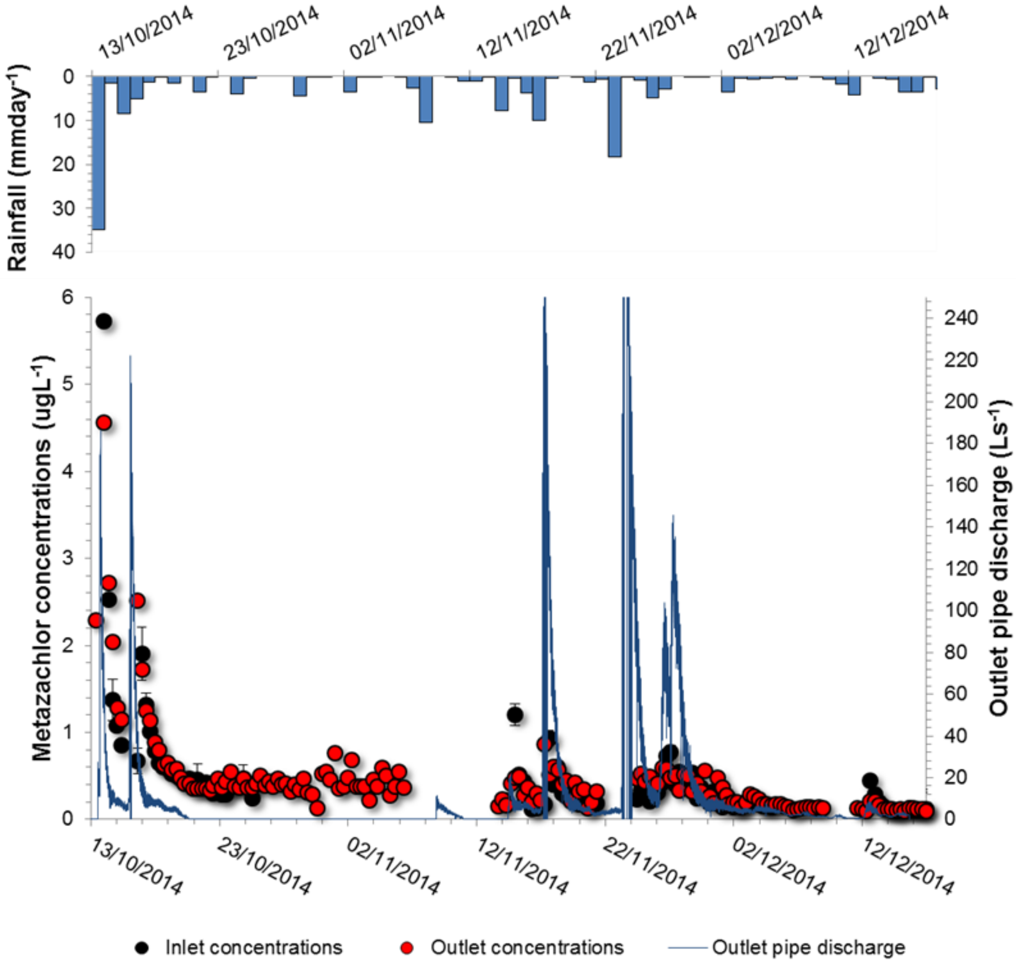

Figure 3.15**. Metazachlor concentrations (µg L^{-1}) at the inlet and outlet of NW, daily rainfall (mm day^{-1}) and outlet discharge (L s^{-1})**

Metaldehyde

Outlet metaldehyde concentrations of 0.5 µg L^{-1} were observed after the rainfall event 13/10/2014 (Figure 3.16). A peak concentration of 1.0 µg L^{-1} was observed during the peak discharge on 15/10/2014 and decreased during the falling limb of the hydrograph. Particularly during mid-November, two peak metaldehyde concentrations of 2.5 µg L^{-1} and 3.7 µg L^{-1} at the inlet were observed on the 15/11/2014 and 17/11/2014. These metaldehyde peaks concentrations suggest that possibly there were remains of slug pellets on the field 5. Thereafter, metaldehyde concentrations decreased to 0.2 µg L^{-1} both at inlet and outlet. Metaldehyde concentrations in paired inlet and outlet samples were plotted against one another. Again, the slope was close to unity suggesting that concentrations were very similar. The paired sample t-test showed no significant difference (p = 0.5) between the 88 samples collected at the inlet and outlet.

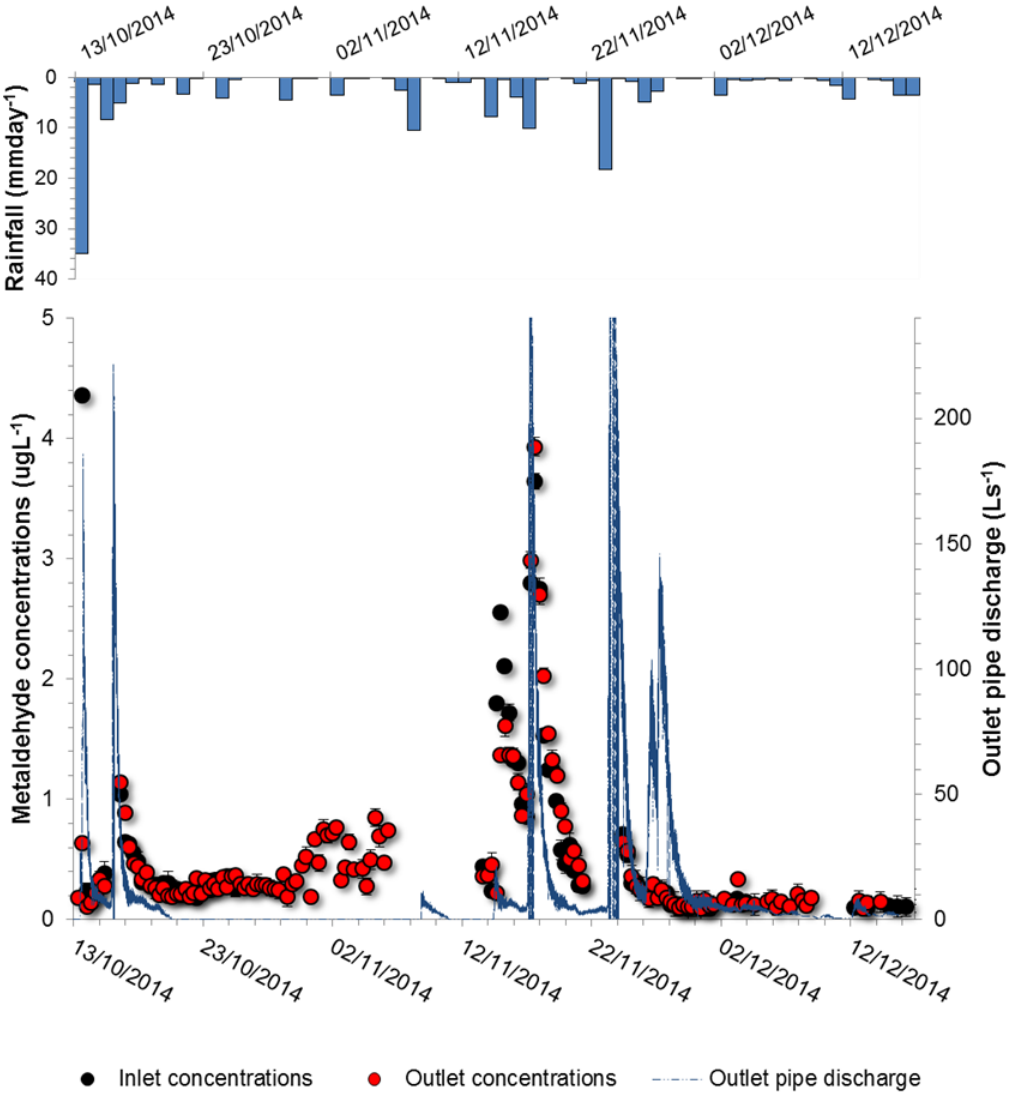

Figure 3.16. Metaldehyde concentrations (µg L^{-1}) at the inlet and outlet of NW, daily rainfall (mm day^{-1}) and outlet discharge (L s^{-1})

Propyzamide

According to the RSPB, Arta flo® (1.05 kg ha^{-1} of propyzamide) was applied to Field 5 in the NW catchment. The event of the 23/11/2014 (18 mm day^{-1}) triggered a significant peak in propyzamide concentrations of 52 µg L^{-1} recorded at the inlet samples (Figure 3.17). Concentrations decrease to 30 µg L^{-1} during the recession period of the hydrograph on 26/11/2014. However, during an increase of peak discharge of 92 L s^{-1} in the same day due to some rainfall events, propyzamide concentrations of 86.1 µg L^{-1} were observed after 6 hours. Propyzamide with a K_{oc} value of 840 L kg^{-1} is considered to be less mobile in soil compared to the other pesticide in this study. However, higher concentrations were observed right after application during a relatively high rainfall event of 19 mm day^{-1}, suggesting that propyzamide can be also easily transferred the application site into surface waters. Propyzamide concentrations decreased to 7.7 µg L^{-1} on the recession period of the hydrograph (1/12/2014). Other two small peak concentrations were observed on the 3/12/2014 and 12/12/2014. The flow was not recorded during this period, but the level logger data confirms that the NW was flowing (Figure 3.17).

Propyzamide concentrations at the inlet and outlet were plotted. The slope was close to unity which suggested that there were few meaningful differences in the concentrations. The paired sample t-test showed that there was no statistically significant difference between the 82 samples collected in total at the inlet and outlet.

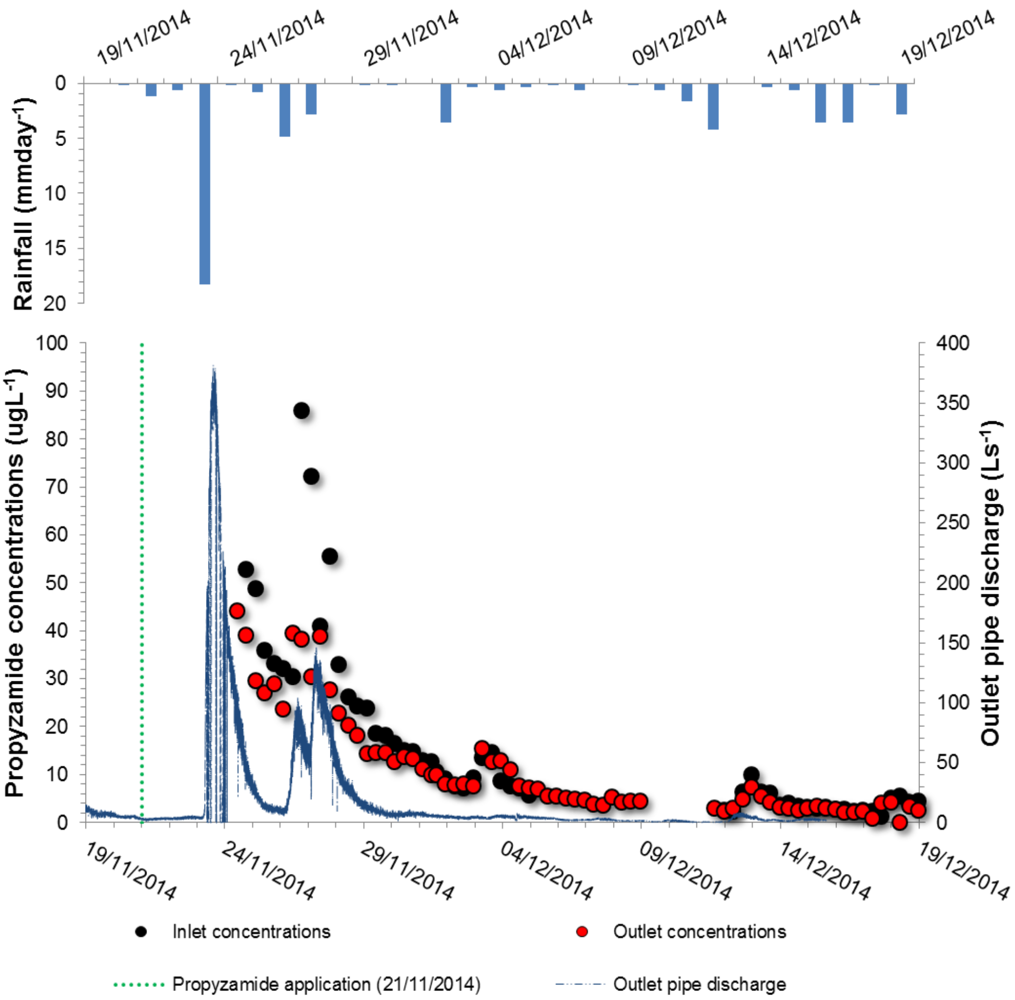

Figure 3.17**. Propyzamide concentrations (µg L^{-1}) at the inlet and outlet of NW, daily rainfall (mm day^{-1}) and outlet discharge (L s^{-1})**

In the similar way for SW, results showed that NW had low potential to remove pesticides when the system was flowing. The most likely explanation is due to the short HRT (~ 40 min) during peak discharges, in which removal mechanisms such sorption and degradation are very unlikely to occur.

3.5 Conclusions

This study focused on monitoring (August to December 2014) two FWS CWs (South Wetland and North Wetland) with different catchment areas in Cambridgeshire, UK to attenuate pesticide transfers. Overall, the findings from SW and NW during water flow periods suggested that these systems were inefficient at mitigating metaldehyde, carbetamide, quinmerac, metazachlor and propyzamide. The main explanation for poor performance was the very short hydraulic residence time (~32 minutes SW and ~40 NW) of these systems which occurred at the time when peak concentrations of pesticides were observed.

At the NW, peak concentrations of metaldehyde (30 µg L^{-1}), metazachlor (150 µg L^{-1}) and quinmerac (130 µg L^{-1}) were observed after application. After this input, the NW behaved as a static system approximately for 41 days. During this period pesticide concentrations decreased over time, suggesting a possible attenuation in the system. However, further experiments need to be addressed to identify and understand the potential removal mechanism.

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4 .Sorption and desorption of five pesticides by wetland sediment

A.M.Ramos[1]; M.J.Whelan[2]; R.Villa[1]; B.Jefferson[1]; I.Guymer[3];

[1]Water Science Institute, School of Water, Energy and Environment, Cranfield University, Bedford, MK43 0AL, UK

[2]Department of Geography, University of Leicester, Leicester, LE1 7RH, UK

[3]School of Engineering, University of Warwick, UK

4.1 Abstract

This study details the sorption-desorption characteristics of metaldehyde, carbetamide, quinmerac, metazachlor and propyzamide in wetland sediment. Batch equilibrium study (OECD, 2000) was used to determine sorption parameters for one pesticide and mixed pesticides solutions. Results showed a linear isotherm for sorption and desorption for all pesticides ($R^2 > 0.97$). The derived sorption partition coefficient (K_d) increased in the sequence: metaldehyde < carbetamide < quinmerac < metazachlor < propyzamide. The desorption coefficient (K_d^{des}) was significantly different for metazachlor and propyzamide, showing a true hysteresis effect ($p > 0.05$). The calculated organic carbon sorption coefficient (K_{oc}) increased in the sequence: metaldehyde (27.6 L kg^{-1}) < carbetamide (32 L kg^{-1}) < quinmerac (41 L kg^{-1}) < metazachlor (194.2 L kg^{-1}) and propyzamide (884 L kg^{-1}). These results showed that metaldehyde, carbetamide and quinmerac have higher mobility in wetland sediment relative to metazachlor and propyzamide.

There was a strong relationship between K_{oc} with water solubility ($R^2 = 0.92$) and with octanol-water partition coefficient (K_{ow}) ($R^2 = 0.85$), showing that the organic content of the sediment responsible for the sorption of the studied pesticides.

The sorption experiment with a mixture of pesticides in wetland sediment showed the presence of other compounds can influence the sorption capacity of the sediment. Results showed a decrease of K_{oc} values for carbetamide, quinmerac and metazachlor, indicating a competitive sorption for the sediment sorption sites.

However, for metaldehyde and propyzamide there was not significant difference between K_{oc} values for single and mixture sorption experiments.

Keywords

Sorption, desorption, pesticides, wetland sediment, competitive sorption

4.2 Introduction

Free water surface constructed wetlands (FWS CWs) can be implemented to mitigate pesticide pollution in surface waters (Alvord and Kadlec, 1996; House *et al.,* 2000). However, the reported efficiency of FWS CWs is variable from negative (outlet concentrations higher the inlet concentrations) (Ramos *et al.,* 2018) to 100% reduction (Passeport *et al.,* 2013).

As pesticides move through a wetland system they interact with sediment, plants and litter. Depending on the physicochemical properties of the pesticide, the characteristics of the solid surfaces in the wetland and the relative concentrations in the water and in the solid matrix, there can be net transfer from water to solid (sorption) or from solid to water (desorption). These processes can, thus, potentially play a key role in the fate of these compounds in wetlands. It is, therefore, important to get an understanding of pesticide sorption dynamics in order to predict their mobility and (possibly) to help optimize wetland design.

There are a very large number of studies on pesticide sorption in different soils and sediments (e.g. Deschauer and Kögel-Knabner 1990; Stuart *et al.,* 2011; Lewis *et al.,* 2016). However, desorption coefficients (K_d^{des}) are less commonly reported. The determination of K_d^{des} values from wetland sediments can allow a better understanding of how quickly pesticides will migrate out of water-sediment systems once concentrations in overlying water reduce and pesticides entrapped in sediments can start to move back into the water column (Wauchope *et al.,* 2002; Rae *et al.,* 1998; Gao *et al.,* 1998). Desorption rates are often not the same and the rate of sorption for the same chemical with the same media and irreversible sorption or very slowly reversible sorption phenomena are quite common. This is known as hysteresis. Hysteresis can be caused by a true hysteresis or several apparent factors (Huang *et al.,* 1998; Weber Jr. and Yu, 1998). True hysteresis is usually explained by an irreversible chemical binding of a pesticide to the matrix of the organic matter or entrapment of the pesticide into organic or mineral microporous structures (Bowman and Sans, 1984; Huang *et al.,* 1998; Kawakami *et al.,* 2007; Alonso *et al.,* 2016; Moyo *et al.,* 2014). Apparent hysteresis is observed due to compound transformation (e.g. (bio) degradation) (Huang *et al.,* 1998) or competitive sorption with other unknown compounds in the sample (Weber Jr. and Yu, 1998). Other reasons could be the failure to reach sorption or desorption equilibrium, measurement errors or artefacts during the experimental method (Chefetz *et al.,* 2004).

The factors influencing sorption include the organic matter content of the solid phase, mineral composition, pH and physicochemical properties of the pesticide, such as water solubility, K_{ow} (Wauchope *et al.,* 2002) and the acid-base ionization constant for ionisable compounds (Guo *et al.,* 2000). For acidic herbicides (*e.g.* quinmerac) sorption mechanisms tend to be pH-dependent and can involve ionic bonding or hydrophobic interactions (Deschauer and Kögel-Knabner 1990).

However, the organic matter content is usually considered as the most important factor for pesticide sorption. The K_{oc} value is often considered to be the most important pesticide-sediment specific parameter, because interactions with organic carbon dominate over interactions with the mineral fraction for many organic compounds (Wauchope *et al.,* 2002; Ahangar, 2011).

Sorption is typically assessed for individual compounds (one at a time). However, in reality other pesticides are often present simultaneously in the water and in the solid matrix. This is because they are applied at the same time – separately or in the same commercial formulation containing different active ingredients (e.g. Palometa$^{®}$ contains - 12.5% (v/v) quinmerac and 35.5% (v/v) metazachlor) (Ramos *et al.,* 2018). This can alter the sorption parameters (Chefetz *et al.,* 2004; Ramos *et al.,* 2018). Several authors have reported that the presence of other chemicals can alter soil or sediment sorption capacity (Farenhorst and Bowman, 1998; Chefetz *et al.,* 2004). Evaluating the sorption of pesticides in mixtures could provide additional information on the nature of the sorption behaviour in wetland sediment, which may be useful for evaluating the efficiency of a wetland but also for fate modelling and environmental risk assessments (e.g. Foo and Hameed, 2010; Warren *et al.,* 2003; Wauchope *et al.,* 2002).

In this paper we evaluate the sorption and desorption characteristics of six different pesticides commonly used in agriculture. We first attempt to quantify their K_d values in wetland sediments. Then we compare their sorption and desorption characteristics when present individually in water-sediment matrices. Finally, we look at their sorption behaviours when present as a complex mixture to ascertain whether any competitive phenomena could be identified.

4.3 Materials and Methods

Adsorption and desorption characteristics of the pesticides quinmerac, metazachlor, carbetamide, metaldehyde and propyzamide were determined in wetland sediment from Hope Farm (Knapwell, Cambridgeshire, UK) using a batch equilibrium method designed to meet requirements of the OECD 106 test guidelines. The wetland sediment pH was 8.1±0.2. Wetland sediment was composed by 11.9±0.3 % of sand, 41.4±0.3% of silt and 46.6±0.5% of clay. The fraction of organic carbon was 0.055 g g^{-1}.

4.3.1 Chemicals

The standards for five pesticides, metaldehyde, quinmerac, metazachlor, carbetamide and propyzamide were purchased from Sigma-Aldrich, Haverhill UK. A solution of calcium chloride (0.01 M) was prepared from >95% calcium chloride powder (Sigma-Aldrich, Haverhill UK). Ultra-pure water was produced by PURELAB ultra, Elga.

4.3.2 Wetland Sediment

Sediment was collected from the South Wetland at Hope Farm (Knapwell, Cambridgeshire, UK) in August 2016. Samples were taken from the top 10 cm with a trowel and stored in zip lock bags. Dead leaves, plant stems and small stones were removed before the sediment was homogenized by hand, air dried at room temperature (20-25°C) for 2 weeks and then passed through a 2 mm sieve (as suggested by the OECD test 106 guidelines to avoid changes the sediment structure). British standard methods were used to determine pH, sand, silt and clay percentage and fraction of organic carbon. All tests were done in triplicate.

4.3.3 Preliminary study

The preliminary study aims were to determine the sediment/solution ratio, the equilibrium time for sorption, the amount of test substance sorbed at equilibrium and the sorption of the test substance on the surfaces of the test tubes.

Selection of sediment to solution ratio

Three sediment to solution ratios were tested (1:2; 1:5 and 1:10) based on 4, 10 and 20 mL of water (with 0.01 M $CaCl_2$) with 2 g of dry sediment. The $CaCl_2$ is used in the aqueous phase to minimise cation exchange. Stock solutions of the pesticides were added to the respective sediment to solution ratio in order to make final mixed solution of 1 mg L^{-1}. All tubes were shaken at 150 rpm (Stuart Orbital Shaker SSL1) for 24 hours and centrifuged (Heraeus Megafuge 16) at 2500 rpm for 15 minutes. The supernatants were filtered through 0.2 µm syringe filters (Millipore Millex^{TM}, Fisher Scientific, UK) and analysed by LC-MS/MS as described by Ramos *et al.,* (2017). All tests were done in triplicate.

Equilibration time

Equilibration time for adsorption and the amount of pesticide sorbed at equilibrium were investigated. The sediment to solution ratio (1:5) was used for investigate the equilibration time for the pesticides studied. Stock solutions of the five pesticides were added to the sediment making the final concentration of 1 mg L^{-1}. All tubes were shaken at 150 rpm for 1, 4, 8, 20 and 24 hours. At specific time intervals, tubes were sacrificed (Parallel method, OECD 106) and centrifuged (Heraeus Megafuge 16) at 2500 rpm for 15 minutes. The concentration in the water phase was analysed by LC-MS/MS (Ramos *et al.,* 2017). All tests were done in triplicate.

Controls and Blanks

Control samples were also prepared in centrifuge tubes with fixed concentrations of 1 mg L^{-1} of each pesticide without sediment. The controls were important to assess if the pesticides were sorbed by the plastic tubes. Results showed no significant sorption in the plastic (<1%).

Blanks were established with sediment and 0.01M of $CaCl_2$ in centrifuge tubes without added pesticides.The blanks were important to check for the presence of any interfering compounds and to quantify residual pesticide concentrations, if present, in the sediment. Results showed no residual presence of pesticides (i.e. all concentrations were below LOD).

4.3.4 Sorption-desorption experiment

Sorption isotherms of pesticides were established in batch mode in the dark according to OECD 106 guidelines (OECD, 2000) with some modifications. The conditions used were: pH 7.0; 21-23 °C of temperature and sediment to solution ratio of 1:5 v/v. To the tubes were added 2 g of dried sediment and 10 mL of 0.01M $CaCl_2$ solutions containing a series of concentrations of single pesticides (0.2, 0.5, 1.0, 2.0 and 5.0 mg L^{-1}). For the sorption study, the range of concentrations (200 to 5000 µg L^{-1}) was chosen based on observations at the field. Lowest initial aqueous concentration in the North Wetland was approximately 200 µg L^{-1} (quinmerac concentration was 160 µg L^{-1} - Ramos *et al.,* 2018) and the highest initial concentration of 5000 µg L^{-1} was chosen based on OECD 106 test guidelines (the highest concentration needs to be one order of magnitude higher than the lowest concentration). Tubes were shaken at 150 rpm for 24 hours. Tubes were then centrifuged at 2500 rpm for 15 minutes and the equilibrium concentration analysed by LC-MS/MS (Ramos *et al.,* 2017).

The sorbed pesticide concentration (Q_e – mg kg^{-1}) (1) was calculated using the difference between the initial pesticide concentration and the equilibrium concentration after 24 hours (i.e. the mass lost from the dissolved phase) (Wauchope *et al.,* 2002)

$$Q_e = \frac{(C_0 - C_e)}{m} . V \qquad (4.1)$$

where C_0 is the initial pesticide concentration (mg L^{-1}), C_e is the equilibrium concentration (mg L^{-1}) at 24 hours, V is the volume of initial solution (L) and m is the mass of sediment in the vessel (kg).

Plotting Q_e versus C_e and establishing the line of the best fit by linear regression yielded a linear isotherm with a slope, K_d (L kg^{-1}), representing solid-water distribution coefficient expressed by equation 4.2:

$$Q_e = K_d C_e \tag{4.2}$$

K_d represents the ratio of the amount of pesticide sorbed in the solid phase to pesticide concentration in the dissolved phase, at equilibrium, without considering the organic matter content (Warren *et al.,* 2003; Kodešová *et al.,* 2011).

The sorption data were described using the Freundlich equation described by Equation 4.3:

$$Q_e = K_f C_e^{1/n} \tag{4.3}$$

where K_f is the sorption coefficient (Freundlich constant) and $1/n$ is adsorption constant. The Freundlich coefficient (K_f), expresses the sorption capacity between the sediment and the pesticide and the $1/n$ constant is defined as sorption intensity parameter. Usually, $1/n$ ranges from 0.7 to 1.0. A value below 1 means that when the concentration of the pesticides increases the relative sorption decreases, suggesting the saturation of adsorption sites available for the pesticide molecules. The linear form of Freundlich isotherm is described by Equation 4.4:

$$\log Q_e = \log K_f + 1/n \log C_e \tag{4.4}$$

The Freundlich model is usually adopted to explain non-linear sorption mechanisms of pesticide in sediments and soils (OECD 106 guidelines, 2000). The Freundlich assumes a non-ideal, reversible and multilayer adsorption in heterogeneous surface. An alternative model is the Langmuir isotherm which assumes monolayer coverage where all adsorption sites are equally probable. This is less representative of a sorbing medium such as sediment and/or soil.

Desorption studies were carried out immediately after the sorption experiment. The supernatant was replaced with the same volume of 0.01 M $CaCl_2$ solution without pesticides. After 24 hours shaking, tubes were centrifuged, and the supernatants were filtered and analysed as previously described. The experiment was performed in triplicate. Desorption behaviour can provide information on the type interaction between the pesticide and the wetland sediment (Katagi, 2016; Weber Jr. and Yu 1998). The Q_e^{des} was calculated using Equation 4.5:

$$Q_e^{des} = \frac{(C_{ads} - C_{eq}^{des})}{m}.V \tag{4.5}$$

where Q_e^{des} is desorption concentration from sediment (mg kg^{-1}), C_{ads} is the concentration sorbed to the sediment from the sorption experiment and C_{eq}^{des} is the equilibrium concentration in the water phase after 24 hours of desorption. The K_d^{des} was calculated using Equation 4.6:

$$Q_e^{des} = K_d^{des} C_e^{des} \tag{4.6}$$

Where K_d^{des} is the ratio between the concentration of pesticide remaining in the sediment and the concentration of pesticide desorbed in the water phase after 24 hours (Chefetz et al., 2004). The higher K_d^{des} the lower is desorption (Kawakami *et al.,* 2007; Gaultier *et al.,* 2009).

The existence of pesticide hysteresis in wetland sediment can be identified using the ratio of desorption (K_d^{des}) and sorption (K_d) isotherm slopes. The hysteresis index (H) was calculated as:

$$H = \frac{K_d^{des}}{K_d} \tag{4.7}$$

The existence of hysteresis in sorption implies that the quantity of pesticide sorbed to wetland sediment is different from the quantity desorbed over the same time period (Gaullier *et al.,* 2017).

4.3 Results and Discussion

A preliminary test was conducted to assess the sediment to solution ratio (1:2; 1:5 and 1:10) which would give between 20 and 80% (preferably 50%) sorption of the studied pesticides. The sediment to solution ratio 1:2 was immediately discarded because it was not possible to separate the water and sediment phases by centrifugation. The sediment to solution ratio of 1:5 proved to be suitable for the test, with pesticide sorption between 30 and 40%. The solution to sediment ratio of 1:10 was discarded because sorption was below 20% for all pesticides.

A second test was conducted to assess sorption equilibration time. The test consisted in measure the concentration in the liquid phase at specific time points of 0, 1, 4, 8, 20 and 24 hours. All pesticide concentrations reached equilibrium between 20 to 24 hours (Appendix 7, Figure 7.8). The equilibrium time of 24 hours was therefore used for the sorption and desorption experiments, which is commonly used by other authors (Formsgaard, 2004; Boivin *et al.,* 2005; Deschauer and Kögel-Knabner, 1990).

4.3.3 Single sorption isotherms

Concentrations of metaldehyde, carbetamide, quinmerac, metazachlor and propyzamide in solution and in the solid phase of wetland sediment from the sorption study are shown in Figure 4.1, together with the fitted lines for sorption and desorption isotherms. The isotherm parameters (K_d and K_d^{des}) were detailed in Table 4.1. The experimental results (sorption and desorption) were described by linear isotherms (R^2 > 0.97) for all pesticides. A linear relationship between sorbate concentrations in the aqueous and solid phases reflects a particular case of the Freundlich isotherm whose intensity parameter (*1/n*) equals 1. The Freundlich coefficients were also calculated and presented in Table 4.1.

According to Warren *et al.,* (2003), pesticides concentrations in water-sediment systems are relatively low and therefore a linear isotherm is common. The K_d values were calculated and varied from 1.38 L kg^{-1} for metaldehyde and 44.2 L kg^{-1} for propyzamide. K_d^{des} varied from 0.97 L kg^{-1} for carbetamide and to 82.67 L kg^{-1} for propyzamide. From the data herein, metaldehyde, carbetamide and quinmerac were the most mobile in wetland sediment. Metazachlor and propyzamide were found to be the most tightly attached to wetland sediment.

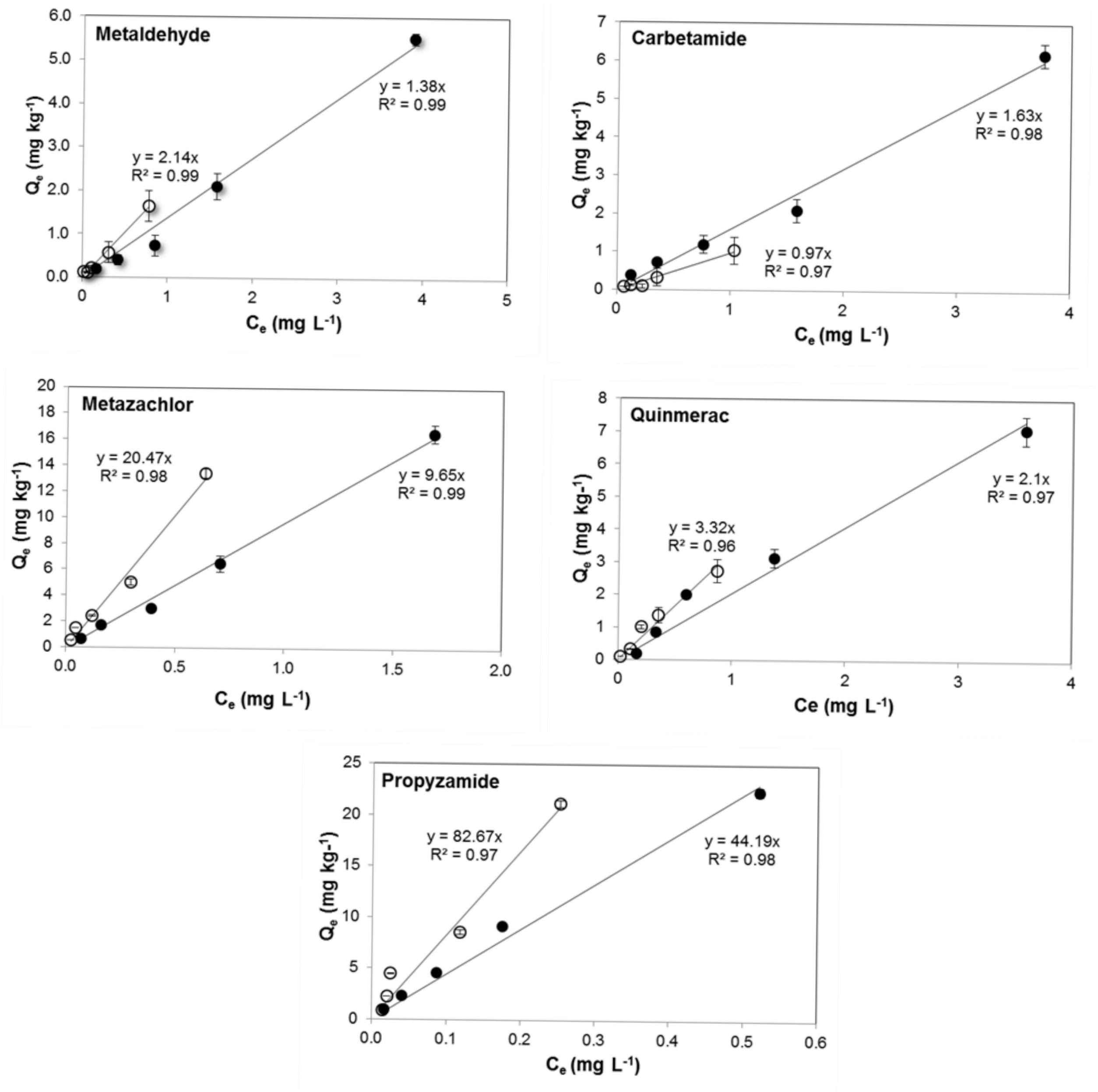

Figure 4.1. Linear sorption (●) and desorption (○) isotherms for metaldehyde, carbetamide, metazachlor quinmerac and propyzamide in wetland sediment. The K_d and K_d^{des} were the slope of the line (L kg $^{-1}$). Error bars denote standard deviation for replicate samples (n=3)

The Hysteresis index was calculated and is presented in Table 4.11. If the value of hysteresis index is close to 1 the coefficients desorption and sorption are the similar and there is no evidence of hysteresis. Hysteresis is considered to have occurred when the K_d^{des} is greater than K_d. To distinguish true from apparent hysteresis a statistical Student's *t* test (95% confidence interval) was performed to assess if the sorption and desorption slopes were statistically different. For quinmerac, metazachlor and propyzamide the sorption and desorption isotherms slopes were significantly different ($p < 0.05$) demonstrating the occurrence of true hysteresis. Higher hysteresis values were observed for metazachlor ($H = 2.1$), followed by propyzamide ($H = 1.8$) and less pronounced for quinmerac ($H = 1.6$). The hysteresis effect for metaldehyde and carbetamide were statistical insignificant ($p > 0.05$) and therefore hysteresis was not evident. In the case of metaldehyde, the slightly difference between the sorption and desorption slopes show a case of apparent hysteresis. Results from the sorption-desorption of hysteresis shown that quinmerac, metazachlor and propyzamide can remain entrapped in the sediment matrix.

Relationship between log K_{oc} with water solubility and log K_{ow}

Organic matter is the major non-polar phase in sediments and it is responsible for sorption between non-polar organic molecules (Wauchope *et al.,* 2002; Warren *et al.,* 2003). The calculated K_d was normalized to the sediment organic carbon content (using the organic carbon concentration in wetland sediment, f_{oc}, 0.055 g g^{-1}) to give the K_{oc} for the different pesticides expressed by:

$$K_{oc} = (K_d/f_{oc}) \tag{4.8}$$

The K_{oc} value was used to predict the fate of pesticides in water-sediment systems (like free-water surface wetlands). The lower the K_{oc} value, the more mobile the pesticide tends to be. Conversely, higher K_{oc} values imply that the pesticide has a higher affinity for the sediment solids and therefore is expected to be less mobile (Wauchope *et al.,* 2002; Warren *et al.,* 2003).

The K_{oc} values increased in the order: metaldehyde (27.6 L kg^{-1}) < carbetamide (32.0 L kg^{-1}) < quinmerac (41 L kg^{-1}) < metazachlor (194.2 L kg^{-1}) and propyzamide (884.0 L kg^{-1}) (Table 4.2). The K_{oc} value obtained for metaldehyde was one order of magnitude lower compared with the value (240 L kg^{-1}) from Pesticides Properties Database (PPDB) (Lewis *et al.,* 2016). K_{oc} values for carbetamide (32 L kg^{-1}) and quinmerac (41 L kg^{-1}) were lower compared with values from Lewis *et al.,* (2016) within approximately a factor of 3 (89 L kg^{-1}) and

2 (86 L kg^{-1}), respectively. The K_{oc} value for metazachlor (194.2 L kg^{-1}) was higher and for propyzamide (884 L kg^{-1}) relatively consistent compared with values from Lewis *et al.,* (2016) (metazachlor, 54 L kg^{-1} and propyzamide 840 L kg^{-1}). The main explanation for the differences between K_{oc} values from the literature and those observed in this study is that the reported K_{oc} values in the pesticide database are mean values calculated for different soils with different qualities of organic carbon. Values of K_{oc} are known to change considerably with different organic matter types (e.g. Whelan *et al.,* 2009; 2010).

According with Food and Agriculture Organization Mobility (FAO) classification based on K_{oc} values, metaldehyde, carbetamide, quinmerac were considered to be mobile (K_{oc} range 10-100 L kg^{-1}) whereas metazachlor and propyzamide were considered to be moderately mobile (K_{oc} range 100-1000 L kg^{-1}) in wetland sediment.

Table 4-11. K_d, K_d^{des}, K_f, 1/n, H and K_{oc} values for the five pesticides and the R^2 value of the regression fits for the sorption and desorption isotherms. $K_{oc}{}^a$ values were obtained from the Pesticide Database PPDB (Lewis *et al.,* 2016)

Pesticide	K_d (L kg^{-1})	K_d^{des} (L kg^{-1})	K_f	*1/n*	*H*	K_{oc} (L kg^{-1})	K_{oc} (L kg^{-1})^a	R^2 Sorption/ Desorption

Metaldehyde	1.38	2.14	1.15	1.08	1.5	27.6	240	0.99/0.99
Carbetamide	1.60	0.97	1.72	0.79	0.6	32.0	59.5-118.2	0.98/0.97
Quinmerac	2.05	3.32	3.99	1.09	1.6	41.0	6.2-126	0.99/0.98
Metazachlor	9.71	20.47	9.21	0.98	2.1	194.2	29.2-73.1	0.97/0.96
Propyzamide	44.21	82.67	42.67	1.09	1.8	884.0	548-1340	0.98/0.97

The most important factor in determining the K_{oc} should be the properties of the chemical under consideration (Wauchope *et al.,* 2002). Several correlations have been observed between the K_{oc} value and different chemical properties (Ahangar, 2011). The most common relations are with K_{ow} and water solubility (Burgos *et al.,* 1999).The K_{ow} is the distribution coefficient of an organic compound between octanol and water and is the most common measure of hydrophobicity (Kawakami *et al.,* 2007). Usually the K_{oc} value has a direct relationship with K_{ow} and an inverse relationship with water solubility (Karickhoff, 1981). Typically, these relationships are given by the Collander equation:

$$\text{Log } K_1 = a \text{ Log } K_2 + b \qquad (4.9)$$

Figure 4.2 shows the relationship between the obtained Log K_{oc} with Log K_{ow} and Log Water solubility average of the values from Lewis *et al.,* (2016) and the EPI software (EPA, 2012).

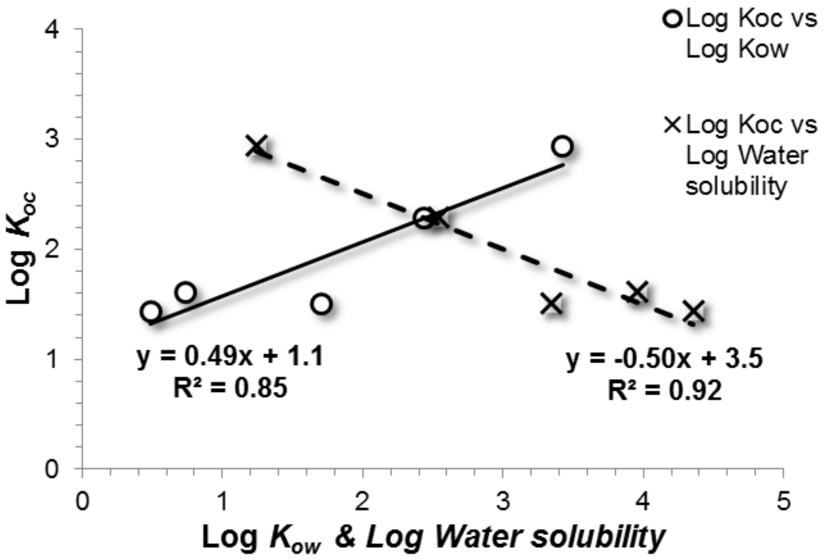

Figure 4.2. Relationship between log K_{oc} with log K_{ow} and log water solubility for the studied pesticides.

Figure 4.2 shows a strong positive relationship between the Log K_{ow} and Log K_{oc} (R^2 = 0.85). According with Jorgensen and Sorensen (1998), the derived relationship (Log K_{oc} = 0.49 Log K_{ow} + 1.1) is within the range for pesticides. Contrastingly, there was a strong negative relationship between Log Water solubility and Log K_{oc} (R^2 = 0.92). Both relations have been extensively reported by many authors (Kawakami *et al.,* 2007; Boivin *et al.,* 2005; Prado *et al.,* 2014). Karickhoff et al. (1979), reported that K_{ow} tends to give a better relationship with K_{oc} compared with water solubility. However, in this study a slightly better relationship was observed for water solubility. The strong relationship between these two chemical properties (Log K_{oc} and Log water solubility) showed the organic carbon content of wetland sediment to be responsible for the sorption of the studied pesticides.

Understanding sorption mechanisms for the studied pesticides

The type of specific sorption mechanisms involved depend on the pesticide chemical structures (Arias-Estévez *et al.,* 2008). Pesticides sorbed by ionic bonding exist as cations or anions in aqueous phase or are pesticides that can protonate or dissociate under different pH conditions (Soubaneh *et al.,* 2015).

Quinmerac as an aromatic acid herbicide has a pKa value of 4.3 and the water and sediment pH in this study was 7. At the pH 7, anionic form of quinmerac will be the dominant (R-COO$^-$) which can form electrostatic interactions with organic matter (Deschauer and Knaber 1990).

For neutral organic compounds as propyzamide, metazachlor, carbetamide and metaldehyde used in this work, sorption usually involves covalent and hydrogen bonding (Martin-Neto *et al.,* 2001; Wu and Laird 2004), general hydrophobic interactions (hydrophobicity) (Passeport *et al.,* 2014) as well as Van der Waals forces (Katagi, 2016). Pesticides which are most likely to bind covalently to organic matter in sediment have similar chemical functionalities to components of humic acids (Gevao, *et al.,* 2000; Formsgaard, 2004; Beulke *et al.,* 2004). Humic material is the remains of decomposition of plants, animals and microorganisms and tends to be dominated by polymers with aromatic structures with polyphenolic units (Li *et al.,* 2002; Prado *et al.,* 2014; Wilkins, 2003). Covalent bonds between pesticide and sediment tend to increase the sorption coefficient. These types of chemical bonds are also extremely stable and very resistant to hydrolysis and/or microbial degradation (Gevao, *et al.,* 2000; Wilkins 2003). Propyzamide and metazachlor belong to a pesticides class of amides (amides herbicides) which are usually less soluble than amines and carboxylic acids (Spliid *et al.,* 2015). This could explain why these two pesticides have higher K_{oc} values compared to the others. The difference between propyzamide and metazachlor is the presence of a triple unsaturated bond in the propyzamide structure, conferring to a high non-polar behaviour molecule. Since a low desorption amount and a true hysteresis was observed for both pesticides (metazachlor 18.1 ± 2.1% and propyzamide 5.4 ± 1.1%), it is possible that some covalent bonding occurred between these pesticides and the organic content of wetland sediment. However, is not possible to know if the sorption is fully irreversible (or low reversible desorption) due to the 24 hours timescale used for this study.

Carbetamide is part of the carbamate pesticide class. Its chemical structure (R-$CONH_2$-R$CONH_2$-R) is responsible for its high polarity. Due to the weak sorption and high desorption of carbetamide from the wetland sediment, carbetamide sorption mechanism is probably based on weak Van der Walls forces (Crovetto *et al.,* 2009).

Metaldehyde has a cyclo-octane structure consisting of four oxygen atoms in a non-aromatic ring (without pi electrons). The presence of four oxygens is responsible for the high molecular polarity which might explain why metaldehyde is very mobile in water and has a low affinity to organic matter. The oxygens in the molecule have non-bonding electron pairs which can easily bind via intermolecular forces of attraction such Van der Walls forces or dipole interactions (Tao and Fletcher, 2013).

The sorption isotherms and associated parameters suggested that the pesticides examined in this study tend to have relatively low sorption to wetland sediment and desorb relatively rapidly once aqueous phase concentrations decrease. However, surface waters are often exposed to mixtures of several pesticides simultaneously. The following results showed the effect on the sorption of pesticide mixtures in wetland sediment.

4.3.4 Sorption of a mixture of pesticides in wetland sediment

The sorption of a mixture of pesticides experiment was performed by adding a solution containing all pesticides to the wetland sediment. Figure 4.3 shows the plot of sorption capacity of the sediment for single pesticide sorption (Q_e^{single}) and for pesticide mixture (Q_e^{mix}). In case of $Q_e^{single} > Q_e^{mix}$, an effect of sorption capacity of the sediment was observed due to the presence of other pesticides and a possible sorption competition was assumed. If $Q_e^{single} = Q_e^{mix}$ (slope of the line = 1), then there was not difference in sorption capacity and there was no sorption competition.

In the case of metazachlor, quinmerac and carbetamide, the sorption capacity was different in the mixture. This means that the presence of other pesticides reduced the sorbed concentration, suggesting that competition for the sorption sites between some of these compounds. For metaldehyde and propyzamide the slope of the line was approximately equal to unity (R^2>0.97), suggesting that the presence of other pesticides in solution does not affect the sorption.

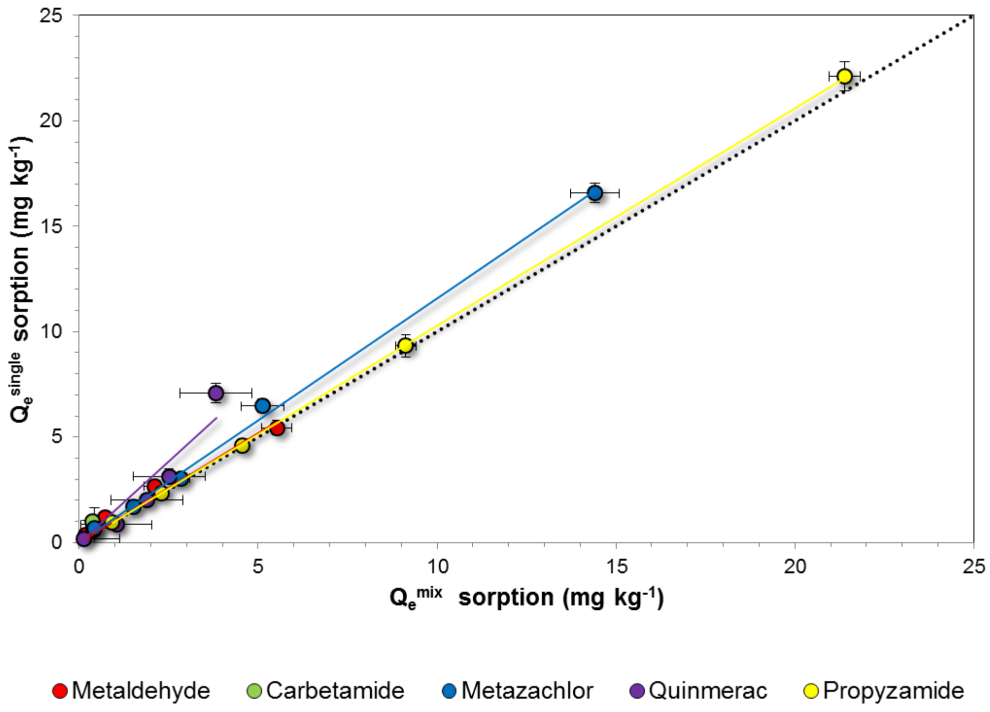

Figure 4.3. Comparison between the sorption capacity of wetland sediment for individual and mixture of pesticides. The dotted line is the 1:1 relationship.

A comparison between K_d and K_{oc} for single and for mixture sorption of pesticides in wetland sediment is shown on Table 4.2. The derived K_{oc} values for metaldehyde and propyzamide for single and for the mixture were relatively the same. For carbetamide, quinmerac and metazachlor the K_{oc} value decreased within factor of 1.6. Results suggested that, when other pesticides were present in the aqueous phase the sorption capacity of the sediment decreased. The explanation for this effect could be due to competitive sorption. Competitive sorption occurs when the presence of two or several molecules compete for the same sorption site in the organic content of the sediment. Xing *et al.,* (1996) study showed the occurrence of competitive sorption between atrazine in different soils with a range of organic matter content, when other pesticides are present.

Table 4-2. Determined K_d, K_{oc} values and respective R^2 values of the isotherm regression fits for the five pesticides tested as a single pesticide solution and as multi-component pesticide solution.

Pesticide	*Single pesticide*			*Mixture of pesticides*		
	K_d (L kg^{-1})	K_{oc} (L kg^{-1})	R^2	K_d (L kg^{-1})	K_{oc} (L kg^{-1})	R^2
Metaldehyde	1.38	27.6	0.99	1.44	28.9	0.97
Carbetamide	1.60	59.5	0.98	1.01	20.2	0.97
Quinmerac	2.05	6.2-126	0.99	1.54	30.8	0.90
Metazachlor	9.71	29.2-73.1	0.97	6.53	130.6	0.98
Propyzamide	44.2	548-1340	0.98	42.5	850	0.98

4.4 Conclusions

All pesticides showed linear sorption and desorption isotherms in wetland sediment over the range of concentrations (0.2-5.0 mg L^{-1}) studied. The calculated K_d values increased in order: metaldehyde (1.38 L kg^{-1}) < carbetamide (1.60 L kg^{-1}) < quinmerac (2.05 L kg^{-1}) < metazachlor (9.71 L kg^{-1}) < propyzamide (44.21 L kg^{-1}).

Results indicated that metaldehyde, carbetamide and quinmerac were the most mobile pesticides, whereas for metazachlor and propyzamide were found to be moderately mobile in wetland sediment. From the desorption experiment was possible to observed a hysteresis effect for metazachlor and propyzamide, which shown that these particular pesticides can remain entrapped in the sediment matrix.

The K_{oc} values were determined by normalizing the K_d values into the organic content of the sediment. The K_{oc} value for metaldehyde (26.6 L kg^{-1}), quinmerac

(41.0 L kg^{-1}), carbetamide (32.0 L kg^{-1}) were lower than those reported previously Lewis *et al.,* (2016), whereas for propyzamide (884.0 L kg^{-1}) was similar and metazachlor (194.2 L kg^{-1}) slightly higher. The calculated K_{oc} showed a strong relationship with K_{ow} and water solubility of the studied pesticides, confirming that organic carbon content is the major sorbent in the wetland sediment examined.

From the experiment of sorption of mixtures of pesticides in wetland sediment, no difference in sorption capacity of the sediment was observed for metaldehyde and propyzamide in the presence of other pesticides. However, differences were observed for metazachlor, quinmerac and carbetamide, suggesting a decreased in sorption capacity of the sediment when pesticides are present as mixtures, due to competition for sorption sites present in the organic content of the sediment.

4.5 References

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5 . Behaviour of pesticides in water-sediment systems

A.M.Ramos[1]; M.J.Whelan[2]; R.Villa[1]; B.Jefferson[1]; I.Guymer[3];

[1]Water Science Institute, School of Water, Energy and Environment, Cranfield University, Bedford, MK43 0AL, UK

[2]Department of Geography, University of Leicester, Leicester, LE1 7RH, UK

[3]School of Engineering, University of Warwick, UK

5.1 Abstract

It is important to quantify degradation rate constants (k) and degradation half-life (DT_{50}) for pesticides in water and sediment in order to be able to understand (and predict) the fate of pesticides in these surface water systems. This study was designed to quantify biodegradation and to examine the influence of microbial inhibition for quinmerac, metaldehyde and metazachlor in laboratory tests containing water and sediment subject to suppression of microbial action using sodium azide (Treatment A) or not (Treatment B). Quinmerac was relatively stable with DT_{50} in order of 84.7 days and there was no difference between treatments. In contrast, there was significant difference between treatments A and B for metaldehyde and metazachlor. In treatment B, there were clear lag phases of 7 days for metaldehyde and 8 days for metazachlor, followed by first-order kinetic curves. This is commonly observed in microbially-mediated biodegradation. Results from the lab experiments were compared with data from a field experiment conducted in a small free-surface wetland during a period of hydrological stasis (i.e. zero outflow). During this period, concentrations of metaldehyde, quinmerac and metazachlor decreased over time approximately according to first order kinetics. The respective DT_{50} values for metaldehyde and metazachlor were 17.3 and 9.9 days. A second objective of this study was to examine the effect of initial concentration on the degradation rate. Results showed an increase in degradation rate for metaldehyde and metazachlor with increasing initial concentrations, but at some stage degradation becomes independent of concentration. The Michaelis-Menten model was employed to

describe the effect of concentration on degradation rate. Values for the half-saturation constant (K_m) were 1.1 µg L^{-1} for metaldehyde and 0.7 µg L^{-1} for metazachlor.

A third objective was to evaluate the influence of water depth (3, 6 and 9 cm) on the degradation rate constant. Here, depth represents the ratio of water volume to the surface area of the sediment-water interface. This is important because it is hypothesised that most microbial activity takes place at this interface (although suspended free colonies of microorganisms will exist in the water column, these represent a minor fraction of the total microbial biomass in the whole system). Thus, biodegradation is limited by mixing rates (diffusion) in the water column and distance from the interface. Results showed no significant effect of depth for metaldehyde and carbetamide on the degradation rates. However, for propyzamide, metazachlor and quinmerac, differences were observed between treatments, mainly in terms of the different rates in the lag phase (rates after this period were very similar).

5.2 Introduction

Pesticides used in agriculture can move from land to aquatic ecosystems such as rivers, lakes and wetlands, particularly during rainfall-runoff events (Boithias *et al.,* 2014; Mantzos *et al.,* 2016; Moore *et al.,* 2001; Tediosi *et al.,* 2012). Several studies have reported that losses in runoff from agricultural land of different classes of pesticides can range between 0.5 and 5% of the amount applied in dry conditions, with these values increasing under severe rainfall conditions (Boopathy, 2000; Lapworth *et al.,* 2012). Similar observations were reported by Ramos *et al.,* (2018a) (Chapter 3) and Tediosi *et al.,* (2012), with higher concentrations (> 600 µg L^{-1}) of pesticides found in the water phase after application generated by rainfall events. The chemical characteristics of the pesticide, in addition to weather conditions, soil type and land use are the controlling factors for pesticides runoff through water, for soluble compounds, or sediments for strongly adsorbed pesticides. Once in the aquatic environment, if not already associated to sediment, the pesticides will tend to sorb to the organic matter in the system and may become less accessible to degradation (Ying and Williams, 2000).

Pesticides dissipation has been reported to be dependent and influenced by the characteristics of the sediments (e.g. organic matter content and clay content) and the water (*e.g.* pH, temperature, ionic strength) (Paszko, 2009, Fogg and Boxall, 2003) but also by the physio-chemical properties of the pesticides (Albrechtsen *et al.,* 2001; Aislabie and Lloyd-Jones 1995). In addition, hydrochemical characteristics such as wetland hydrology, intermittent flow conditions, hydraulic retention time and the presence of plants are also important factors for regulating pesticide removal (Maillard *et al.,* 2011; Gregoire *et al.,* 2009). Very little information is available on the impact of the water : sediment ratio, or the depth of the water column on pesticide behaviour in either laboratory mesocosm or ponds/wetlands. Exceptions include Radke and Maier (2014) who identified differences in DT_{50} values for the pharmaceuticals metoprolol and propranolol from previously reported values (Ramil *et al.,* 2009). They suggested that the water:sediment ratio used in their study (5:1) compared to that previously used (3:1) was responsible for the differences in removal rates observed, with a higher proportion of water to sediment leading to slower dissipation. Similarly, Kunkel and Radke (2012) reported that rate constants for several pharmaceuticals in a field dissipation study were higher in the river Grundlach (Germany) compared with those in the river Roter-Main, despite the fact that Radke and Maier (2014) reported that there was a more rapid dissipation in lab studies using sediments from the Roter-Main compared with those using sediment from the Grundlach. This is explained by the fact that, in the field, the Grundlach was shallower and had a greater hyporehic exchange. Water depth represents the ratio of water volume to the surface area of the sediment-water interface. This is important because it is hypothesised that most microbial activity takes place at this interface (although suspended free colonies of microorganisms will exist in the water column, these represent a minor fraction of the total microbial biomass in the whole system). Thus, biodegradation is limited by mixing rates (diffusion) in the water column and distance from the interface.

Pesticide dissipation in water-sediment systems can occur via several processes (Warren *et al.,* 2003): transfer processes, such as volatilization, plant uptake (Moore *et al.,* 2013), sorption that transfer substances to different environmental compartments (Wu *et al.,* 2011; Vallée *et al.,* 2015); and degradation processes such as photolysis (Kiss and Virág, 2009), hydrolysis and biodegradation (Aislabie and Lloyd-Jones,1995; Singh, 2008). However, it is commonly accepted that the most important removal processes affecting the fate of pesticides in water-sediment systems are sorption (Williams, 2002) and degradation (Vymazal and Tereza, 2015).

Ramos *et al.,* (2018a) (Chapter 3) showed a decrease in metaldehyde, quinmerac and metazachlor concentrations in a free-water surface constructed wetland during a non-flowing period. The aim of this work was to elucidate the removal processes of pesticides under static conditions similar to those periodically observed in this system (the North Wetland).

One of the hypotheses to be tested was that pesticide degradation over time was due to microbial-mediated biodegradation. The calculation of degradation kinetic parameters (lab and field data) are a fundamental component of environmental risk assessments and also for pesticide fate modelling.

A second objective of the work was to understand the influence of pesticide initial concentration on the degradation rate. Pesticide microbial-mediated biodegradation is an enzyme-catalyzed reaction (Tien *et al.,* 2013) and therefore the degradation rates are dependent on the initial concentrations of pesticides (Foog and Boxall, 2003). Pesticide biodegradation cannot be simply be extrapolated by testing at high concentrations and extrapolated to lower concentrations.

A third objective of this study is to test the hypothesis that pesticide degradation rate is inversely proportional to water depth. Work done in our laboratories on the same water-sediment system showed a strong inverse relationship between nitrification rates and water depth (in agreement with Tanner *et al.,* 1999). The basis of this hypothesis is that the microbes (which degrade the pesticides) predominantly inhabit the sediment. As depth increases most water is not in contact with the sediment surface and so the rate constant decreases.

5.3 Materials and Methods

5.3.1 Pesticides, wetland sediment and water

Pesticides and sediment (collected during August 2016) used in this experiment were the same as those used by Ramos *et al.,* (2018b) (Chapter 4). Wetland water was collected from North Wetland (Hope Farm, Cambridgeshire, UK) on 15th of August 2016. Water was filtered through Whatman® qualitative filter paper, Grade 1 (Sigma-Aldrich, Dorset, UK) to remove suspended particles and analysed for pesticides residues (all below LOD).The water pH was 6.5 ± 0.1.

5.3.2 Degradation Experiments

Water-sediments degradation experiments were carried out according to OECD 308 standard test (OECD, 2002) with modifications. The water-sediment experiment was set up in a 1 L glass container. Wetland sediment (200 ± 0.1 g dry weight – 3 cm height) was added to each container followed by 500 mL of wetland water (15 cm – average water depth during the static period in North Wetland). The glass containers were covered with a lid to avoid evaporation. All containers were set at laboratory temperature 21-23°C in the presence of sunlight. To investigate if microbially mediated biodegradation degraded pesticides, half the containers (Treatment A) were treated with 0.05% sodium azide to suppress microbial growth, and half were not (Treatment B).

Sediment was allowed to settle and acclimate for five days before spiking the water with a pesticide working standard solution to mimic surface water runoff. The initial concentrations of the three pesticides were 30 µg L^{-1} for metaldehyde and 100 µg L^{-1} for quinmerac and metazachlor. These initial concentrations were chosen to replicate approximate concentrations observed in the North Wetland in late August 2014 (Ramos *et al.,* 2018a - Chapter 3). Water samples were subsequently collected periodically from each container for 26 days and analysed for pesticides concentrations by LC-MS/MS (Ramos *et al.,* 2017).

Blanks consisted of water and sediment without spiked pesticides. Controls consisted of water with spiked pesticides but without sediment (OECD 308 Guidelines). Sodium azide was also added to the controls, denominated as CA (with 0.05% sodium azide) and CB. Controls were used to evaluate if the pesticides degradation undergoes in the water phase and to differentiate degradation in the water phase from degradation on the sediment interface. All experiments, including blanks and controls, were conducted in triplicate.

5.3.2 Effect of initial concentrations on degradation rates

To test the effect of initial concentration on degradation rates, the water was spiked with individual pesticides metaldehyde and metazachlor to initial concentrations of 1, 5, 10, 20, 30, 80 and 100 µg L^{-1}. Water samples were taken periodically for 22 days and analysed for pesticide concentrations by LC-MS/MS (Ramos *et al.,* 2017).

5.3.3 Effect of water depth on degradation rates

To test the effect of water depth on degradation rates, wetland sediment (200 ± 0.1 g dry weight – 3 cm height) was added to each container followed by 235 ml, 470 ml or 700 ml of wetland water to represent 3 cm, 6 cm and 9 cm respectively. The water was spiked with a pesticide solution containing four pesticides (metaldehyde, quinmerac, metazachlor and propyzamide) at a concentration for each of 10 µg L^{-1}. Water samples were collected periodically over time and analysed for pesticide concentration in solution by LC-MS/MS (Ramos *et al.,* 2017).

5.3.4 Data Analysis

Pesticide degradation commonly assumes first-order kinetic (FOCUS, 2006). First-order kinetics occurs when the rate of change in concentration is directly proportional to the pesticide concentration. The integration of this model in time is described by:

$$C_t = C_0 \, e^{-k.t} \qquad (5.1)$$

where C_t is the concentration at time t, C_0 is the initial concentration, k is the rate constant and t is time. The first-order rate equation is considered unacceptable if the determination coefficient (R^2) falls below 0.7 (Fogg and Boxall, 2003).

A plot ln (C_t/C_0) versus time yields a straight line with slope (determined from linear regression) equal to k. The half-life degradation (DT_{50}) can be calculated by:

$$DT_{50} = \frac{\ln(2)}{k} \tag{5.2}$$

Pesticide biodegradation is commonly accepted to be an enzyme-catalyzed transformation (Okpokwasili and Nweke, 2005). The rate of an enzyme-catalysed reaction can be described by Michaelis-Menten kinetics:

$$v = \frac{V_{max}[C]}{K_m + [C]} \tag{5.3}$$

where C is the concentration in solution, V_{max} is maximum reaction rate and K_m is the half saturation (or Michaelis-Menten) constant (i.e. the concentration at which the rate v is half the maximum rate V_{max}). The Lineweaver-Burk Equation (5.4) was used to calculate V_{max} and K_m (by plotting 1/V vs 1/C):

$$\frac{1}{V} = \frac{1}{V_{max}} + \frac{K_m}{V_{max}} . \frac{1}{C} \tag{5.4}$$

5.3.5 Pesticide analysis

Pesticide concentrations were quantified by the LC-MS/MS method described by Ramos *et al.,* (2017). All analyses were performed with a Waters Alliance 2695 liquid chromatography system coupled to a Quattro Premier XE tandem quadrupole. A Kinetex C18 column (Phenomenex, UK) was used for chromatographic separation. Samples were filtered with 0.2 µm syringe filters (Millipore Millex^{TM,} Fisher Scientific, UK) and analysed in triplicate.

5.4 Results and Discussion

5.4.1 Degradation experiments: quinmerac, metaldehyde and metazachlor (suppressed vs unsuppressed)

Results reported in Figure 5.1 show observed changes in the concentrations of quinmerac, metaldehyde and metazachlor over time in glass vessels incubated in the laboratory with microbial suppression using sodium azide (Treatment A/suppressed) and without microbial suppression (Treatment B/unsuppressed). These three pesticides were selected because they were observed to decrease over time in the North Wetland during the static conditions reported in Chapter 3.

For quinmerac (Figure 5.1a), first-order kinetics (equation 5.1) fitted the measured degradation data well ($R^2 = 0.85$). There was no difference in rate of degradation between treatment A ($k = 0.009$ day^{-1}) and treatment B ($k = 0.009$ day^{-1}) (i.e. DT_{50} = 84.7 days). The initial spiked concentration of 100 ± 0.85 µg L^{-1} decreased to around 80 ± 0.71 µg L^{-1} at the same rate over the 26 days on both treatments. Results indicated that suppressing the microbial activity does not have any effect on quinmerac degradation. Quinmerac is known to be a very stable compound, and previously published DT_{50} values in water, soil and water-sediment systems are 88.7, 30.0 and 179.4 days (Lewis *et al.,* 2016). The calculated DT_{50} (84.7 days) is consistent with the DT_{50} in water (88.7 days) reported by Lewis *et al.,* (2016) but lower than the value of 138.8 days reported by the European Food Safety Authority (EFSA) (EFSA, Quinmerac, 2008). EFSA reported that quinmerac is stable to hydrolysis at pH 5 to 9 but can slowly be degraded under artificial light (photolysis) (EFSA, Quinmerac, 2008). The pH of the water phase (pH = 6) suggests that hydrolysis rate would be very low. Therefore, it is reasonable to assume that the observed changes in quinmerac concentrations were due to photolysis since the experiment was performed at normal sunlight. The decrease in quinmerac concentrations was also observed in Controls A and B (water only, no sediment).

For metaldehyde samples (Figure 5.1b) there is a clear difference in the rate of degradation between treatment A (0.01 day^{-1}) and treatment B (0.09 day^{-1}). In treatment A, initial metaldehyde concentrations of 30 ± 1.2 µg L^{-1} decreased to

22.7 ± 3.9 µg L^{-1} over the 26 day period. Distinctively, in treatment B, metaldehyde concentrations decreased from the initial 30 ± 0.9 µg L^{-1} to 5.5 ± 1.5 µg L^{-1} during the same period. The calculated DT_{50} values for treatment A and B were 69.3 and 14.7 days, respectively. Thus, there is clear evidence that adding sodium azide as a microbial inhibitor has an effect on metaldehyde removal, implying a microbial degradation for this compound. In Treatment B (Figure 5.3b) there is an initial period of 7 days where metaldehyde concentrations decrease slowly and thereafter follow first-order kinetics. This initial period was assumed to be equivalent to the microbial lag-phase reported by other authors for pesticide mineralization in soil (Boivin *et al.,* 2005; Kah *et al.,* 2007), water (Larsen *et al.,* 2001) and water-sediment systems (Warren *et al.,* 2003; Katagi, 2016; Albrechtsen *et al.,* 2001). It is often explained as an acclimation period in which the microbial community adapts to the introduction of a new carbon and energy source (Albrechtsen *et al.,* 2001; Pesce *et al.,* 2010; Paszko, 2009). Adaptations include the induction of relevant enzyme synthesis and the preferential growth of competent organisms which can utilise the new energy source (Okpokwasili and Nweke, 2005). During the initial lag-phase, metaldehyde concentration decreased from the initial 30 ± 0.7 µg L^{-1} to 22.4 ± 2.2 µg L^{-1}, similar to the decrease observed in the control samples.

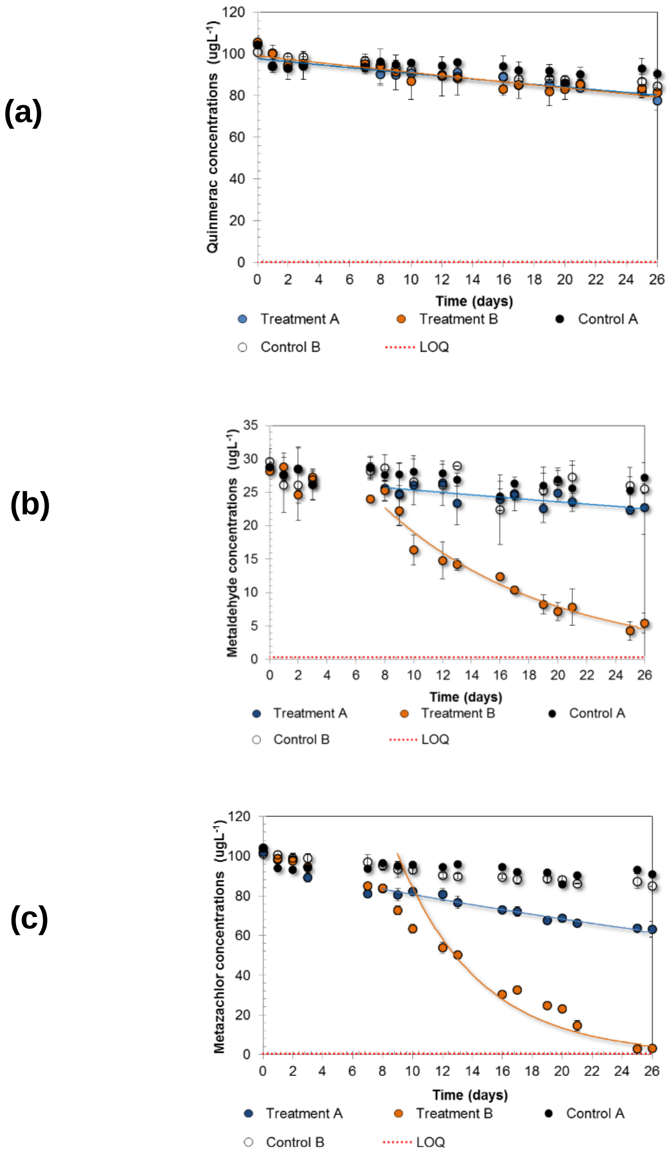

Figure 5.1. Quinmerac (a), metaldehyde (b) and metazachlor (c) concentration (μg L^{-1}) over time in Treatment A (microbial suppression with 0.05% sodium azide), Treatment B (without microbial suppression), controls A and B. Error bars denote standard errors for replicates (n=3). The red dashed line is the LOQ (0.03 μg L^{-1} for quinmerac, metaldehyde and metazachlor).

The DT_{50} for Treatment B was calculated including the lag phase period (as recommended by the OECD, 2002). The value of 14.7 days is consistent with the value reported by Lewis *et al.,* (2016) in water-sediment systems (12.2 days) and from values reported by EFSA (EFSA, metaldehyde, 2009). The report results showed a lag phase period of 7 days with DT_{50} values in water ranging from 10.3-11.4 days. The report also highlighted that metaldehyde can be biodegraded under oxidising conditions but is more persistent under reductive conditions. Unfortunately, dissolved oxygen was not measured as a controlling parameter, and further experiments will be necessary to understand how the presence of oxygen can influence metaldehyde biodegradation.

The K_{oc} value (23.1 L kg^{-1}) for metaldehyde in wetland sediment derived from Ramos *et al.,* (2018a) (Chapter 4) indicated low sorption to sediment and it is expected the majority of metaldehyde molecules remain in the water phase. Metaldehyde is known to be very stable in water (Bieri *et al.,* 2003; Lu *et al.,* 2017; Stuart *et al.,* 2011) and degradation in the water phase is unlikely to occur (Dolan *et al.,* 2014; Dolan *et al.,* 2013). This was also observed in controls A and B (water only controls with and without sodium azide), where metaldehyde concentrations remained relatively constant throughout the study period (Figure 5.1b). This suggests that the degradation of metaldehyde observed in the active treatment B (and partially in the microbially-suppressed A) occurs mainly at the water-sediment interface. The changes in concentration observed in the microbially-suppressed treatment (A) suggests that some biodegradation may have taken place and the percentage of sodium azide added was not enough to inhibit the microorganisms responsible for metaldehyde degradation during a long experiment.

In the case of metazachlor (Figure 5.1c), there is a clear difference in the rate of degradation between Treatment A (0.02 day^{-1}) and Treatment B (0.11 day^{-1}). In the Treatment A, metazachlor concentrations decrease quasi-linear to 62.9 ± 2.9 µg L^{-1} during the studied period. The reaction fitted first-order kinetics well with a derived DT_{50} value of 34.7 days. In Treatment B (unsuppressed) there was a clear lag-phase period of 8 days, where concentrations decreased from 100 ± 0.8 µg L^{-1} to 83.7 ± 2.4 µg L^{-1}. After this period, concentrations decreased over time following first-order kinetics, characteristic of microbial biodegradation. Metazachlor concentrations decreased to 2.9 ± 0.8 µg L^{-1}, reaching a plateau on day 25. In Treatment B, the best-fit DT_{50} value was 14.3 days, which is consistent with the values from an EFSA report (13.4 to 27.8 days) (EFSA, Metazachlor, 2008) and lower than the value of 20.6 days reported by Lewis *et al.,* (2016). EFSA reported metazachlor to be hydrolytically stable at pH 5 to 9 and photo-catalytically stable under the influence of sunlight (EFSA, metazachlor, 2008). This was also observed in Controls A and B (Figure 5.3c), where metazachlor concentrations remained constant throughout the studied period. Since metazachlor is hydrolytically and photo-catalytically stable, the decrease in concentrations in Treatment A can be explained by the fact that, as for the case of metaldehyde, the percentage of sodium azide (0.05%) added to the system might not be enough to fully inhibit the microbial activity for the whole length of the experiment.

Comparison to field data

Figure 5.2 shows the concentrations of quinmerac, metaldehyde and metazachlor in Treatment B of the water-sediment systems (microbially active) together with field data collected from the North Wetland at Hope farm during a static (stagnant) period (see Chapter 3). Quinmerac concentrations in the wetland decreased over time from 100 µg L^{-1} to 50 µg L^{-1} in four days due to minor rainfall events that promoted dilution. After day 5, quinmerac concentrations remained relatively constant for the following 26 days. Here, first order kinetics did not fit the data well ($R^2 < 0.7$) and therefore the degradation rate constant was assumed to be zero. From laboratory degradation experiments, the decrease in quinmerac concentrations could have been due to photolysis. However, this was not observed in the field data from the North Wetland. The reason could be that quinmerac photolysis is expected to be lower in the wetland water phase due to the presence of vegetation that can extinguish solar radiation in the water column. The experiment showed that quinmerac exhibited high persistence in the water-sediment system (DT_{50} = 84.7 days) and even higher persistence at the North Wetland, showing low potential to mitigate this herbicide. Due to the low degradation of quinmerac in water-sediment systems, this herbicide was not studied for the effect of initial concentrations on degradation rates.

Similarly to the observed behaviour of quinmerac, the decrease in metaldehyde concentrations in the first four days at North Wetland was due to minor rainfall events that promoted dilution. Thereafter, metaldehyde concentrations in the North Wetland decreased following first-order kinetics in a similar way to that observed in Treatment B.

The metaldehyde data at the North Wetland fitted first-order kinetics with a degradation rate constant of 0.04 day^{-1} ($R^2 = 0.76$) equivalent to a DT_{50} of 17.3 days. Interestingly, the lag phase phenomenon was not apparent in the North Wetland data (Figure 5.2b). This may be due to the development of a competent microbial community in this system as a consequence of repeated exposure to metaldehyde. Although the sediment used in the degradation experiments had been previously exposed to these pesticides, the sediment was collected several months prior to the experiments. It has been observed that the competence of a microbial consortium to degrade organic pollutants can be lost if the time between exposures is long. For example, Rolf (2016) observed that the rate constants for metaldehyde associated with microbial biofilms in slow sand filters used in water treatment decreased when metaldehyde concentrations were low or absent. When these organisms were then exposed to high concentrations a lag phase was observed before removal rates increased to their optima.

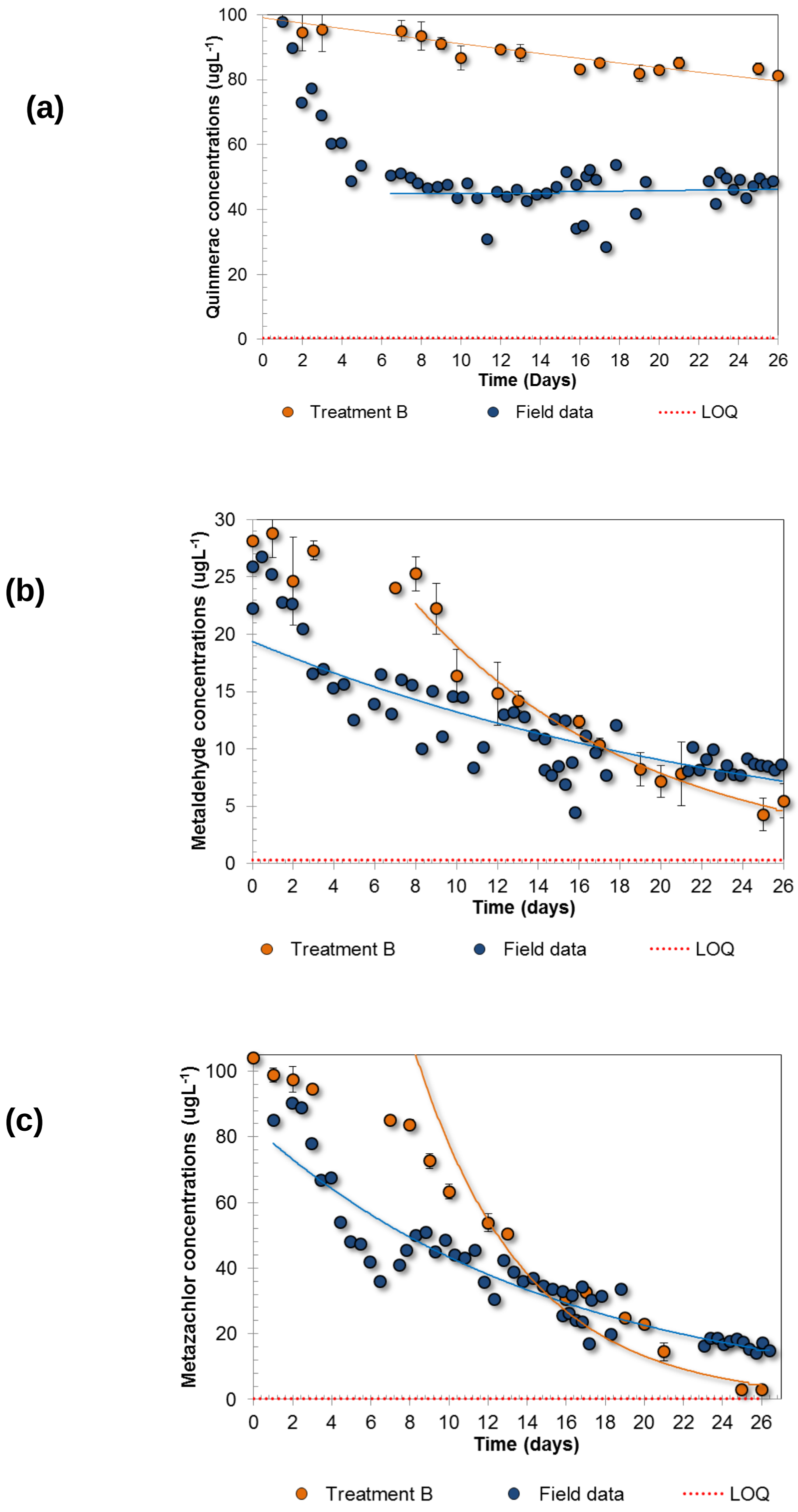

Figure 5.2. Quinmerac (a), metaldehyde (b) and metazachlor (c) concentrations over time in the lab-water-sediment system microbially active and from field data collected at the North Wetland (static period).

The decrease in metaldehyde concentrations observed during a static period in the North Wetland was the first field observation for this pesticide with a major concern for water treatment companies in the UK. The findings suggest that shallow free-water surface constructed wetlands can mitigate metaldehyde to some extent and that the main removal mechanism is biodegradation. However, the biodegradation rate is slow (0.04 day^{-1}) and a residence time of at least 17.3 days is needed to observe a 50% reduction in its concentration.

Metazachlor (Figure 5.2c) concentrations were diluted in the first four days of the static period due to minor rainfall events. Thereafter, metazachlor concentrations in the North Wetland decreased following classic first order kinetics, characteristic of microbial biodegradation activity as observed in Treatment B. The metazachlor data at North Wetland fit a first-order kinetic and the degradation rate is 0.07 day^{-1} (R^2 = 0.89) and DT_{50} is 9.9 days.

A summary of the data is reported in Table 5.1. The DT_{50} value for field-biodegradation of metaldehyde, 17.3 days, is higher than that measured in the lab (14.7 days). However, when a temperature correction factor (Q_{10}) is introduced for the difference in temperature between the lab (22°C) and the field (where the average temperature during the static period was 12°C), the values become more similar. The Q_{10} is a temperature coefficient describes the change in the rate constant with changing temperature in a biological or chemical system. It represents the increase in rate constant for an increase in temperature of 10°C resulting from increased microbial activity (and, implicitly, changes in the temperature-dependent partition coefficients of the pesticide). The Q_{10} value often used for pesticides is 1.2. From Equation 5.5 it is possible to extrapolate the rate to compare lab and field data.

$$Q_{10} = (R2/R1)^{10°/(T2-T1)} \qquad (5.5)$$

where R is the rate (day^{-1}) and T is temperature (°C).

The calculated DT_{50} value of 16.2 days for metaldehyde (with the temperature correction factor) becomes closer to the observed one of 17.3 days in the field. This discrepancy can be partly explained by the nature of the chemical (difficult to quantify) and the assumptions made during the calculations (e.g. field temperature and height of the water level in the pond).

Metaldehyde degradation intermediates (acetaldehyde and paraldehyde) are easily uptaken and used by the microbial population in the sediments and do not accumulate in the environment, suggesting that the window of values reported (8-17 days) are the time required for the full removal of metaldehyde. Whereas metazachlor metabolites were not investigated in this study, Vonk *et al.,* (2012) reported the isolation of two metazachlor metabolites (BH-518-2 and BH-518-5) and calculated DT_{50} values were higher than 300 days.

Results from the laboratory experiments and from the field data showed that both pesticides can be degraded (fully or partially) in water-sediment systems by microbial action, but that the degradation rates are too low to allow for an effective *in-field* treatment.

Table 5-1.Degradation rate constants, DT_{50} and R^2 for quinmerac, metaldehyde and metazachlor in Treatment A, Treatment B and from the field data collected at North Wetland

Pesticide	Water-sediment system	Deg. Rate (day^{-1})	DT_{50} (days)	R^2
Quinmerac	Treatment A	0.009	84.7	0.85
	Treatment B	0.009	84.7	0.85
	North Wetland – Field data	-	-	-
Metaldehyde	Treatment A	0.01	69.3	0.73
	Treatment B	0.09	14.7	0.96
	North Wetland – Field data	0.04	17.3	0.76
Metazachlor	Treatment A	0.02	34.9	0.97
	Treatment B	0.11	14.3	0.92
	North Wetland – Field data	0.07	9.9	0.89

5.4.2 Effect of initial concentrations on degradation rates

Metaldehyde and metazachlor degradation rates were calculated for the water-sediment system. The degradation curves of metaldehyde and metazachlor over 22 days at different initial concentrations followed a first-order kinetic model. Figure 5.3 shows the plot of rates of degradation against initial pesticide concentration following a Michaelis - Menten saturation curve, characteristic of microbial reactions mediated by enzymes. Rates of degradation at different initial concentration, DT_{50} values, V_{max} and K_m are shown in Table 5.2.

This experiment showed that there is an influence of the initial concentration on the degradation rate of metaldehyde and metazachlor. At lower initial concentrations, the reaction rate is proportional to initial concentrations for both pesticides and as pesticide concentrations increases, the degradation rates (k) eventually become independent of the concentration. The calculated V_{max} for metaldehyde and metazachlor are 0.03 day^{-1} and 0.05 day^{-1}. V_{max} is the maximum rate of reaction which is dependent on the microbial concentrations in the wetland sediment. More important is the value of K_m which is the pesticide concentration at which a reaction rate is half of $V_{max.}$ The calculated K_m values for metaldehyde and metazachlor were 1.1 µg L^{-1} and 0.7 µg L^{-1}.

There was a marked decrease in the DT_{50} values of metaldehyde up to 50 µg L^{-1} concentration, at concentrations above 50 µg L^{-1}, degradation rates did not change, suggesting the reach of a saturation level for the enzymes involved in the degradation or a change of uptake mode. The initial rate of degradation was very slow with a DT_{50} value of 43.3 days.

The rate of degradation of p-chlorobenzoate and chloroacetate at initial concentrations of 0.05 µg L^{-1} to 50 µg ml^{-1} fell noticeably below 2 µg L^{-1}. The authors suggested the existence of a threshold below which no significant mineralization would occur (Boethling and Alexander, 1979). The data on metaldehyde suggest a similar behaviour (DT_{50} decreased from 43.3 to 27.3 days when concentration increased from 1 to 5 µg L^{-1}. It is likely that the energy released from the oxidation of the compound is too little to meet the energy demands of the small number of microorganisms able to degrade the compound.

It should be mentioned, however, that organic compounds can be degraded by co-metabolism in addition to being degraded directly as a carbon and energy source. Co-metabolism is the simultaneous degradation of two compounds, in which one compound is used for energy and growth and the other (the secondary substrate) is degraded only as a consequence of the first compound being present (Dalton and Stirling, 1982). Metazachlor DT_{50} values showed comparatively lower decreases in magnitude with a similar trend.

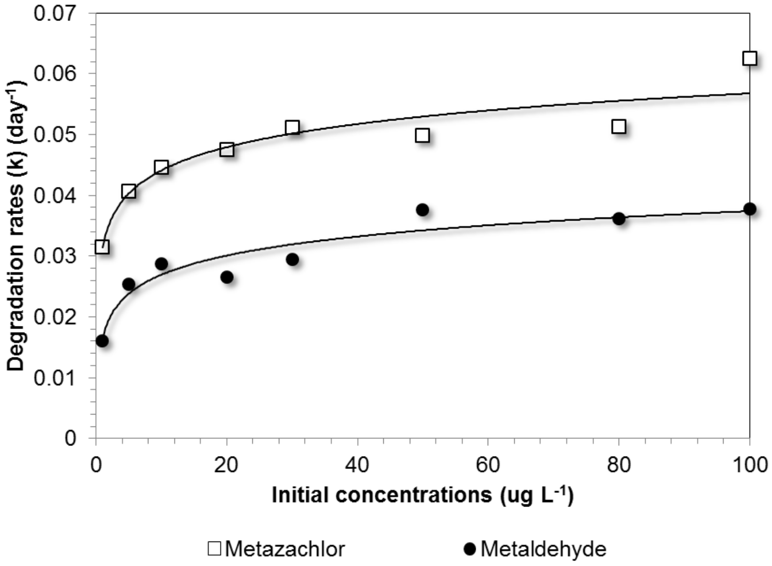

Figure 5.3. Degradation rates versus Initial pesticide concentration (● metaldehyde □ metazachlor)

Besides the clear evidence of the effect of the initial concentrations on the degradation rates, the values obtained in this experiment for metaldehyde (0.029 day^{-1}) and for metazachlor (0.062 day^{-1}) were lower compared with the values in treatment B (metaldehyde 0.09 day^{-1} and metazachlor 0.11 day^{-1}), when the initial concentrations were 30 µg L^{-1} for metaldehyde and 100 µg L^{-1} for metazachlor. The current hypothesis is that the presence of other pesticides in solution (treatment B contained quinmerac, metaldehyde and metazachlor) could enhance the degradation of pesticides (Swarcewiz and Gregorczyk, 2012; Fogg and Boxall, 2003). Further experiments need to be done to test the influence of presence other pesticides on the biodegradation rate.

Table 5-2. Degradation rates constants (day^{-1}), DT_{50} values (days), V_{max} (day^{-1}) and K_m (µg L^{-1}) for metaldehyde and metazachlor in water-sediment systems

	Metaldehyde				**Metazachlor**			
Initial Concentration (µg L^{-1})	**Deg. rates (day^{-1})**	**DT_{50} (days)**	**V_{max} (day^{-1})**	**K_m (µg L^{-1})**	**Deg. Rates (day^{-1})**	**DT_{50} (days)**	**V_{max} (day^{-1})**	**K_m (µg L^{-1})**
1	0.016	43.3	0.03	1.1	0.032	22.1	0.05	0.7
5	0.025	27.3			0.041	17.0		
10	0.029	24.2			0.047	15.5		
20	0.027	26.1			0.048	14.6		
30	0.029	23.5			0.051	13.6		
50	0.037	18.5			0.049	13.9		
80	0.036	19.2			0.051	13.5		
100	0.037	18.4			0.062	11.1		

5.4.1 Effect of water depth on degradation rates

Changes in pesticide concentrations over time in the mesocosm with different water depths are reported in Figure 5.4 In all cases, there is an initial lag phase of about 5 days with little or no concentration change over time for most treatments, followed by a marked decrease in concentrations over the following week. In this experiment, the hypothesis was that the rate constants would be inversely proportional to water depth because the majority of the degrading microbes are assumed to inhabit the sediment in fixed biofilms (*e.g.* freely suspended cells and cells associated with suspended solids are relatively unimportant as degraders). The water column to sediment surface area (i.e. water depth), would, therefore, be expected to control the concentration change in the water column.

In the case of metaldehyde (Figure 5.4B), the concentration in the initial spike (time zero) was lower than the expected 10 µg L^{-1}, probably due to an operator error. As LC-MS/MS analysis was done after the end of the trial, the concentration could not be corrected in time during the trial to match the concentration of the other pesticides in the system. This error produced values close to the LOQ of the method. Notwithstanding this, the samples showed a small difference between treatments and produced DT_{50} and k values comparable to those obtained in the field and in the jars trials. For propyzamide, metazachlor and quinmerac, differences were observed between treatments (Table 5.3).

The effective rate constants for metaldehyde, metazachlor, propyzamide ranged from 0.010 day^{-1} for quinmerac at 9 cm depth to 0.285 day^{-1} for metazachlor at 3 cm depth, which translate into a half-life of 68 and 2.4 days respectively. This range of DT_{50} values is similar to those values reported in Table 5.1 for these compounds, derived from laboratory water-sediment experiment.

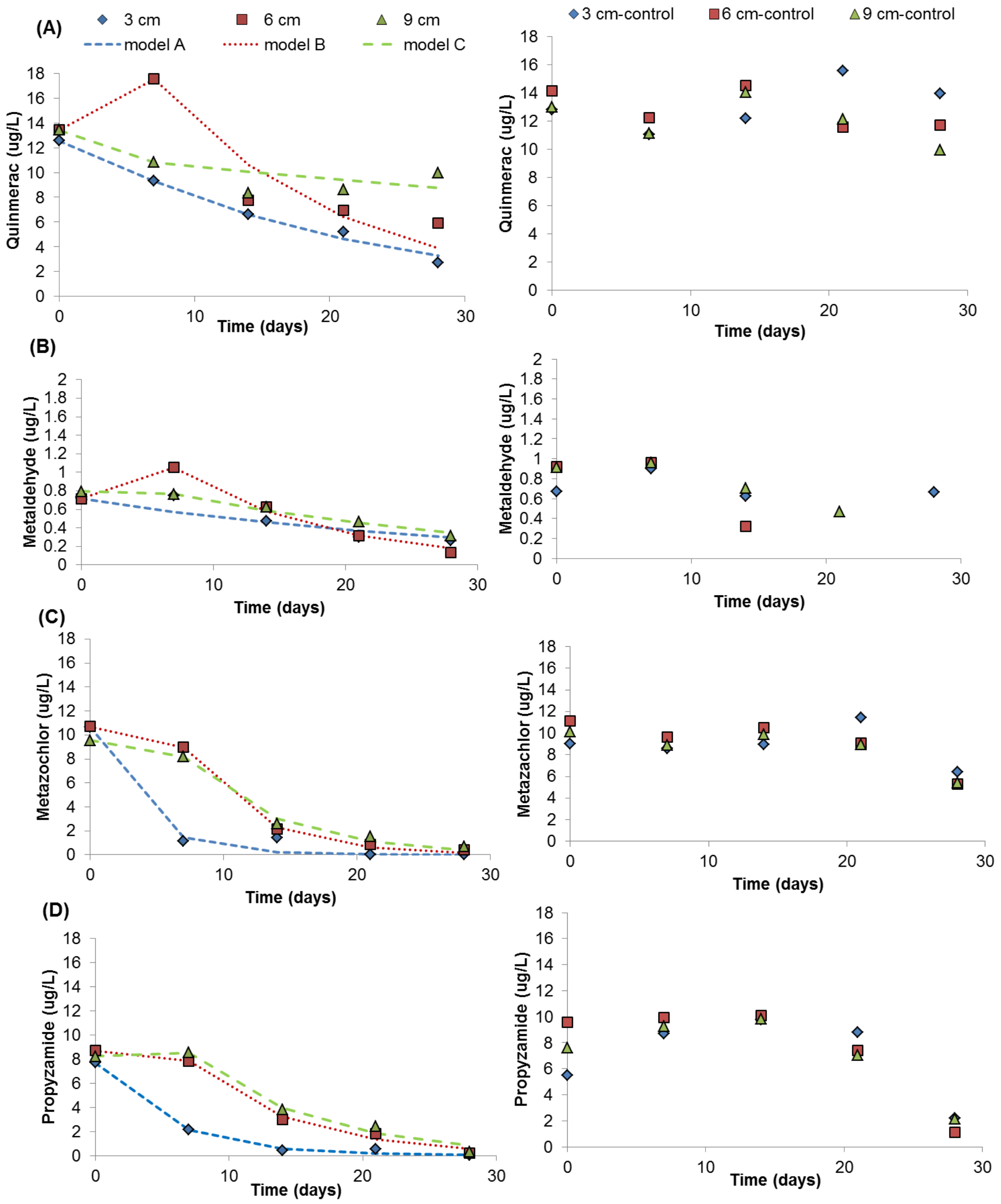

Figure 5.4.Changes in pesticide concentrations (A) quinmerac, (B) metaldehyde, (C) metazachlor and (D) propyamide over time in mesocosm containing sediments (200g = 3cm) and different volumes of wetland water representing different depths (3 cm, 6 cm and 9 cm).

The rate of quinmerac dissipation was the slowest of all five compounds investigated (range for 0.03-0.05 day^{-1}), which reflects the fact that quinmerac is generally slower to degrade than the other compounds (Table 5.3). However, the *DT_{50}* for quinmerac observed here was also relatively short (13-24 days) compared to value from the water-sediment experiment (84.7 days).

Table 5-3.Degradation rate constants (k) (day^{-1}), *DT_{50}* (days) of first order kinetic curves on the mesocosm data

Pesticide	**Water depth (cm)**	***k* (day^{-1})**	**DT_{50} (days)**
Quinmerac	3	0.05	13.9
Quinmerac	6	0.072	9.7
Quinmerac	9	0.01	68
Metaldehyde*	3	0.032	21.9
Metaldehyde*	6	0.085	8.2
Metaldehyde*	9	0.038	18.5
Metazachlor	3	0.285	2.4
Metazachlor	6	0.193	3.6
Metazachlor	9	0.142	4.9
Propyzamide	3	0.184	3.8
Propyzamide	6	0.126	5.5
Propyzamide	9	0.109	6.4

This experiment reinforces the hypothesis that the presence of other pesticides could possibly enhance the degradation rates (e.g. via co-metabolism), since the calculated rates from the mesocosm experiment are significant higher compared with the laboratory experiments and the field data. However, in this case, it is very unlikely that the presence of other pesticides would have increased the degradation rate by factor of 10.

5.5 Conclusions

The fate of pesticides quinmerac, metaldehyde and metazachlor were studied in water-sediment systems. Two treatments were set, in which microbial activity was supressed in one (Treatment A) but not in the other (Treatment B). Results were also compared with the observations of these pesticides in the North Wetland during a static period. Quinmerac degradation rates followed a first-order kinetic and it was similar (0.008 day^{-1} i.e. DT_{50} = 71 days.) in both treatments. The possible loss for quinmerac in the vessels was due to photolysis. Comparing to quinmerac concentrations at the North Wetland during the static period, degradation rate did not fit a first-order kinetic and concentrations remained relatively constant.

Metaldehyde degradation followed first order kinetics in both systems. However, there was different rate of degradation in Treatments A and B. In Treatment A, the reaction rate was 0.01 day^{-1} (DT_{50} = 69.3 days). In Treatment B, the reaction rate was 0.09 day^{-1} (DT_{50} = 14.7 days). In treatment B, it was observed a lag phase period of 7 days, followed by first-order kinetic model, which is observed to on microbial-mediated biodegradation reactions. Metaldehyde concentrations at the North Wetland also fitted a first order kinetic and the reaction rate was 0.04 day^{-1} (DT_{50} = 17.33 days). The lag phase period was not observed in the field and the explanation is due to the consecutively repeated exposure to metaldehyde.

Metazachlor concentrations fitted a first order kinetic model, but there was a distinct difference between Treatment A and Treatment B. In Treatment A, metazachlor degradation rate was 0.02 day^{-1} (DT_{50} = 34.9 days) and in Treatment B, metazachlor degradation rate was 0.11 (DT_{50} = 14.3 days). Metazachlor concentrations on North Wetland also fitted a first-order kinetic and the rate was 0.07 day^{-1} (i.e. DT_{50} = 9.9 days). The degradation experiments suggested that metaldehyde and metazachlor were degraded by microbial activity and the results were used to confirm by extent that it was the same removal mechanism responsible for the deceased in concentrations in the North Wetland.

The effect of initial concentration of metaldehyde and metazachlor on the degradation rate was observed. The degradation rate increased with the concentration, but at certain level the increase in concentration did not have an effect on the reaction rate. The Michaelis-Menten parameter K_m for metaldehyde and metazachlor were 1.1 µg L^{-1} and 0.7 µg L^{-1}, which shows the pesticide concentration at which the enzyme is more effective.

The mesocosm experiment was used to test the hypothesis that degradation rate is inversely proportional to the water depth. Results showed no significant difference for metaldehyde and carbetamide. However, for propyzamide, metazachlor and quinmerac, differences were observed between treatments, mainly in the different rates during the lag phase but the rates after this period were very similar.

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6 . General Discussion and Conclusions

6.1 Meeting the aim and objectives

Article 7 of the Water Framework Directive promotes a prevention-led approach to achieve the DWD compliance for pesticides in drinking water of 0.1 µg L^{-1} for individual pesticides and 0.5 µg L^{-1} for total pesticides at the point of supply

(Dolan *et al.,* 2013). The prevention-led approach is based on several potential catchment solutions, such as application control (amount and timing), the use of buffer (and no-spray) zones and, potentially, the use of constructed wetlands (Gregoire *et al.,* 2009) to attenuate the impact of pesticide contamination from agricultural land (Dolan *et al.,* 2014). Natural and man-made wetlands are well known to provide efficient removal of organic materials, nutrients and metals (*e.g*. CEH, 2001; Newman *et al.,* 2015), via a combination of sorption and biodegradation before these compounds are released into the natural drainage network or reach water supply reservoirs. Several experiments have indicated that pilot constructed wetlands in the laboratory have potential to mitigate pesticides but the evidence at field scale is rather limited and the reported efficiency is variable (Reichenberger *et al.,* 2007).

The overall aim of this thesis was to improve understanding of the processes affecting pesticide fate and transport in free-water surface constructed wetlands (FWS CWs) in order to assess their utility as potential mitigation features. This study focused on six pesticides: metaldehyde, quinmerac, carbetamide, metazachlor, propyzamide and pendimethalin. Metaldehyde is a molluscicide and the other five are herbicides which are commonly applied to arable crops in the UK. Metaldehyde has been reported as the biggest pesticide challenge currently facing the UK water industry and has been responsible for several compliance failures in recent years (Environmental Agency, 2009; Kay and Grayson, 2014).

Pesticide monitoring for all these compounds in this project was a challenging task because several different methods are needed. Existing methods at Cranfield University were based on individual techniques – many employing pre-concentration steps (using solid-phase extraction) before analysis. This was time-consuming and unreliable. Several errors were found in the determination of concentrations in samples and standards. A new method was, therefore developed which simultaneously determines the pesticides of interest in a single sample run.

Objective 1: To develop a direct aqueous injection multi-component method for the determination of six pesticides by LC-MS/MS in environmental waters.

The specific requirements of the method were to be accurate and rapid in order to permit an efficient processing of a large number of samples. The method was validated according to the performance criteria established by ICH guidelines (ICH, Harmonised Tripartite Guideline, 2005). The method showed a good range of linearity (R^2 ranged from 0.995 to 0.999), accuracy (84 to 100%) and RSD precision (4 to 15) and there was negligible matrix effect compared to the same pesticides in ultra-pure water. The limit of quantification (LOQ) ranged from 0.2 to 1.0 µg L^{-1}. Although not appropriated for assessing DWD compliance, the method was acceptable for detecting pesticide concentrations in natural waters from Hope Farm (Cambridgeshire, UK) where pesticide concentrations can exceed 100 µg L^{-1}. The method was relatively straightforward to implement with simple sample preparation, which reduced the analysis time improved laboratory efficiency practices. At the time this thesis was written, the method described in Chapter 2 (Ramos *et al.,* 2017), was the starting point for more complex methods, including several additional pesticides (15 in total, including insecticides). It has also been adapted for ultra-performance liquid chromatography (UPLC) which can analyse a sample less than 6 minutes.

The analytical method was used as a key tool to determine concentrations in water samples collected from FWS CWs at Hope Farm and for the laboratory experiments developed to study sorption and degradation behaviour.

Objective 2: To determine the effectiveness of existing free-water surface constructed wetlands for retaining and mitigating pesticides transfers from land to surface waters.

The main aim of this research was to investigate the effectiveness of existing FWS CWs (e.g. ponds) to mitigate pesticides transferred from land to surface waters. Generally, these features are recognised as effective, ecologically friendly and low- cost solutions for dealing with nutrient pollution and, more recently, pesticides. In the case of pesticides, a wide range of removal efficiencies has been reported, ranging from 0% (Passeport *et al.,* 2014) to 100% (Vymazal and Tereza, 2015), depending on the system considered (e.g. residence time, depth, vegetation distribution) and the type of pesticides monitored.

Chapter 3 presented data from monitoring two FWS CWs (the South Wetland and the North Wetland) situated at the RSPB's Hope Farm in Knapwell Cambridgeshire, UK. These wetland systems are simple structures which were built on the stream and ditch network at the farm using diggers and loaders. The South Wetland has a large catchment area of 3.9 km^2 which includes other farms. In contrast, the North Wetland has a smaller catchment of just 0.66 km^2 which is entirely within the boundaries of Hope Farm. All monitored wetlands had a free water surface with emerging vegetation that covered the wetland surface by at least 70%. In all systems, a set of hydraulic flow control structures (weirs and flumes) were constructed to monitor discharge continuously and automatic water samplers were positioned at strategic locations (the inlets and outlets of each pond). Water samples were taken approximately every 8 hours from August to mid-December 2014.

Several dye tracing tests were carried out together with Vassia Ioannidou, Ian Guymer and Ian Bayliss from the School of Engineering at the University of Warwick. The dye tracing tests were used to determine the hydraulic residence time (HRT) of the wetlands. Results of these exercises showed that, in general, mixing of the dye was incomplete, resulting in short-circuiting. This reduced effective residence time and will consequently have reduced attenuation potential because the time available for pesticide losses (e.g. biodegradation, net sorption, volatilisation) is low.

The South Wetland system consisted of two FWS CWs in series. The hydrometric data for this system showed an average discharge of 19 L s^{-1} over the monitored period, and the recorded flows were very similar at each monitored station. Several discharge peaks were observed after rainfall events, with lag times to peak discharge typically in the range of 24 hours. All recession curves were approximately exponential. From the dye tracing exercises the average HRT was estimated to be approximately 1.9 hours but during peak flows (e.g. 13/10/2014 and 22/11/2014) the HRT decreased to about 30 minutes.

Highest peak pesticide concentrations were typically observed during the falling limb of the hydrograph. This is consistent observations reported for other pesticides in other catchments (e.g. Passeport *et al.,* 2014; Tediosi *et al.,* 2012). Whilst an 8 hour sampling regime probably captured (approximately) the overall pattern of concentration changes during storm events, including the peak, more frequent sampling would have been useful at least to confirm the validity of the choice of an 8 hour sample interval. Further work with more frequent sampling could focus on specific rainfall events after pesticide application in order to obtain better event resolution. In terms of assessing wetland removal efficiency the 8 hour sampling regime was not consistent with the short hydraulic residence time of each wetland system, although staggering sample times by (say) 1 hour between inlet and outlet was probably able to capture the overall picture of removal efficiency reasonably accurately because the time scale for concentration change in the inlet (i.e. the catchment concentration response time) appears to be longer than this. Nevertheless, strictly speaking, sampling for the detection of removal should actually be staggered by a best-estimate of residence time of the system at the time of sampling (e.g. determined by dye tracing at this time: Fox *et al.,* 2000; Whelan *et al.,* 2007; Lange *et al.,* 2011). Better still, composite samples collected with an automatic water sampler over, say, 24h (e.g. Rühmland *et al.,* 2015), which should also be staggered by the residence time. All too often the solute residence time is not considered in input-output studies of pond and wetland performance for pollutant removal and samples are often collected simultaneously from the inlet and the outlet, even in systems with long residence times (e.g. Bundschuh et al., 2016). This approach is flawed unless the systems are approximately in steady state (common for wastewater treatment but not in stormwater ponds during storm events: Verlicchi and Zambello, 2014).

Overall, the findings from South Wetland data suggested that this system was inefficient at mitigating metaldehyde, carbetamide and propyzamide transfers (i.e. metaldehyde, carbetamide and propyzamide concentrations in paired inlet and outlet samples were not significantly different). The main explanation for poor performance was the very short hydraulic residence time of the monitored system at the time when peak concentrations of pesticides were observed.

In the case of carbetamide the concentration pattern appears to be inconsistent with the hydrological data – at least for the first half of the data set shown – with elevated concentrations during hydrograph recessions. The explanation for this phenomenon is currently uncertain, but we have retained the data because they add information value in terms of pesticide behaviour in the wetland system. It is possible that the carbetamide concentration pattern could be a consequence of a dilution effect (where loads are maintained but where concentrations decrease due to increased contributions of runoff with low-concentrations – e.g. from parts of the catchment in which carbetamide has not been used or from hydrological pathways which are not in contact with sources). It is known that a relatively small fraction of the soil porewater needs to be mobilized to generate significant concentrations in drainflow (Tediosi et al., 2012) which suggests that most runoff is essentially pesticide free diluent.

Unfortunately, the reliability of the flow data in the North Wetland was poor overall and on several occasions, failures occurred to the hydraulic structures (*e.g.* undermining and leakage). The outlet pipe discharge and the level logger located at the outlet were considered to be most reliable. The North Wetland data cover two distinct periods: static and flowing. During the static period concentrations of metaldehyde, metazachlor and quinmerac decreased quite rapidly over time initially due to a combination of minor rainfall events that promoted dilution and advective outflow. Subsequently, pesticide concentrations decreased exponentially (suggesting first-order kinetics). The current hypothesis is that the decreases in concentrations were due to microbial activity. These findings are the first field observations of metaldehyde, quinmerac and metazachlor decreases within a static FWS CW and they highlight that FWS CWs can mitigate pesticides transfers in principle, albeit as a low rate.

During the flowing period several pesticide peaks were observed but, again, no significant differences between the inlet and outlet concentrations could be detected. This also reflects low hydraulic residence time in this system during the flowing period (*c.a.* 1 hour). Bendoricchio *et al.,* (2000) suggested that an HRT of 5 to 14 days is probably needed for effective attenuation of organic compounds in constructed wetlands, so it is unsurprising that no removal was detected at Hope Farm. That said, Passeport *et al.,* (2013) reported load reductions of 45 and 96% for 11 herbicides and 5 fungicides in an artificial free surface wetland with large surface area (1280 m^2) and an average hydraulic retention time of 8 hours and Braskerud *et al.,* (2003) reported removal of 3 to 67% of pesticides in a small free-water constructed wetland covering 0.4% of the catchment area.

In hindsight, the small size of the wetlands at Hope Farm was a major limitation. The wetland surface area to catchment area was just 0.001% for the South wetland and 0.03% for the North wetland. Since residence time will be inversely proportional to catchment area and proportional to wetland volume, increases in the removal potential of FWS CWs can only be realistically achieved with a low ratio between catchment area and wetland surface area. If wetlands are large in relation to the catchment area, the relative retention time is usually high. However in agricultural catchments this possibility is always limited due to land availability (Gregoire *et al.*, 2009). Furthermore, increases in discharge during storm events mean that residence times tend to decrease at exactly the same time that pesticide concentrations are increasing, confounding attenuation potential. Further studies are needed to understand the best catchment size required to reduce pesticide concentrations and loads in a wetland of given dimensions. Hydrochemical models (e.g. Whelan, 2013; Krogseth et al., 2017) can be useful in this context in order to help determine the best ratio for optimal performance.

Other options to improve wetland performance by increasing actual (theoretical) retention times include changing the inlet strategy (Tournebize *et al.,* 2016). FWS CWs can be placed either in-stream (on line) or off-stream. In-stream wetlands are often under-dimensioned for pesticide attenuation (as was the case here). Off-stream wetlands may help in this respect. These could consist of wetlands within or at the edge of field. Alternatively they could be designed along the lines of many flood retention basins (i.e. by-pass structures), in which the inlet is an overflow from the main channel which is triggered only during high stages. If such structures are relatively empty prior to the first post-application storm event, they may be able to attenuate the highest concentrations – particularly if they have sufficient capacity, such that they do not fill up completely before the peak concentrations have subsided. This could be minimised using active open and close strategies (e.g. sluice gates) – although with the disadvantage that these gates need to be managed and operated (e.g. by farmers). Such a system has been implemented in the Bray watershed, France (Passeport et al., 2013) where results showed a reduction of less polar pesticides of about 20%. Although attractive in many respects, this strategy could be difficult to manage in practice since different pesticides are applied at different times for different pests and because most catchments contain several farms where the pesticide application information is not always available. Finally, flooding large areas of otherwise productive land could be unpopular with many farmers.

It should be noted that, mass load reduction is often used to assess pesticide removal efficiency of FWS CWs. This approach can be complicated because requires a good assessment in terms of flow and concentration data, which in practice can be challenging. Several problems occurred during monitoring; including v-notches weirs and flumes being washed away during flood events, logger malfunctions and autosampler failures (e.g. blocked tubes and faulty batteries). This resulted in data gaps for either discharge or concentration. The assessment of performance via mass balance was, therefore, not performed.

Objective 3: To understand the relative contribution of different mechanisms (sorption and degradation) of pesticide attenuation in constructed free-water surface farm wetlands.

Chapter 4 focused on sorption and desorption of metaldehyde, quinmerac, metazachlor, carbetamide and propyzamide in wetland sediment. Although data for K_d were available for these compounds from previous studies desorption coefficients (K_d^{des}) were unknown. The desorption coefficient is an important parameter because it can allow possible sorption mechanisms to be identified and can show if hysteresis effects exist (*e.g*. retardation in desorption relative to sorption). It is now well recognised that sorption may not be constant in time and that affinity for solids often increases over time (aged sorption) (FOCUS, 2006). Some pesticide may never be desorbed, even using strong solvents. This fraction is often referred to as a bound (or non-extractable) residue. The experiments were designed to understand the sorption-desorption behaviour of individual pesticides but also to explore the effect of the presence of other pesticides on sorption in wetland sediment (Chefetz *et al.,* 2004).

Linear isotherms were observed for both sorption and desorption for all the pesticides examined ($R^2 > 0.97$). The desorption experiment showed a true hysteresis effect for metazachlor and propyzamide, suggesting that these pesticides can remain entrapped in the sediment matrix (temporarily or permanently). K_{oc} values increased in the sequence: metaldehyde (27.6 L kg^{-1}) < carbetamide (32 L kg^{-1}) < quinmerac (41 L kg^{-1}) < metazachlor (194.2 L kg^{-1}) < propyzamide (884 L kg^{-1}). These results suggest that metaldehyde, carbetamide and quinmerac have higher mobility in the studied wetlands sediment relative to metazachlor and propyzamide. Importantly, the observed sorption kinetics suggested that the studied pesticides needed at least 24 hours to achieve equilibrium between the water and the sediment phases. To some extent these results explain why net sorption is probably an ineffective removal mechanism for the Hope Farm wetlands due to low HRT (rate of sorption << rate of advection through the system). Furthermore, the rate of net removal of chemical from water by sorption to sediment will be proportional to the disequilibrium gradient. If a pesticide is already sorbed to sediment, such that the ratio of sediment to water concentration is already close to K_d (i.e. the fugacity in sediment is similar to the fugacity in water: Mackay, 2001) then there will be little net loss via sorption from the water column, regardless of the HRT. Alternatively, if the concentration in the water phase decreases, the pesticide can desorb (or "bleed") from the sediment back to the water column in an attempt to restablish the equilibrium. This may explain the occasional occurrence of a higher concentration of metaldehyde observed at the outlet compared to the inlet of the South wetland 1 (Chapter 3).

One disadvantage of pesticide sorption to sediment is that accumulation may have toxic effects on sediment dwelling organisms (Cooper, 1993; Brock et al., 2018) particularly if they are persistent to degradation (Budd *et al.,* 2009; Katagi, 2016). It would have been interesting to have sampled the sediment in the Hope farm wetlands over the course of the sampling period to evaluate the extent to which pesticide concentrations changed with changes in the water column concentration. However, this was practically infeasible in view of the large numbers of water samples which needed to be processed and given the complex and time-consuming nature of sediment extraction and analysis procedures for pesticides (Pastor et al., 1997). Further studies should focus on understanding the evolution of pesticide concentrations in wetland sediment, both individually and in the presence of other pesticides. This work could also evaluate the toxicity of the studied pesticides individually and together (e.g. via the OECD 218 test on the effects of prolonged exposure sediment-dwelling Chironomid larvae).

Where organic matter is the major non-polar (sorbing) phase for pesticides, retention will be a function of hydrophobicity (Wauchope *et al.,* 2002; Warren *et al.,* 2003). In this case, sorption capacity may decrease if sorption is competitive for particular sites. This was explored in the experiment examining sorption of pesticides as mixtures. This showed that the presence of other pesticides (along with other organic contaminants present at different concentrations) can indeed influence the sorption capacity of the sediment. This was observed for carbetamide, quinmerac and metazachlor where the K_{oc} values decreased in the presence of a mixture compared to when it was spiked as an individual compound. For metaldehyde and propyzamide, the K_{oc} was unaffected by the presence of a mixture. This suggests that not all pesticides compete for sorption sites in the sediment.

The sorption studies were limited by the fact that only one sediment was used. Further work could explore the influence of different sediment characteristics (e.g. organic matter content and quality). Another limitation was the fact that the contribution of plants stems and roots to sorption was not evaluated. Since the 70% of the wetland surface is covered with vegetation, it would be interesting to understand the capacity of live plant stems, roots and litter for pesticide sorption.

Chapter 5 focused on the study of pesticide degradation in water-sediment systems. Degradation rates (k) and half-life (DT_{50}) are important for understanding the fate of pesticides in water-sediment systems. In the first part of Chapter 5 the influence of microbial inhibition on quinmerac, metaldehyde and metazachlor was investigated. Pesticides were added to two treatments (A and B) containing water and sediment in glass vessels. In Treatment A, sodium azide (0.05%) was added to inhibit microbial activity. Quinmerac was relatively stable in water-sediment systems with dissipation half-life of 84.7 days and there was no difference between the suppressed (A) and unsuppressed (B) treatments. For metaldehyde and metazachlor, there was a significant difference between treatments. In Treatment B, there was a clear lag phase period of 7 days for metaldehyde and 8 days for metazachlor, followed by a concentration decrease which could be approximately described by first-order kinetics. It is pertinent to note that no lag phase was observed for metaldehyde and metazachlor in the static period in the North wetland. This could have been due to the development of a competent microbial community in this system as consequence of repeated exposure to these pesticides. This phenomenon has been reported previously by Pesce *et al.,* (2010) and Rabiet *et al.,* (2010). Although the sediment used in the degradation experiments had been previously exposed to these pesticides, the sediment was collected several months prior to the experiments, which could have had an effect on acclimation (Rolf, 2016). DT_{50s} estimated for metaldehyde and metazachlor in the field (17.3 and 9.9 days, respectively) were similar to those observed in the lab (approximately 14 days for both compounds). The loss of these pesticides during the static period suggested that constructed FWS CWs do have potential to mitigate metaldehyde and metazachlor but that several days are needed to obtain substantial reductions in concentration. This reinforces the idea that HRT and DT_{50s} should be considered in future designs of artificial wetland systems.

The second part of Chapter 5 investigated the effect of initial concentration of metaldehyde and metazachlor on degradation rates. This experiment showed that there is an influence of the initial concentration on the degradation rate of metaldehyde and metazachlor. At lower initial concentrations, the reaction rate is proportional to concentration for both pesticides (first order kinetics). As pesticide concentration increased, the degradation rate became increasing more independent of concentration (suggesting a saturation level for the enzymes), indicating that Michelis-Menten kinetics can describe the behaviour of these chemicals across the whole range of concentrations. The calculated V_{max} values for metaldehyde and metazachlor are 0.03 day^{-1} and 0.05 day^{-1}. V_{max} is the maximum rate of reaction which is dependent from the microbial concentrations in the wetland sediment. The other parameter in the Michelis-Menten model is K_m which is the pesticide concentration at which the reaction rate is half of $V_{max.}$ Calculated K_m values for metaldehyde and metazachlor were 1.1 µg L^{-1} and 0.7 µg L^{-1}. Boethling and Alexander (1979) observed a similar effect during the degradation of p-chlorobenzoate and chloroacetate at initial concentrations of 0.05 µg L^{-1} to 50 µg L^{-1}, where the degradation rate was similar above 2 µg L^{-1}. These authors suggested the existence of a threshold below which no significant mineralization would occur. At low concentrations the energy released from the oxidation of the compound is too little to meet the energy demands of the small number of microorganisms able to degrade the compound, although co-metabolism may still occur (Dalton and Stirling, 1982).

The third part of Chapter 5 was to study the effect of water depth on degradation rates in laboratory systems containing wetland sediment and water. The central hypothesis here is that the rate constants should be inversely proportional to water depth because the majority of the degrading microbes are assumed to inhabit the sediment in fixed biofilms. Work done in Cranfield Laboratories (Gnata, 2016) showed a strong inverse relationship between nitrogen removal and water depth. The same principle should apply to pesticide degradation. Furthermore, any net losses to sediment by partitioning may also be inversely proportional to depth for similar reasons and could explain the fact that concentrations in the shallow treatments are systematically lower than for the other depths for metazachlor and propyzamide. However, this is unlikely to be a significant contribution to the temporal patterns because a clear lag phase exists in almost all cases (presumably a relating to the development of microbial competence). Results were mixed. For metaldehyde, depth did not appear to control the rate constant. However, for propyzamide, metazachlor and quinmerac, depth did appear to be an important factor controlling the rate constant – mainly in the lag phase.

6.2 Contribution to knowledge

This work has made significant contributions to further understanding the potential (or not) of constructed free-water surface farm wetlands for mitigating pesticide from agricultural land to surface waters. Table 6.1 summarizes the contributions to knowledge from the individual chapters.

Table 6-1. Contribution to knowledge in the different technical chapters

	Contribution to Knowledge
Chapter 2	• A novel multi-component method was developed to determine metaldehyde, quinmerac, carbetamide, metazachlor, propyzamide and pendimethalin in water samples simultaneously by liquid-chromatography tandem quadrupole mass spectrometry; • The method was suitable for detecting pesticide concentrations in surface water rapidly and with simple sample preparation;

	Contribution to Knowledge
Chapter 3	• Free-water surface constructed wetlands were ineffective in reducing pesticide concentrations due to short hydraulic residence times (typically less than 2 hours, and considerably lower during storm events according to dye tracing) • In principle, metaldehyde and metazachlor can be mitigated by 50% in FWS CWs if the hydraulic residence times are similar to the apparent DT_{50}'s of these compounds in the field (17.3 and 9.9 days, respectively);

	Contribution to Knowledge
Chapter 4	• Sorption coefficients (K_d, K_d^{des} and K_{oc}) were determined for metaldehyde, carbetamide, metazachlor, quinmerac and propyzamide in wetland sediment; The determination of K_d^{des} represents a novel contribution to our understanding of the behaviour of these compounds in water-sediment systems. • Metaldehyde, carbetamide and quinmerac have higher potential mobility in wetland sediment relative to metazachlor and propyzamide; • The presence of other pesticides reduced the sorption capacity of the sediment for carbetamide, quinmerac and metazachlor; probably due to competitive sorption for sorption sites in the sediment.

	Contribution to Knowledge
Chapter 5	• Quinmerac is a relatively stable pesticide in water-sediment systems with a DT_{50} value of 84.7 days • Metaldehyde and metazachlor are more easily degraded with respective DT_{50s} of 14.7 and 14.3 days (post-lag phase) in experimental mesocosms in the laboratory. The pattern of degradation in water-sediment systems was dependent on initial concentration, implying that Michaelis-Menten kinetics may be able to describe degradation rates over the whole concentration range. The calculated K_m values for metaldehyde and metazachlor were 1.1 µg L^{-1} and 0.7 µg L^{-1}. • Laboratory studies suggest that degradation rate constants might be dependent on water depth, as hypothesised, but the data were not consistent for all pesticides.

6.3 Recommendations for further work

Several areas for further work have been identified:

1. It would be useful to explore the processes of pesticide transfer from the upstream catchment areas to the studies wetlands using the data collected. If information on pesticide application rates and timing could be made available, it may be possible to use a mathematical model of pesticide transfers from land to water (e.g. Tediosi et al., 2012; 2013) to

evaluate the relationship between land management and pesticide transfer;

2. The collected data could be compared to the predictions generated using hydrochemical models (e.g. multimedia fate and transport models: Whelan, 2013; Krogseth et al., 2017) to predict the fate of pesticides in wetland systems. Provided such a model could be properly validated, it could be used to explore the influence of wetland dimensions (depth, surface area etc.), sediment properties and upstream catchment characteristics on pesticide attenuation. It is likely, for example, that increasing the system volume, will increase residence time and enhance any losses. The size to wetland required for a particular target reduction in concentration or load could be estimated, for example, as part of studies to better understand the importance of catchment size to wetland volume ratio;
3. Further work is required to better understand sorption of pesticides in different types of wetland sediment, in order to inform potential behaviours of pesticides in different wetland systems with different sediment characteristics;
4. Further understanding of the contribution of wetland plants to pesticide behaviour is required. Plants can affect pesticides via uptake (e.g. Trapp, 2004), sorption and biodegradation (e.g. via epiphytes growing on the surfaces of stems: Kalwasińska *et al.,* 2011);
5. A better understanding is required of the composition and competence of the microbial community responsible for pesticide degradation, especially for metaldehyde (cf Rolf, 2016);
6. Further experiments are needed to investigate the mechanistic details of sorption and biodegradation – particularly, the role of competitive effects of due to the presence of other pesticides.

6.4 Conclusions

The research presented in this thesis considered the potential of free-water surface constructed wetlands to mitigate pesticides in agricultural runoff. The behaviours of five pesticides (metaldehyde, quinmerac, carbetamide, metazachlor and propyzamide) in water-sediment systems were explored using (1) field monitoring in two wetland systems and (2) laboratory tests. Overall, the results of the study suggest that on-line (in ditch or in stream) free-water surface constructed wetlands are relatively ineffective in reducing diffuse-source pesticide concentrations in the systems examined – primarily due to short hydraulic residence times.

Laboratory experiments were performed to improve our understanding of sorption in wetland sediment. These sorption studies showed that the pesticides examined were relatively mobile in wetland sediment with relatively low affinities for sediment and relative slow rate of equilibration (slower than the rate of chemical advection out of the studies systems). Sorption for some of the pesticides examined is expected to be lower when they are present in mixtures due to competitive effects.

The fate of quinmerac, metaldehyde and metazachlor was studied in laboratory water-sediment systems. The dominant removal mechanism was believed to be biodegradation (as revealed by microbial suppression treatments). There was some evidence that the rate constant for degradation was dependent on water depth, although results were not consistent for all pesticides.

6.5 References

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7. Appendices

A.1 Scatter plots of inlet and outlet concentrations of metaldehyde, carbetamide and propyzamide at South Wetland system

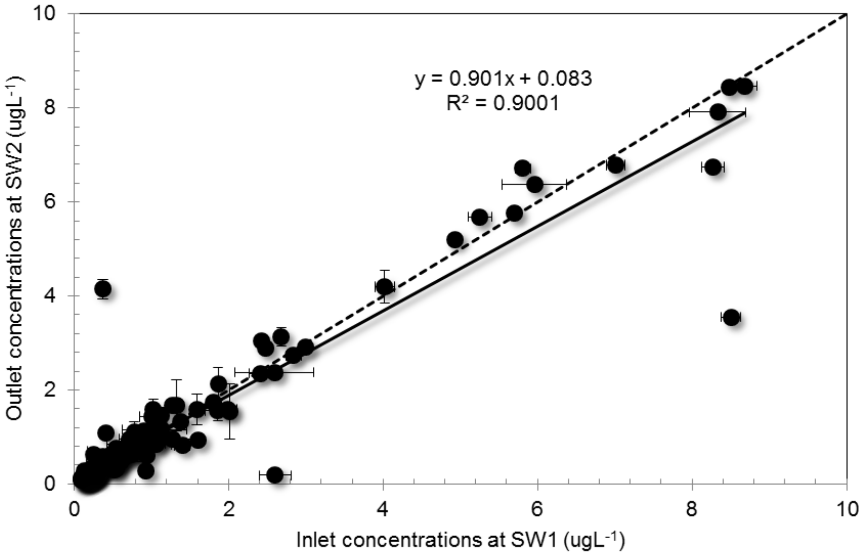

Figure 7.1. Scatter plots of inlet and outlet concentrations of metaldehyde (µg L^{-1}) at South Wetland

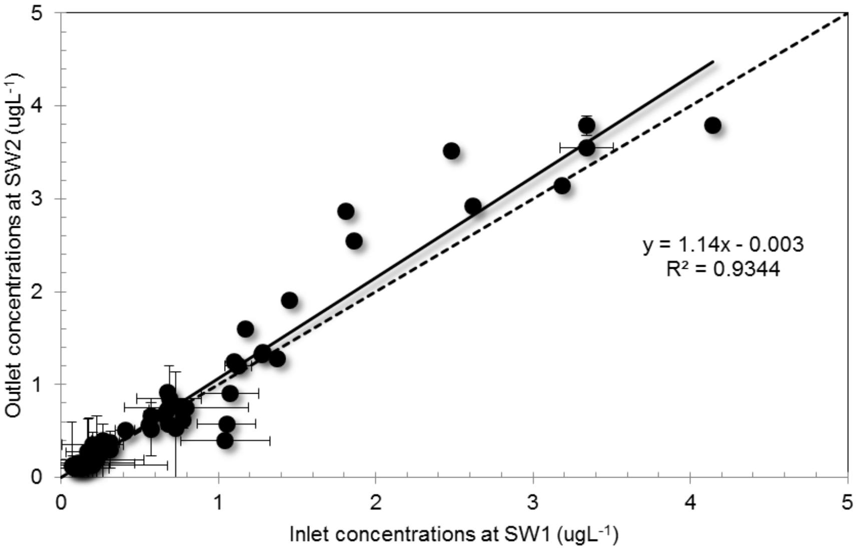

Figure 7.2. Scatter plots of inlet and outlet concentrations of carbetamide (µg L^{-1}) at South Wetland

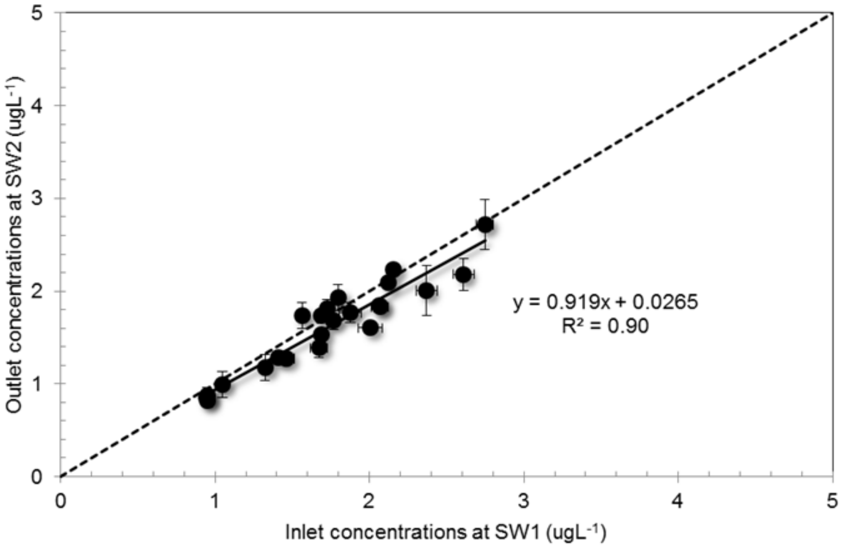

Figure 7.3. Scatter plots of inlet and outlet concentrations of propyzamide (µg L^{-1}) at South Wetland

A.2 Scatter plots of inlet and outlet concentrations of metaldehyde, carbetamide and propyzamide at North Wetland system

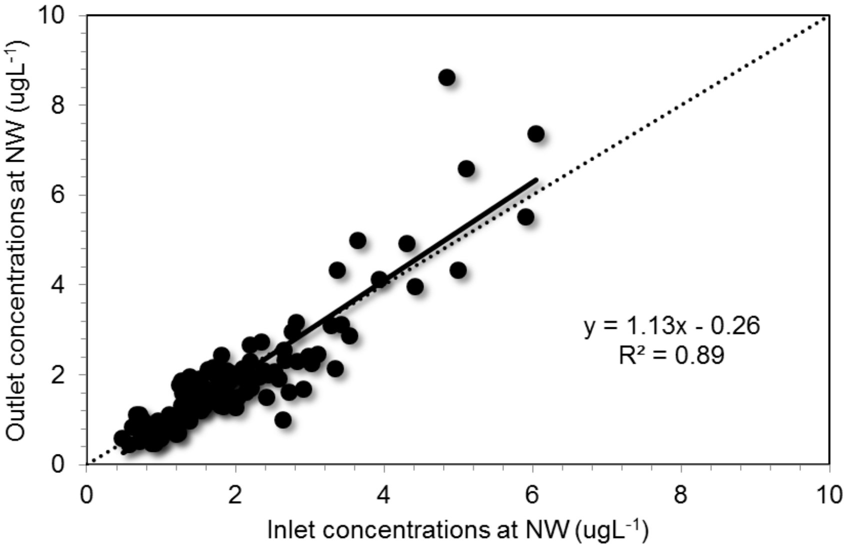

Figure 7.4. Scatter plots of inlet and outlet concentrations of quinmerac (µg L^{-1}) at North Wetland

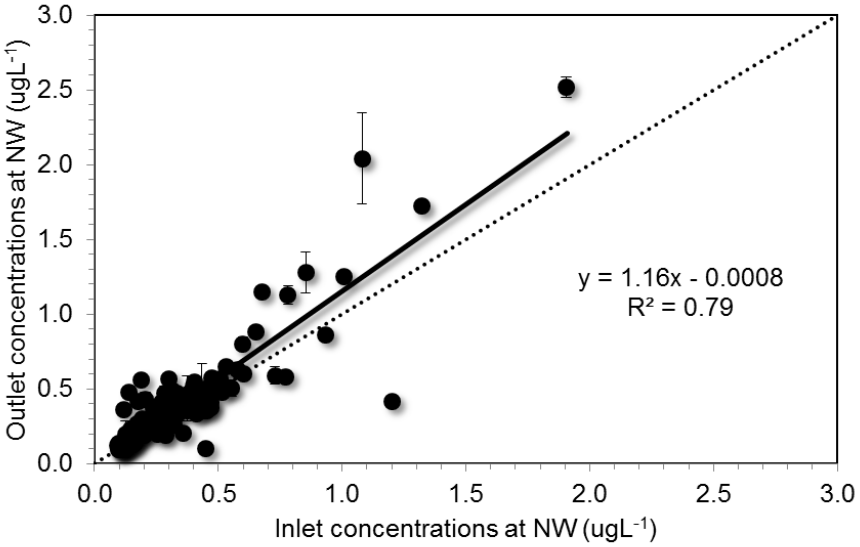

Figure 7.5. Scatter plots of inlet and outlet concentrations of metazachlor (µg L^{-1}) at North Wetland

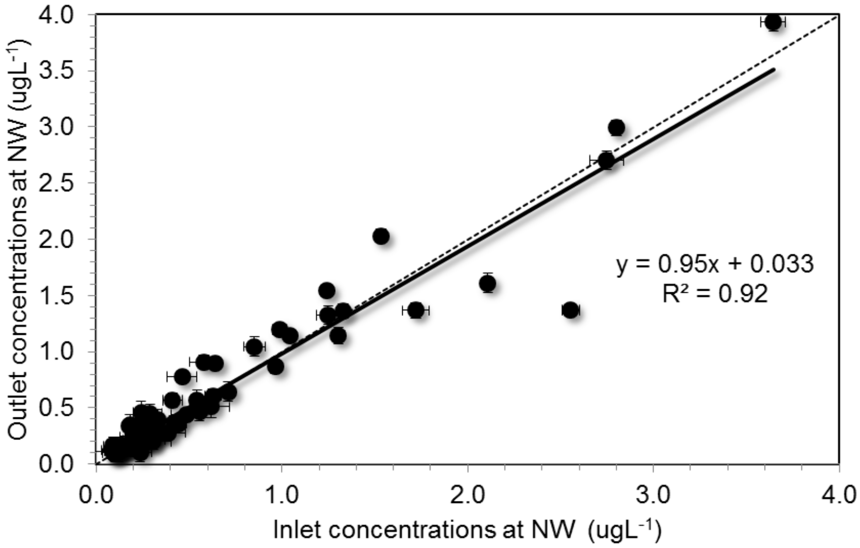

Figure 7.6. Scatter plots of inlet and outlet concentrations of metaldehyde (µg L^{-1}) at North Wetland

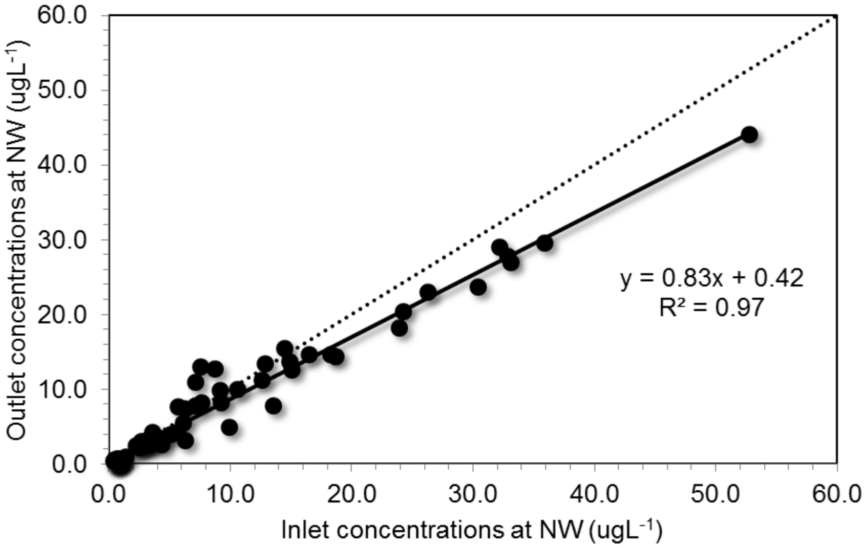

Figure 7.7. Scatter plots of inlet and outlet concentrations of propyzamide (µg L^{-1}) at North Wetland

A.3 Sorption equilibration time

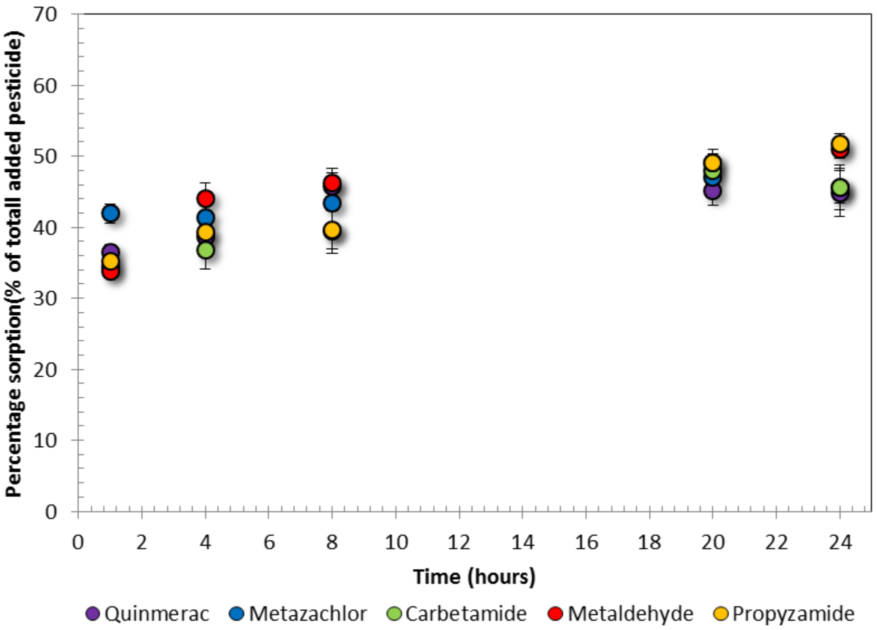

Figure 7.8. Change in sorption of all pesticides on wetland sediment with varying equilibration time. Error bar represents the standard deviation (n=3)