CRANFIELD UNIVERSITY

Stephanie Leanne Cosgrove

Pesticide removal from farm run-off using in-field treatment systems

School of Water, Energy and Environment
PhD Thesis

PhD
Academic Year: 2014 -2018

Supervisor: Peter Jarvis
Associate Supervisor: Bruce Jefferson
December 2018

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

ABSTRACT

The use of pesticides in modern agriculture is necessary in order to maintain high crop yields, however this use of pesticides can risk contamination of potable water sources. In order to prevent potable water contamination, the movement of pesticides out from agricultural environments must be prevented. In this work, adsorption media has been considered as a means to do this as it can be used without external energy requirements and so can be used in remote locations such as farmland catchments. To understand the issue of pesticides in drinking water in the UK, a study on pesticide water quality compliance was conducted using data available from the Drinking Water Inspectorate water quality regulator. From this, a number of pesticides were identified to be of particular concern. The physico-chemical properties of these pesticides were then established and adsorption media suitable for their removal from water was identified. A field study was conducted to understand the specific conditions under which pesticide run-off occurs using a new sampling methodology that was proportional to the local rainfall. The work then researched in-field adsorption solutions for pesticide removal. This was investigated by using different activated carbon media and determining their speed and efficiency at removing three identified pesticides: metaldehyde, metazachlor and propyzamide. The practical applicability of each medium was then considered by understanding the headlosses that might be observed at a range of realistic flow rates as observed in the field study. This resulted in the selection of an activated carbon fabric for pilot testing in flowing water as a result of its superior kinetic uptake and its effective performance in a complex matrix (raw water) when compared with the other media tested. In addition, the ability to orientate the fabric into a range of practical and flexible configurations will enable reduced headlosses in agricultural environments. The results showed that the activated carbon medium had great potential, achieving approximately 46% removal of the pesticide metaldehyde during flume experiments.

Keywords:

Activated carbon, Adsorption, Metaldehyde, Rainfall, Pesticides

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LIST OF ABBREVIATIONS

AC	Activated carbon
AOP	Advanced oxidation processes
BET	Brunauer-Emmett-Teller
DI	Deionised
DT50	Degradation time to 50% of initial concentration
EFSA	European Food Safety Authority
FI	Farm inlet
FO	Farm outlet
GAC	Granular activated carbon
Ha	Hectare
IBC	Intermediate bulk container
IC	Inorganic carbon
I/O	Input/output
IDF	Intensity-duration-frequency
IOT	Internet of things
K_d	Adsorption partition coefficient
K_f	Freundlich coefficient
K_{oc}	Soil organic carbon/water partitioning coefficient
K_{ow}	Octanol-water coefficient
LC	Liquid chromatography
Leca	Light expanded clay aggregate
MS	Mass spectrometry
NPOC	Non-purgable organic carbon
OSR	Oilseed rape
PAC	Powdered activated carbon
PDACB	Polymer derived activated carbon bead
PI	Pond inlet
PKa	Acid dissociation constant
PO	Pond outlet
PPDB	Pesticide properties database
PZC	Point of zero charge
QC	Quality control
RSuDs	Rural sustainable drainage systems
SSA	Specific surface area

STW	Severn Trent Water
TC	Total carbon
TN	Total Nitrogen
TOC	Total organic carbon
UK	United Kingdom
UPLC	Ultra performance liquid chromatography
USB	Universal serial bus
UV	Ultraviolet
WTW	Water treatment works

1 Introduction

Pesticides are an integral part of modern agriculture, where increasing demand for crops that produce food and fuel must keep up with a growing population. Pesticide use is extensive, for example approximately sixteen and a half thousand tonnes of pesticides were used in the UK in 2016 (FERA, 2018). Pesticides help to ensure a high crop production by protecting the crops against competing weeds, insect pests and fungal diseases. However, the use of pesticides on such a large scale has caused a number of issues for the water industry. The movement of pesticides from the agricultural environment into water sources that are subsequently used for abstraction for potable water can cause water quality compliance failures. In Europe, drinking water quality regulations are controlled by the Drinking Water Directive (Council of the European Union, 1998). For pesticides, the concentration must not exceed 0.1 µg L^{-1} per single pesticide compound or 0.5 µg L^{-1} for the total amount of pesticides.

Pesticides are composed of a wide range of molecular structures. As such, they have very different characteristics that mean their mobility from land to water differs and the ability to remove them from water varies considerably. Important features of a pesticide that control its behaviour are its solubility, polarity and adsorption coefficient (Franco and Matamoros, 2016). A number of different pesticides have caused compliance failures in the recent past, however metaldehyde is currently the pesticide of greatest concern in the UK (Busquets *et al*., 2014; Drinking Water Inspectorate, 2016; Castle *et al*., 2017; Salvestrini *et al*., 2017). Metaldehyde is a molluscicide used to deter and control molluscs and has caused more compliance failures in the last ten years than all other pesticides put together. The main reason for this is that it is difficult to remove from water and so conventional treatment using granular or powdered activated carbon (PAC) adsorption and ozone oxidation has been relatively ineffective (Busquets, 2014). Other means of pesticide treatment include ultraviolet (UV) photolysis and advanced oxidation processes, which are effective but expensive and energy intensive (Boudesocque *et al*., 2008).

Beyond direct treatment of contaminated water, a number of catchment management schemes have also been used across the UK to try and lessen the impact of pesticides and to minimise their movement outside of their intended location. Catchment management schemes have included proposals such as paying farmers to substitute the pesticides that have caused problems for others that are less harmful to the environment. For example, in the case of metaldehyde, switching to ferric phosphate (Severn Trent Water, 2014). Other methods focus on the means of pesticide application for example planting crops across a slope in order to avoid making tramlines down a gradient that encourages flow of rainfall down a path of least resistance. Programmes such as ‘Get Pelletwise’ and ‘The Voluntary Initiative’ aim to educate and encourage pesticide users about the risks and best practice of their use (Metaldehyde Stewardship Group, 2015; Voluntary Initiative, 2015).

Constructed wetlands are another means of controlling the movement of pollutants from farm land. They are primarily used as a final polishing step for wastewater treatment (Sultana *et al*., 2015) and have been successfully used for the mitigation of phosphorus (P) and nitrogen (N) (Xu *et al*., 2014). However, they have been more commonly used for treatment of high nutrient loaded livestock waste streams rather than for dilute arable farming run-off (Sultana *et al*., 2015). Much of the pollutant removal is reliant upon microbial degradation that can take place due to the long hydraulic retention times (typically in excess of 24 h) present in most wetland systems (Xu *et al*., 2014; Vymazal and Březinová, 2015). Constructed wetlands have, however, been explored in numerous studies for control of pesticides in run-off from arable agricultural environments, but there is large variation in the removal efficiency. For example in a review by Vymazal and Březinová (2015), when pesticide removal was analysed according to chemical group it was found that there was removal of only around 20% for those in the triazinone group (metamitron, metribuzin) but removal was in excess of 90% for those in the organochlorine (endosulfan, pentachlorophenol) and strobilurin/strobin (kresoxin methyl, trifloxystrobin, azoxystrobin) groups. Pappalardo *et al*. (2015) found good, but reversible, adsorption of up to 98% of two herbicides under artificial flooding conditions in a surface flow constructed wetland. Other studies used specific media within the wetland in order to enhance pollutant removal. This has included materials such as steel slag, light expanded clay aggregates (leca) and alum sludge. The leca was used for treatment of the pesticide MCPA and achieved between 56-97% removal whereas the steel slag and alum sludge were both used for P removal and both achieved removal rates in excess of 80% (Babatunde and Zhao, 2007; Dordio and Carvalho, 2013; Yun *et al*., 2015).

This project was carried out in collaboration with the catchment management team at Severn Trent Water (STW). STW covers an area of 21,000 km^2 in the Midlands and mid-Wales, providing potable water to approximately 7.7 million people (Severn Trent Water, 2014). Twelve pesticides had been identified by the company that were considered to be threats to potable water abstraction sources, five of which were of particular interest. These included four herbicides: propyzamide, metazachlor, quinmerac and clopyralid and the molluscicide metaldehyde which is of major concern (Severn Trent Water, 2014). STW have been challenged with developing innate catchment solutions to improve water quality in wider catchment areas. The approach taken in this research was to focus on the application of engineered solutions to be applied 'in-field'.

The overall aim of this research was to therefore understand the critical risk factors and associated management tools for elevated pesticide concentrations in field run-offs. This aim consisted of two objectives:

1) To understand the conditions that lead to elevated pesticide presence in agricultural run-off
2) To understand the impact of design and operating conditions on the efficacy of adsorptive processes to manage elevated pesticide concentrations in agricultural run-off

The thesis has been written so that each chapter has been formatted in the style of a paper for publication (Figure 1.1). The papers have been written entirely by the first author Stephanie Cosgrove with support provided by Prof Peter Jarvis and Prof Bruce Jefferson. All experimental work was carried out by Stephanie Cosgrove at Cranfield University or the field site, Hattons Farm located in Wolverhampton. Technical support was provided by Oliver Heard for the monitoring equipment solution used in chapter 3.

Chapter 2 is a literature review that looked at the water quality issues caused by pesticides in the UK. This focuses on pesticide compliance failures that have occurred in England and Wales and includes analysis of data contained in DWI reports and historical environmental datasets. The review then focused on a number of pesticides and potential adsorption media that could be used for their removal from water.

Chapter 3 reports on results from field experiments conducted on a working farm site in Wolverhampton. A rain-dependant sampling method was developed in order to best describe the pattern of pesticide run-off under storm conditions.

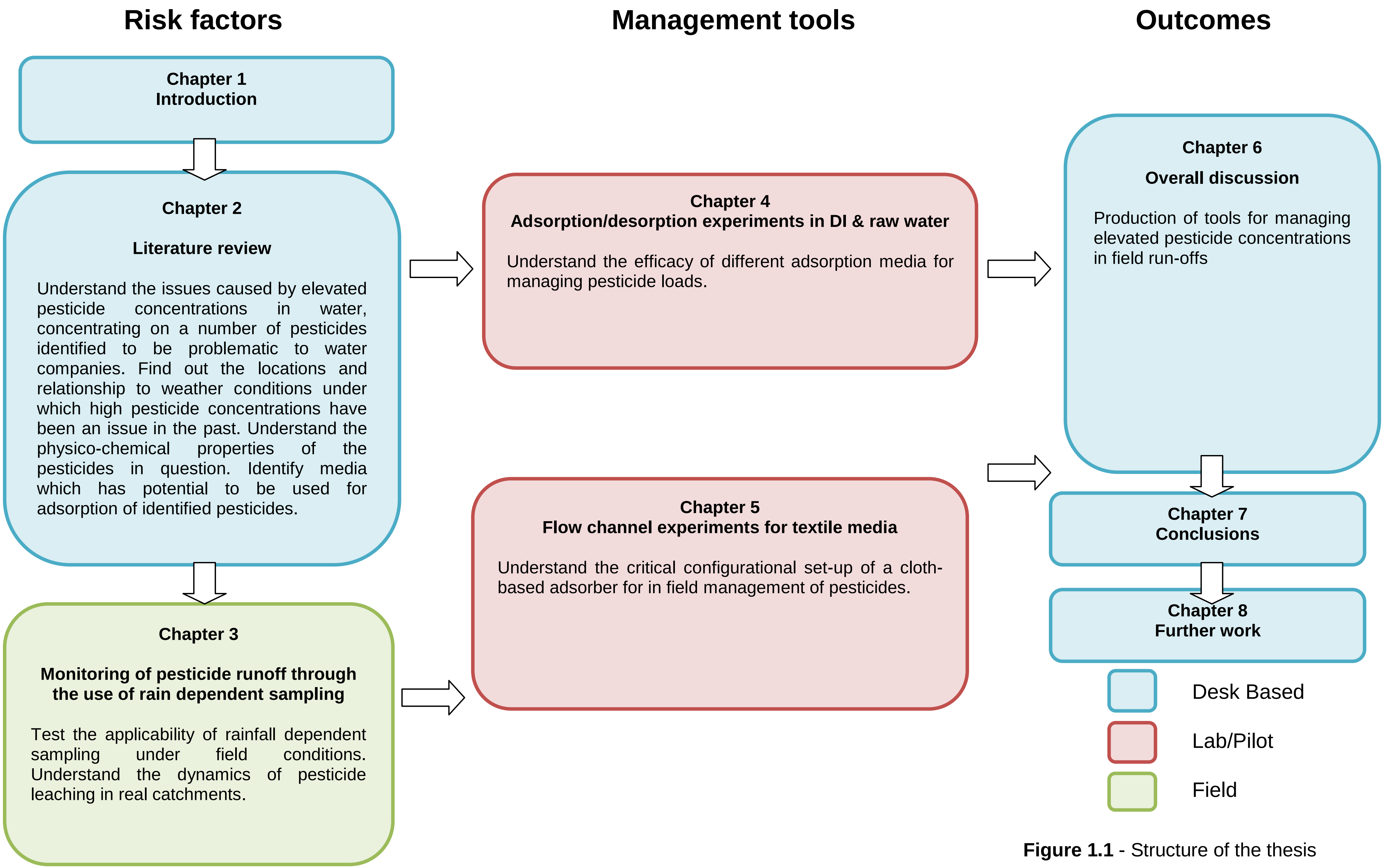
Chapter 4 presents experimental data from adsorption tests investigating the capacity and speed of adsorption of different pesticides from water using different adsorbent media.

Chapter 5 describes further testing of the selected adsorption medium (activated carbon fabric) under continuous flow conditions for removal of the pesticide metaldehyde. Firstly, a lab scale experiment was designed using a membrane cell set-up to understand the kinetics of removal under different flow rates and contact times in a re-circulating batch experiment. This was then expanded to a pilot scale setup using 2 m^2 and 8 m^2 of fabric inside a flow channel with faster flow rates (2 L min^{-1} and 10 L min^{-1}) and a single pass design in order to more closely mimic the conditions that would be present under working environmental conditions.

Chapter 6 presents the key findings of the thesis in an overall discussion focussing on how the in-field adsorption system could be used and applied in farm catchments.

Chapter 7 summarises the key findings and conclusions of the work.

Chapter 8 proposes the further research that is required in order to deliver a technically feasible in-field adsorption solution that will be robust enough to be deployed in the environment.



Chapter 1
Introduction

Chapter 2

Literature review

Understand the issues caused by elevated pesticide concentrations in water, concentrating on a number of pesticides identified to be problematic to water companies. Find out the locations and relationship to weather conditions under which high pesticide concentrations have been an issue in the past. Understand the physico-chemical properties of the pesticides in question. Identify media which has potential to be used for adsorption of identified pesticides.

Chapter 3

Monitoring of pesticide runoff through the use of rain dependent sampling

Test the applicability of rainfall dependent sampling under field conditions. Understand the dynamics of pesticide leaching in real catchments.

Chapter 4
Adsorption/desorption experiments in DI & raw water

Understand the efficacy of different adsorption media for managing pesticide loads.

Chapter 5
Flow channel experiments for textile media

Understand the critical configurational set-up of a cloth-based adsorber for in field management of pesticides.

Chapter 6

Overall discussion

Production of tools for managing elevated pesticide concentrations in field run-offs

Chapter 7
Conclusions

Chapter 8
Further work

🟦 Desk Based
🟥 Lab/Pilot
🟩 Field

Figure 1.1 - Structure of the thesis

1.1 Publications

The literature review section of this thesis has been published in the journal 'Environmental Technology Reviews' (Cosgrove *et al*., 2019. Stephanie Cosgrove was also a contributing author to a method paper (Ramos *et al*., 2017) published in 'Water and Environment Journal' that describes the development and use of the analytical method used in this research.

1.2 References

Babatunde, A.O. and Zhao, Y.Q. (2007) ‘A novel alum-sludge based Constructed Wetland system to reduce pollution effects of agricultural run-off: first results’, *International Journal of Water*, 3(3), pp. 207-213.

Boudesocque, S., Guillon, E., Aplincourt, M., Martel, F. and Noël, S. (2008) ‘Use of a Low-Cost Biosorbent to Remove Pesticides from Wastewater’, *Journal of Environment Quality*, 37(2), pp. 631-638.

Busquets, R., Kozynchenko, O.P., Whitby, R.L.D., Tennison, S.R. and Cundy, A.B. (2014) ‘Phenolic carbon tailored for the removal of polar organic contaminants from water: a solution to the metaldehyde problem?’, *Water Research*, 61, pp. 46–56.

Castle, G.D., Mills, G.A., Gravell, A., Jones, L., Townsend, I., Cameron, D.G. and Fones, G.R. (2017) ‘Review of the molluscicide metaldehyde in the environment’, *Environmental Science: Water Research & Technology*, 3(3), pp. 415–428.

Cosgrove, S., Jefferson, B. and Jarvis, P. (2019) ‘Pesticide removal from drinking water sources by adsorption: a review’, *Environmental Technology Reviews*, 8(1), pp. 1–24.

Council of the European Union (1998) ‘Drinking Water Directive 98/83/EC’, *Official Journal of the European Communities*

Dordio, A. and Carvalho, A.J.P. (2013) ‘Constructed wetlands with light expanded clay aggregates for agricultural wastewater treatment.’, *The Science* *of the Total Environment*, 463–464, pp. 454–61.

Drinking Water Inspectorate (2016) *Annual Report., DWI Annual Report* Available at: http://www.dwi.gov.uk/about/annual-report/index.htm (Accessed: 13 June 2016).

FERA (2018) *Pesticide usage statistics*.

Franco, J. and Matamoros, V. (2016) ‘Mitigation of polar pesticides across a vegetative filter strip. A mesocosm study’, *Environmental Science and Pollution Research*, 23(24) pp. 25402–25411.

Metaldehyde Stewardship Group (2015) *Get Pelletwise*. Available at: http://www.getpelletwise.co.uk/ (Accessed: 16 April 2015).

Pappalardo, S.E., Otto, S., Gasparini, V., Zanin, G. and Borin, M. (2015) ‘Mitigation of herbicide runoff as an ecosystem service from a constructed surface flow wetland’, *Hydrobiologia*, 774(1), pp. 193–202.

Ramos, A.M., Whelan, M.J., Cosgrove, S., Villa, R., Jefferson, B., Campo, P., Jarvis, P. and Guymer, I. (2017) ‘A multi-component method to determine pesticides in surface water by liquid-chromatography tandem quadrupole mass spectrometry’, *Water and Environment Journal*, 31(3), pp. 380–387.

Salvestrini, S., Vanore, P., Bogush, A., Mayadevi, S. and Campos, L.C. (2017) ‘Sorption of metaldehyde using granular activated carbon’, *Journal of Water Reuse and Desalination*, 7(3), pp. 280–287.

Severn Trent Water (2014) *Final Water Resources Management Plan 2014*. Coventry.

Sultana, M.-Y., Akratos, C., Vayenas, D. and Pavlou, S. (2015) ‘Constructed wetlands in the treatment of agro-industrial wastewater: A review’, *Hemijska Industrija*, 69(2), pp. 127–142.

Voluntary Initiative (2015) *The Voluntary Initiative: Promoting responsible pesticide use*. Available at: http://www.voluntaryinitiative.org.uk/en/home (Accessed: 20 September 2015).

Vymazal, J. and Březinová, T. (2015) ‘The use of constructed wetlands for removal of pesticides from agricultural runoff and drainage: A review’, *Environment International*, 75, pp. 11–20.

Xu, J., Lo, S.L., Xu, L. and Gong, R. (2014) ‘Comparison of semi-natural and constructed wetlands for agricultural wastewater treatment’, *Desalination and Water Treatment*, 54(11), pp. 2959–2968.

Yun, Y., Zhou, X., Li, Z., Uddin, S.M.N. and Bai, X. (2015) ‘Comparative research on phosphorus removal by pilot-scale vertical flow constructed wetlands using steel slag and modified steel slag as substrates’, *Water Science & Technology*, 71(7), pp. 996–1003.

2 Literature review: The use of pesticides in the UK and their potential for removal by adsorption within farm catchments

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2.1 Abstract

Pesticides are an important part of crop production in the UK, however their use poses a threat to potable water sources. Seasonal use of pesticides can cause increased concentrations to be detected at potable water abstraction sites as a shock load which can be difficult for conventional treatment processes for pesticide removal to deal with. Concentrations of pesticides above 0.1 μg L^{-1} in drinking water contravene the regulations as laid out in the Drinking Water Directive (Council of the European Union, 1998) and cause significant reputational and financial impact to water companies. This review considers the relationships between the pesticides that have caused compliance failures and historical weather data. It was found that over 50% of the compliance failures due to pesticide detection in the UK have been caused by the molluscicide metaldehyde and that the majority of the problematic pesticides causing these compliance failures are considered to be polar and mobile. An increase in the number of metaldehyde compliance failures was found in years when a 40 mm deficit of rainfall was experienced between the months of October and August + September. The review looks in further detail at five different pesticides with differing physico-chemical properties known to

have caused compliance failures and to be of particular concern for water companies. In addition adsorption media which could be utilised in agricultural environments were investigated to understand whether they could be applied to prevent the onward contamination of potable water sources.

2.2 Introduction

Pesticides are a major part of most arable crop production processes. It is estimated that around a third of crop losses are due to pests and diseases. The use of pesticides therefore is the main way by which crop losses are minimised and yields maximised when practicing intensive agriculture in order to provide food and resources for a growing global population (Rowell, 1994; Carvalho, 2006). The movement of pesticides into water courses via processes such as run-off, leaching, sub-surface drainage and spray drift (Margoum *et al*., 2006; Vallée *et al*., 2014) has become a major problem for water utility companies, particularly with respect to contamination of water sources used for drinking (ADAS UK Ltd, 2011; Tediosi *et al*., 2012; Severn Trent Water, 2014). The removal of pesticides and other micropollutants from drinking water typically involves using ozone oxidation and granular activated carbon (GAC) adsorption during the final treatment stages (Rakness, 2005; Giribaldi, 2013). However a number of pesticides have been shown to be difficult to remove using these conventional treatment processes. For example, pesticides such as metaldehyde do not adsorb effectively to activated carbon (AC) over long periods of time and ozone is unable to oxidise the compound using economically feasible doses (Giribaldi, 2013; Tao and Fletcher, 2013). In Europe, the amount of pesticides allowed in drinking water is strictly regulated under the Drinking Water Directive legislation (Council of the European Union, 1998). Limits for single pesticides are set at 0.1 µg L^{-1} and there is a 0.5 µg L^{-1} limit for total pesticides. Thus, non-compliance to these standards can have negative impacts, both to human health and financially to the water companies.

In England and Wales between 2000 and 2016 there have been a total of 1571 water company compliance failures due to the detection of pesticides in drinking water above the 0.1 µg L^{-1} limit (Drinking Water Inspectorate, 2016). These compliance failures comprised 35 different pesticides from the 248 compounds approved for use in the UK. Over two thirds of these failures have been caused by a single pesticide, namely metaldehyde (Figure 2.1). However, metaldehyde is not one of the most widely used pesticides as since 2009 its application has dropped out of the top ten applied by weight (FERA, 2018). The most regularly used pesticides in the UK between 2000 and 2016 include glyphosate, chlorothalonil, pendimethalin, mancozeb and mecoprop-p. However these compounds have caused relatively few compliance failures.

Pesticides are grouped into four main categories based on their application, namely fungicides for treating plant fungal diseases, herbicides for combating weeds, insecticides for reducing crop damage caused by insect pests and molluscicides for targeting slugs and snails. Metaldehyde is an example of a molluscicide and is the only representative in this category that has caused compliance failures (Figure 2.1; 2.2).

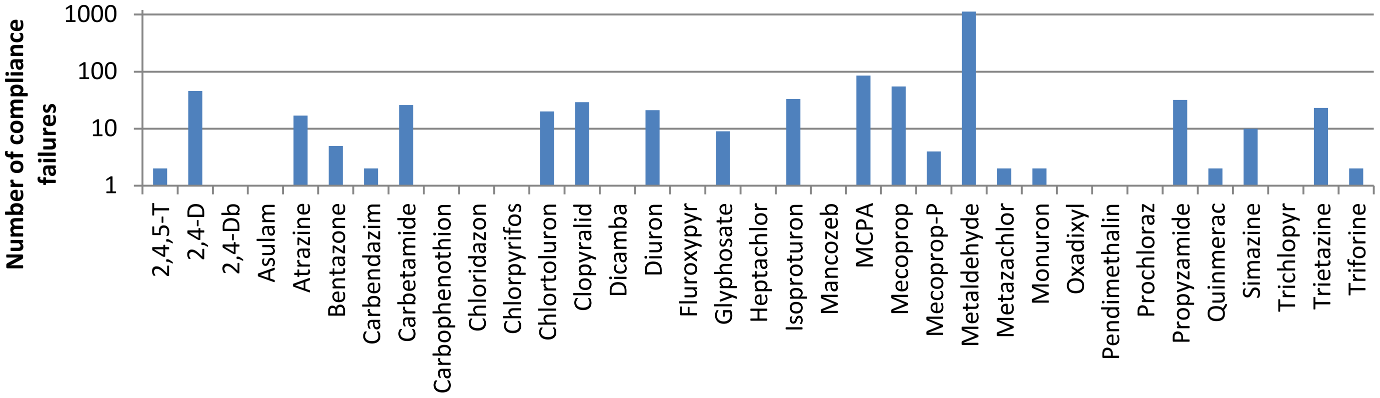


Figure 2.1 – Number of compliance failures caused by all pesticides detected by UK water companies between the years 2000 and 2016 (Drinking Water Inspectorate, 2016)

After metaldehyde, the herbicide group are the next most important group of pesticides impacting on water quality in the UK (Figure 2.2). There are two main types of herbicide; contact and systematic. Contact herbicides only affect the part of the plant with which they come in to contact and systematic herbicides are absorbed by roots and/or foliage and are subsequently translocated where they affect other parts of the plant. Contact herbicides tend to have a shorter half-life and are more strongly sorbed to soils as compared to systematic herbicides (Malone *et al*., 2004; Shipitalo *et al*., 2008). Due to the need of systematic herbicides to be taken up in diluted form by the target weed in order to be effective, they tend to be compounds that are polar and mobile.

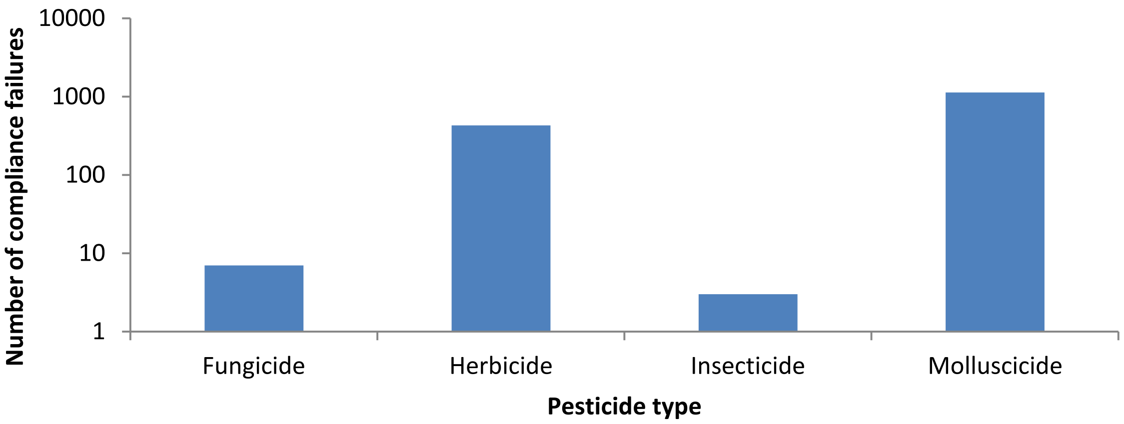


Figure 2.2 – Number of pesticide compliance failures by pesticide type between the years 2000 – 2016 (Drinking Water Inspectorate, 2016)

Whether a pesticide is found in drinking water is dependent on a number of factors, including: how the water has been treated and the treatability of the pesticide; the amount of pesticide applied; the prevailing weather conditions and the underlying physico-chemical properties of the pesticide. For instance, it has been assumed that the detection of these pesticides in drinking water originated from run-off events. In this scenario, the pesticides would be washed out from their intended location during rainfall events rather than from acute pollution sources such as spillages of concentrated pesticides into water courses. These are fair assumptions given previous correlations that have been seen between pesticide detection in watersheds and storm events (Bingham, 2007; Pérez *et al*., 2017). This is supported by other studies which have found between 84 and 90% of pesticide losses occurred during storm events (Kay and Grayson, 2014). The treatability of a pesticide is also important. For example, between 1990 and 2016 approximately 33,540 tonnes of glyphosate was used in UK agriculture, while only 5,360 tonnes of metaldehyde was used during the same period

(FERA, 2018). The number of compliance failures for metaldehyde (1131) far exceeded that of glyphosate (9) even though glyphosate has a higher reported half life (DT_{50}) of 15 days compared to 5.1 days for metaldehyde (PPDB, 2014) as glyphosate is more easily removed during the water treatment process. The structure of glyphosate is much more susceptible to breakdown by oxidation by ozone due to its amino group (Assalin *et al*., 2010) compared to metaldehyde that has a more stable ring structure. In addition, glyphosate also has a higher affinity for adsorption with a K_{oc} of 3.1 compared to 2.4 for metaldehyde meaning glyphosate is more likely to be retained in soil.

Compliance failures caused by pesticides were most prominent in the eastern region of England, notably in East Anglia (Figure 2.3). This region of England and Wales is responsible for much of the country’s agricultural production, especially in terms of cereals and combinable crops, with 1.42 million hectares of cereals and oilseed rape (OSR) planted in the eastern and East Midlands regions out of a total of 3.18 million hectares planted in England (AHDB, 2016; NFU, 2016). In cereal production, crop rotations with the associated use of break crops are used to control pests, diseases and nutrient cycling and ensure a good soil structure (White, 1997). A break crop is a crop that reduces the build-up of weeds, pests and diseases in cereal crops, hence ‘breaking’ the cycle of cereals and reducing the risk of pesticide resistance through the use of pesticides containing alternative active ingredients (Finch *et al*., 2014). OSR is an important break crop and is often the most profitable option for many farmers.

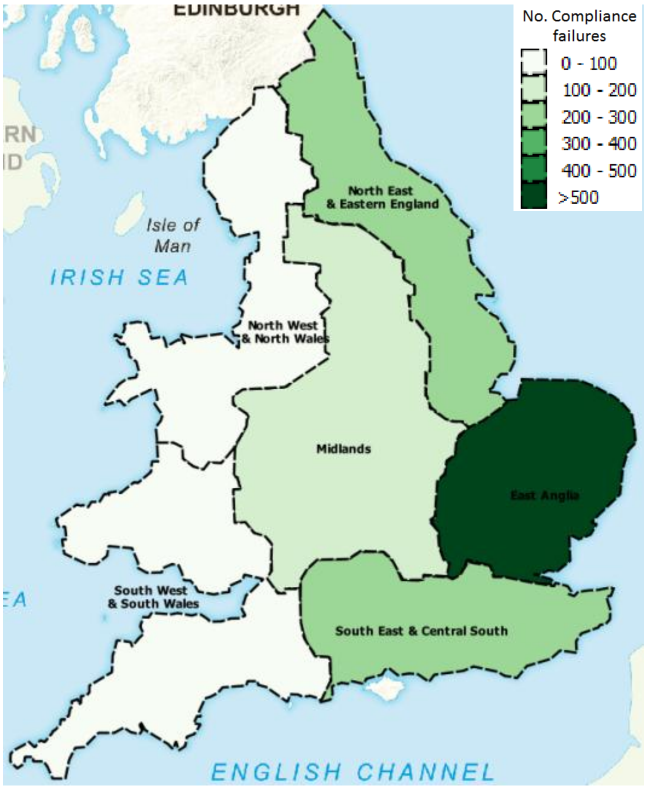


Figure 2.3 – Combined number of compliance failures for pesticide detection within UK regions between 2000 and 2014 (Drinking Water Inspectorate, 2016)

In the UK the amount of OSR being grown has greatly increased in recent years. This is particularly noticeable in the Eastern regions where croppage has increased from 68 thousand hectares in 2000 to 137 thousand hectares in 2016 (Figure 2.4). The map regions presented in Figure 2.4 are different from those in Figure 2.3 due to differences in how the source data was partitioned. OSR is a crop that requires intensive use of pesticides during the early stages of growth in order for the plant to become established (Twining *et al*., 2009). There is concern amongst farmers and agronomists about the future of a number of OSR pesticides. This is because these pesticides are the ones that are frequently found in drinking water. For example, metaldehyde, clopyralid, and propyzamide were all within the top ten pesticides for compliance failures in the period from 2008 to 2016 (Twining *et al*., 2009; Clarke, 2014; Drinking Water Inspectorate, 2016). A number of voluntary initiative schemes have been set up to try and tackle the problem but, particularly in the case of metaldehyde, regulatory bodies and government agencies fear that this may not be enough to sufficiently control the presence of these pesticides in drinking water (Pendergrast, 2014).

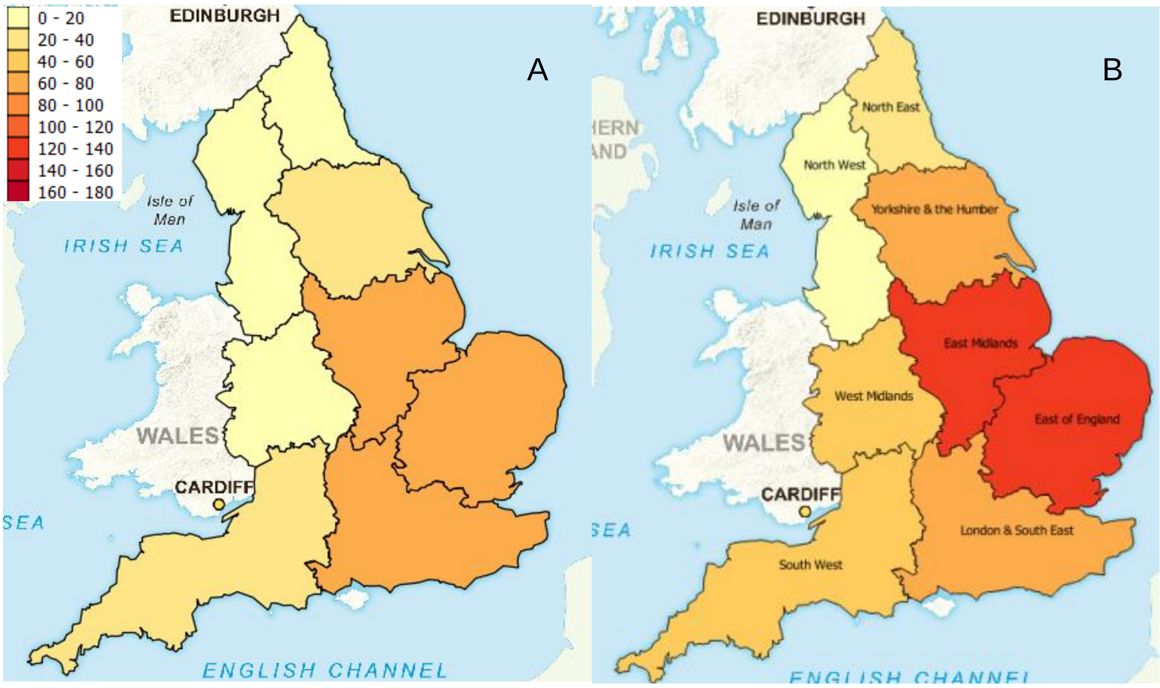


Figure 2.4 – Area of OSR grown in the UK (per thousand hectares) between years 2000 (A) and 2016 (B) Source: (AHDB, 2016)

The review now focuses on five important pesticides: metaldehyde, clopyralid, metazachlor, propyzamide and quinmerac. These have been selected based on: their importance in causing compliance failures in drinking water; that they are representative of a range of pesticide physico-chemical properties; their inclusion within voluntary initiative schemes and their wide-scale use in OSR crop production. With the increase in OSR croppage, wider use of these pesticides is expected. In addition, the interest surrounding these particular pesticides includes a number of factors such as their persistence in the environment and the difficulties involved in removing them from potable water sources. A high number of compliance failures occurred for these pesticides in the years 2009 and 2013, 388 and 349 respectively. The compliance failures were dominated by metaldehyde which accounted for 361 failures in 2009 and 324 failures in 2013 (Figure 2.5). In 2009, compliance failures also occurred for clopyralid (11) and propyzamide (1). In 2013 clopyralid, propyzamide and quinmerac were also the causes of a small number of compliance failures with 2, 3 and 2 respectively. In the years following 2013, there were 50% fewer failures. The applications of the identified pesticides has increased by weight over the time period covered (Figure 2.5), with applications for metazachlor and quinmerac reaching a stabilised maximum since 2013 and clopyralid and propyzamide applications reaching a steady state in more recent years. The exception has been metaldehyde, which has had inconsistent applications over the time period studied. There was no obvious correlation between the amount of pesticide applied and the number of compliance failures for the identified pesticides (Figure 2.5). For example, in the case of metaldehyde, 480,440 kg and 112,547 kg were applied in 2009 and 2013 while the numbers of drinking water compliance failures in these years was 361 in 2009 and 324 in 2013. Likewise, for the other identified pesticides there was no obvious link between compliance failures and the amount of pesticide that was applied in England and Wales.

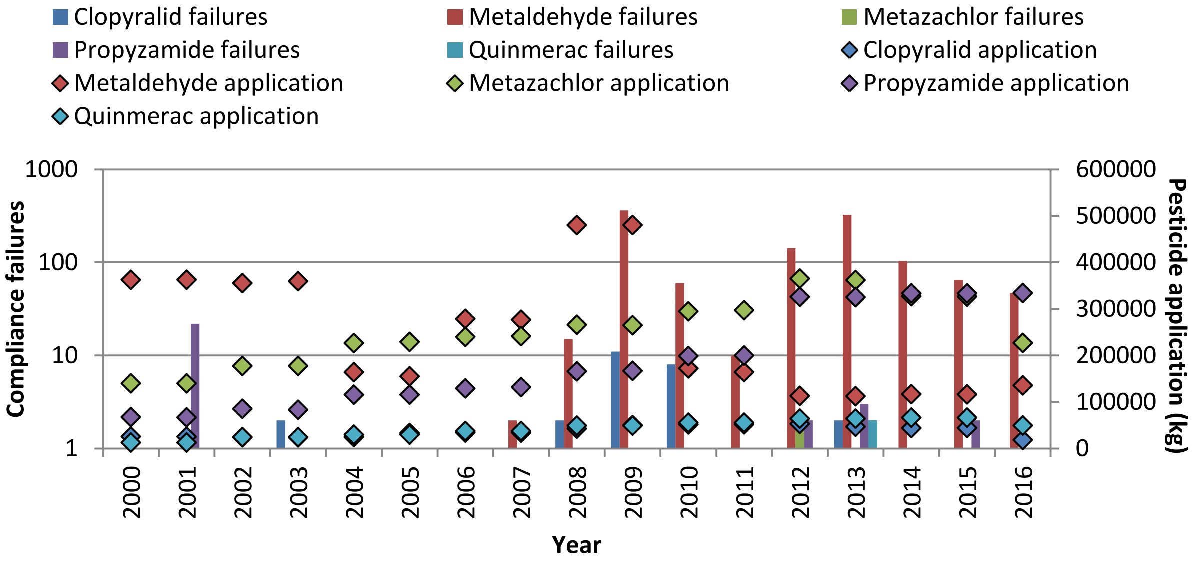


Figure 2.5 – Compliance failures caused by identified pesticides across England and Wales by year alongside the application (kg) for each identified pesticide (Drinking Water Inspectorate, 2016; FERA, 2018)

As noted, there are other factors to consider other than total application when considering whether a pesticide is likely to cause a drinking water compliance failure. This section therefore considers the relationship between rainfall and compliance failures by region. This is because relationships between storm events and pesticides in run-off has been seen before in many previous studies (Chen *et al.*, 2002; Bingham, 2007; Ulrich *et al*., 2013). The three regions of East Anglia, the South East and the Midlands have been chosen for this analysis due to the high numbers of compliance failures and the extensive arable agricultural activity that takes place in these regions. Analysis was carried out looking at the localised regional rainfall patterns with rainfall data from the Met Office (2015) for average monthly rainfall from 2007 to 2014 against the rate of compliance failures for each region. The only correlation observed was found between the rainfall patterns in August to October and the number of compliance failures seen. These months are significant as they cover the period during which metaldehyde (Lu et al., 2017) is usually applied and when winter crops such as OSR are sown for the autumn/winter growing period (although there is always some variability in this due to the weather dependent nature of agricultural production). Metaldehyde is the main pesticide considered here as it is the most significant one with regards to the number of compliance failures it has caused. For Southern and Eastern regions (Figure 2.3), the large numbers of metaldehyde failures coincide with regional weather conditions that consist of a dry August and September relative to an increase in the average rainfall during October. The impact of the relative differences in rainfall over the three months of August to October can be seen when the difference in rainfall between these months is plotted against the number of compliance failures (Figure 2.6). The general trend shows that as the rainfall in October gets closer to equalling and/or exceeding the amount of rainfall that occurred in the previous 2 months, the number of compliance failures increases. The data shows that a 40 mm deficit of rainfall in October compared to the combined rainfall during August and September, is where the threshold for the increasing number of compliance failures starts to occur. These data suggest that dry to wet conditions during this period pose the highest risk of compliance failures occurring as compared to wet to wet, wet to dry or dry to dry conditions over the same time period. The highest numbers of failures occurred in East Anglia, although the same pattern was seen in the other regions. The extent of these patterns therefore was a reflection of the relative magnitude of agricultural activity that occurs in each of these regions. This implies that when considered at a regional level, the amount of pesticides applied has an impact in terms of the potential for compliance failures but it is the rainfall patterns that are the main factor that affects the extent of the number of compliance failures seen.

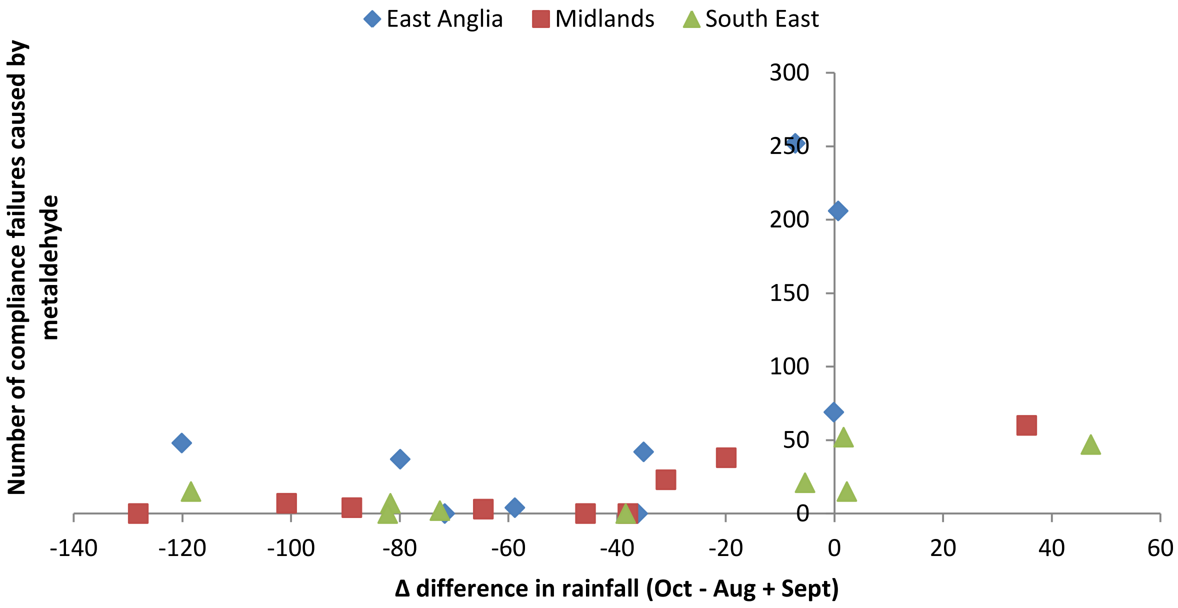


Figure 2.6 – Compliance failures for metaldehyde against Δ difference in rainfall between the months of October and August to September for three regions in the UK between 2007 and 2014

These results align well with previous research on the mechanisms of pesticide mobility. Storm-flow events where increased flow is seen in drainage systems are a large contributor to the movement of pesticides from the field into water courses through leaching or run-off of water soluble pesticides (Maillard *et al*., 2011). Heavy rainfall is therefore a contributing factor to the pollution of drinking water sources by pesticides from agricultural run-off. The effects of climate change are likely to impact upon the regularity at which extreme weather events are experienced in temperate climates. As temperatures increase, so does the ability of the atmosphere to hold moisture (Met Office, 2011; Trenberth, 2011). The evidence suggests that this will lead to longer dry periods followed by intense periods of precipitation. This pattern would in turn lead to a decrease in overall soil moisture coupled with an increase in run-off (Trenberth, 2011). This outcome agrees with that seen here (Figure 2.6) meaning in the event of these weather patterns, a likely increase in the amount of pesticides running into water courses and subsequent compliance failures will occur.

In order to deal with this potential increase of pesticides in run-off, expansion and improvement of existing potable water treatment methods would be needed. The most common means of treatment that water companies currently utilise to deal with pesticides in drinking water is GAC, often coupled with pre-treatment by ozonation (Evans *et al*., 2003; Giribaldi, 2013). Other treatment options for pesticide removal include chlorination, reverse osmosis and advanced oxidation processes (AOPs) where hydroxl radicals are used to break down the pesticide compounds (Assalin *et al*., 2010). However, chlorination is not effective at oxidising many pesticides and the other methods are capitally and operationally expensive and require high energy inputs when used in drinking WTW. Adsorption using GAC is effective for treatment of a range of pesticides, although compounds such as metaldehyde break through GAC filters quickly. However, the use of adsorption media is a simple and low energy input approach to reduce pesticide concentrations (Sophia and Lima, 2018). The relative ease of application and low energy requirement of adsorption systems make them potentially suitable for use in agricultural environments where they could be used to reduce pesticide concentrations. This in turn would reduce the pesticide concentrations entering water courses and subsequently the potential to enter into water used for potable supply. The use of pesticide treatment ‘at source’ in the field would, if successful, reduce any health risks associated with the presence of pesticides in potable water. It would also reduce the risk of non-compliance, have a potential beneficial financial impact by reducing the amount of treatment needed at the treatment works and financial consequences from exceeding Drinking Water Directive limits in addition to reducing the extent of shock loads during treatment. Furthermore, this approach would benefit the environment by reducing pesticide contact with non-target organisms.

The effectiveness of adsorption is dependent on both the properties of the individual pesticides (the adsorbate) and the material being used as the adsorbent. The mechanism of pesticide adsorption is usually considered in terms of physisorption by Van der Waals forces, London dispersion forces, hydrophobic interactions and hydrogen bonding. These are relatively weak forms of intermolecular forces that involve attractions between the adsorbent and the adsorbate (Lewis and Evans, 2006; Worch, 2012; Sophia and Lima, 2018). Factors such as temperature, pH, presence of other organic molecules, pore size distribution, external surface area and the properties of the pollutant all have an impact on adsorption processes (Worch, 2012). The presence of other organic contaminants present in the water is of particular importance when considering the use of an adsorption medium in environmental applications as preferential adsorption may occur which may inhibit the adsorption of the target pollutant (Ayranci and Hoda, 2004; Worch, 2012).

The following section of the review considers an overall look at pesticide physico-chemical properties and how these properties may affect the extent to which the pesticides will adsorb to soil or associated adsorption media. The review then focuses in on the five selected pesticides with differing physico-chemical properties that are important both in their role in agricultural production and of concern for potable water treatment.

2.3 Pesticide properties and their influence on removal by adsorption

The physico-chemical properties of the selected pesticides of interest have been compared using various coefficients that provide an indication of the likely adsorption behaviour that will be displayed by each pesticide (see Table 2.2 for mathematical expressions and unit derivations for each coefficient). The adsorption partition-coefficient (K_d) is a measure of how organic molecules such as pesticides partition at equilibrium between a sorbent and solution. In environmental fate studies, the sorbent is usually soil. Although these tests are usually carried out using soil, they still give an indication of how well a pesticide will adsorb to other substrates and so are still useful indicators when considering other adsorption media. K_d is empirically derived from adsorption isotherm experiments. Batch adsorption tests are carried out using a fixed mass of a medium and by varying pesticide concentrations, or by having a set concentration of pesticide and varying the amount of adsorption medium used. The adsorption isotherm can then be modelled from which the theoretical adsorption capacity can be obtained. In these experiments adsorbate and adsorbent are mixed and a sample taken from the liquid phase after equilibrium has been reached. The difference between the concentration of the original solution and the concentration in the liquid phase determines the amount adsorbed. Different K_d values may be obtained depending on the soil type used in the experiments, making comparisons between studies difficult (Howard, 1993; Hemond and Fechner, 2015). However, the higher the K_d value, the greater the affinity there is between the adsorbate and the adsorbent, which in turn indicates that the compound is less likely to leach from the soil. Researchers have proposed guidelines for pesticide chemicals, with K_d values greater than 5 mL g^{-1} being indicative of compounds where the risk of leaching into surface run-off is low (Trautmann *et al*., 2012). The K_d also gives an indication of the efficiency of adsorption based treatment processes. For example glyphosate, with a K_d of 222 mL g^{-1}, should be relatively easier to remove by adsorption than clopyralid which has a K_d value of 0.071 mL g^{-1}.

The soil organic carbon/water partitioning coefficient (K_{oc}) value is K_d normalised to the organic carbon content by mass of the soil. The process of determining the organic content of soils is described by Schumacher (2002). This value is important because the soil characteristics, particularly the organic carbon content, affect adsorption due to hydrophobic interactions of the organic surface of the adsorbent with the organic adsorbate (Trautmann *et al*., 2012; Washington State Department of Ecology, 2015). The higher the carbon content of a soil, the greater the chance a pesticide will be adsorbed (PPDB, 2014) meaning that the mobility of pesticides in run-off or from leaching into water sources in high concentrations, is less likely (Table 2.1). This is related to the polarity of the compound. A polar compound in water is more likely to remain in solution as a result of dipole–dipole forces between the pesticide molecule and the highly polar water molecule (Linde, 1994). Conversely, less polar compounds display increased hydrophobicity which leads to a preference for the organic compound to sorb to the non-polar regions of a sorbent surface as a result of these hydrophobic interactions (Faust and Aly, 1998).

Table 2.1 – Pesticide mobility as a function of K_d and K_{oc} values. (Guertin *et al*., 2001)

Mobility	**K_d (mL g^{-1})**	**Log K_d**	**K_{oc} (mL g^{-1})**	**Log K_{oc}**
Immobile	> 10	>1	> 2000	>3.3
Low mobility	2 – 10	0.3 - 1	500 - 2000	2.7 - 3.3
Intermediate	0.5 – 2	-0.3 - 3.3	150 – 500	2.2 - 2.7
Mobile	0.1 – 0.5	-1 - -0.3	50 – 150	1.7 - 2.2
Very mobile	< 0.1	<-1	< 50	<1.7

K_f is the Freundlich coefficient that provides an indication of the capacity of the adsorbent to adsorb an adsorbate. The Freundlich model is fitted to data obtained from adsorption isotherm experiments as already described for K_d.

The model assumes that adsorption occurs through a process of multilayer adsorption onto a heterogeneous surface. K_f is derived from a log-log plot of the final equilibrium concentration, obtained against the amount of pesticide adsorbed per mass of adsorbent. K_f is obtained from the intercept of the regression line through the data (Tan, 2011). For the Freundlich model, 1/n is an experimental value derived from the slope of the regression line. It is linked to the surface heterogeneity of the medium being used, a value close to 1 indicates a more linear sorption (Saha *et al*., 2013). Other models such as the Langmuir model, which describes monolayer adsorption, are also often used, however it is often the Freundlich model that gives a better fit to the experimental data when describing pesticide adsorption (Baskaran *et al.*, 1996; Crittenden *et al.*, 2012; Ghafoor *et al*., 2013; Khan and Brown, 2017).

The octanol-water coefficient (log K_{ow}) is a measure of the hydrophobicity of a compound. This shows whether a pesticide has a preference for being in water or whether it is more likely to dissolve in the organic phase. Octanol is used due to its similar carbon to oxygen ratio to that of lipids (8:1), which are very hydrophobic. This means that octanol is non-miscible with water and so clearly separates the organic and non-organic liquid phases (Harrison, 2007). The polarity of a pesticide is inferred from its associated K_{ow} value.

The solubility of a compound in water is the amount of pesticide (in mg) that can dissolve in 1 L of water at a set temperature (usually 20°C). Initially, the solubility of a compound is estimated by increasing the volume of water until the solute is visually dissolved. Then, one of two methods is followed to more accurately determine solubility (OECD, 1995). In the column method an inert substance is coated in the solute material and solubility is determined by the mass concentration eluted from the column once equilibrium is reached. In the flask method, a known volume of water is saturated by the compound of interest at a temperature higher than the set temperature. After 24 h of agitation at the higher temperature, the solution is cooled to the test temperature then centrifuged. A sample is then taken from the aqueous phase and the compound analysed using the most appropriate means, for example liquid chromatography (LC) or gas chromatography (GC) coupled with mass spectrometry (MS) (OECD, 1995). A compound with a high solubility would indicate a preference to be in the water phase and therefore is likely to have a higher mobility (Müller *et al*., 2007; Dordio and Carvalho, 2013).

The acid dissociation constant (pKa) is an indicator of the pH at which a pesticide will dissociate and change ionic state. The maximum amount of adsorption is expected to occur at a pH close to the pKa of the pesticide (Schwandt *et al*., 1992; Clayden *et al*., 2001; PPDB, 2014). This is because at these pH, the molecules exist in an undissociated state where they are protonated and uncharged and so are in a more hydrophobic state and therefore have a preference to adsorb rather than be in solution (Baskaran *et al*., 1996; White, 1997; Strawn *et al*., 2015). The most common method of determination is by titration through the addition of an acid or base of a known concentration to a known volume of pesticide solution until a neutral pH is reached (Environmental Protection Agency, 1996).

Table 2.2 – Summary of co-efficient parameters used to define physico-chemical properties of pesticides and adsorbents.

Coefficient parameter	**Symbol**	**Units**	**Equation**	**Function**	**Reference**
Adsorption partition coefficient	K_d	mL g^{-1}	$K_d = \frac{A_i}{C_i}$ A_i = Mass of sorbate adsorbed C_i = Mass of sorbate in solution	Describes the extent of adsorption for a given sorbent	(Thrasher *et al.*, 2004; Tran *et al.*, 2015)
Soil organic carbon/water partitioning coefficient	K_{oc}	mL g^{-1}	$K_{oc} = K_d \times \frac{100}{\%oc}$ %oc =percentage of organic carbon in soil sample	Describes the partitioning of the sorbate between the organic carbon in the soil and water	(Environment Protection Agency, 2000; Chemicals Regulation Directorate, 2012; PPDB, 2014)
Freundlich coefficient	K_f	(μg g^{-1})(μg L^{-1})$^{1/n}$	$q = K_f C^{\frac{1}{n}}$ K_f = adsorption capacity C = chemical concentration in solution K& n = empirical constants	Describes the adsorption capacity of an adsorbent material	(Environment Protection Agency, 2000; PPDB, 2014)
Octanol water coefficient	K_{ow}	mg L^{-1} or mol L^{-1}	$K_{ow} = \frac{A_{(oc)}}{A_{(aq)}}$ $A_{(oc)}$ = Amount of substance dissolved in octanol at equilibrium $A_{(aq)}$ = Amount of substance dissolved in water at equilibrium	Describes the hydrophobicity of a compound dependent upon its partitioning between an organic solvent (octanol) and water	(Finizio *et al.*, 1997; Worch, 2012; Molyneux, 2014)
Solubility in water	-	mg L^{-1}	-	Describes the amount of chemical that will dissolve into a given amount of water at a given temperature (usually reported at 20°C)	(Ulrich *et al.*, 2013; PPDB, 2014)
Log of dissociation constant	pKa	Dimensionless	pKa = -log K_a Where K_a is: $k_a = \left(\frac{[H^+]\,[A^-]}{[HA]}\right)$ H^+& A^- = ions HA = acid	Describes the strength of an acid via the ratio of ions to acid. Usually reported in log form	(Montgomery, 2007; Pillai *et al.*, 2009; Paszko, 2014)

To determine whether there were any relationships between the frequency of compliance failures and the physico-chemical properties of the pesticides, the mobility (log K_{oc}) and polarity (log K_{ow}) indicator values for each chemical were plotted against the failure frequency (Figure 2.7) for the 35 pesticides that have been recorded as causing compliance failures between 2000 and 2016. This gives an overall indication of the trends between pesticide physico-chemical properties and compliance failures. Pesticides were categorised as mobile if their log K_{oc} was <2.7 mL g^{-1} based on the definition of mobility (Guertin *et al*., 2001). Above this value, pesticides were considered to have low mobility or be immobile. A pesticide was considered polar if its log K_{ow} was <3 based on values in the PPDB (2014). This is because there is a low chance of bioaccumulation (low-moderate) at this K_{ow} compared with K_{ow} >3 which are non-polar compounds where high bioaccumulation is seen. This is because these molecules prefer to partition in the octanol rather than water phase.

A polar compound with a low K_{oc} value infers that the compound has a preference to be in water rather than be adsorbed on to the organic content within the soil. This in turn means that during storm events, these are the compounds that are more likely to be removed from the field by water run-off and therefore these are the compounds that are most likely to influence drinking water quality. The data in Figure 2.7 generally agrees with these principles in that the majority of compliance failures were found for pesticides within or close to the boundary of the polar, mobile category. The average number of failures in the polar mobile category was 67 as compared to the other categories where the average numbers of failures were all lower: polar immobile 8.5; non-polar mobile 6.25; non-polar immobile 7.2.

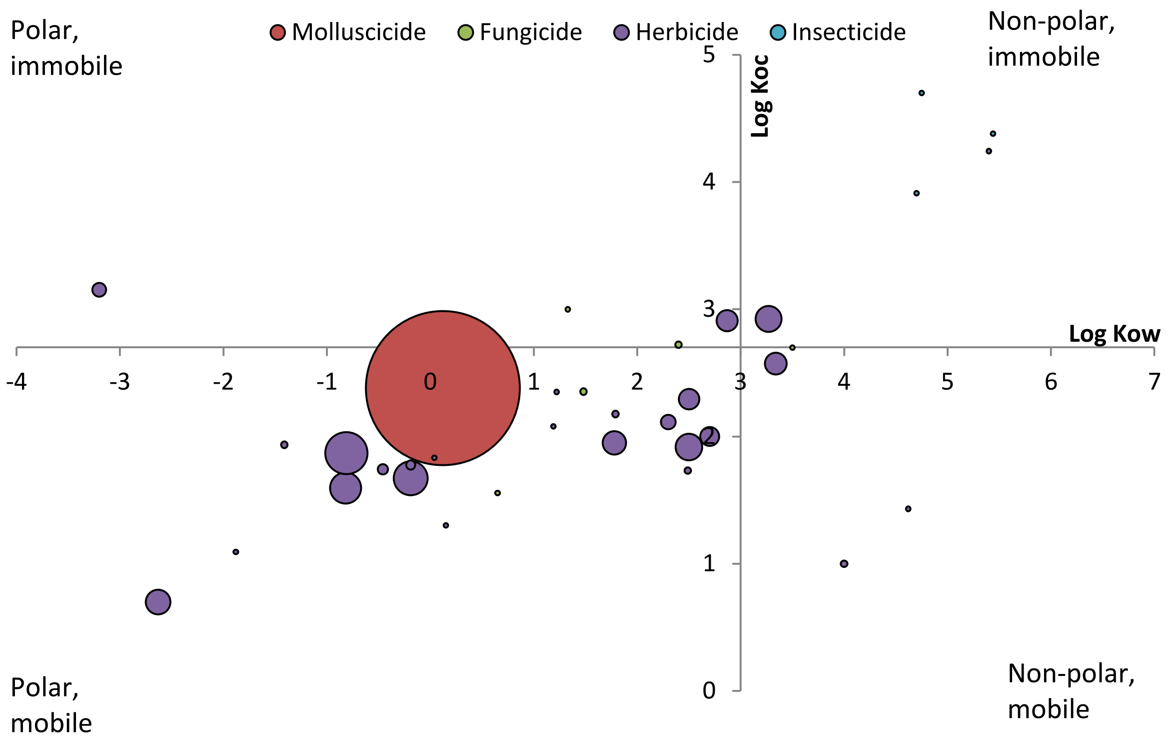


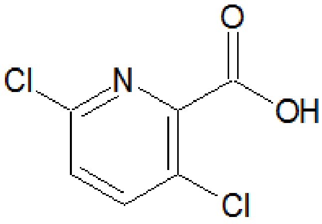
Figure 2.7 – The relationship between the physico-chemical properties of pesticides and drinking water compliance failures within the UK between 2000-2016. Size of the bubble is relative and indicates number of failures out of a total of 1571. Adapted from (De Smedt *et al*., 2015). Sources: (EFSA, 2006a, 2006b, 2007b, 2009b, 2009c, 2014; PPDB, 2014; Drinking Water Inspectorate, 2016; Kegley *et al*., 2016)

The next section looks in detail at specific problem pesticides in potable water in the UK. The physico-chemical properties of each pesticide are described alongside a review of the literature for studies which describe associated adsorption studies.

2.3.1 Clopyralid

Clopyralid is a synthetic herbicide which affects cell elongation and respiration of the target weed (Tomlin, 2009). It is described as an auxin-like compound, meaning that it mimics a specific type of plant hormone (the auxin class). Clopyralid is used for the control of broad-leaved weeds (Gu *et al*., 2011; Momcilovic *et al*., 2014). It has a structure (Table 2.3) based around the pyridine molecule (Momcilovic *et al*., 2014; PPDB, 2014). Clopyralid is acidic and under most natural environmental pH conditions and is likely to be found in its anionic form (Celis *et al*., 2012). Its acidic nature means that the solubility in water of clopyralid is dependent upon pH. Due to its low K_d value of 0.071 mL g^{-1} (Table 2.3), clopyralid does not adsorb well to soil particles and so is highly mobile (Table 2.1) with the potential to contaminate groundwater (Šojić *et al*., 2009) and surface water. The low K_{oc} (5 mL g^{-1}) coupled with its low K_{ow} value (-2.63) suggests that organic matter will not be a suitable adsorbent for the removal of clopyralid and that the pesticide will have a strong preference towards being in the water phase.

Table 2.3 – Clopyralid pesticide properties

Coefficient parameter	Value	Range	Medium	Reference
Molecular mass	192	-	-	
Chemical formula	$C_6H_3Cl_2NO_2$	-	-	
Structure				(Advanced Chemistry Development Inc., 2015)
K_d	0.071 ml g^{-1}	0.032 – 0.151 mL g^{-1}	Soil	(EFSA, 1997; PPDB, 2014)
K_{oc}	5 ml g^{-1}	3.43 – 7.34 mL g^{-1}	Soil	(EFSA, 1997; PPDB, 2014)
K_f	0.0126 ml g^{-1}	0.0054 – 0.0267 mL g^{-1}	Soil	(EFSA, 1997)
1/n	0.6473	0.3881 – 0.8602	Soil	(EFSA, 1997)
Log K_{ow}	-2.63	-	-	(PPDB, 2014)
Solubility in water	143000 mg L^{-1}	118000 – 157000 mg L^{-1} (pH range 5 – 9)	-	(EFSA, 2005a; PPDB, 2014)
pKa	2.01	-	-	(PPDB, 2014)

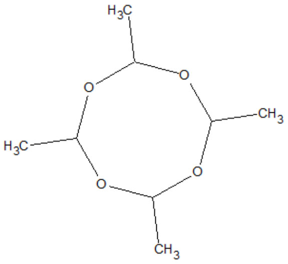
The main route of environmental degradation of clopyralid is through microbial degradation, with the rate being dependent upon the initial pesticide concentration and the soil practices such as tillage (Schütz *et al*., 1996; Tomlin, 2009). Microbial degradation is decreased under cold, dry or anaerobic conditions (Marin Municipal Water District, 2010). Clopyralid has been seen to be persistent in immature composts of grass clippings where it can cause problems for some sensitive plant species which show phytotoxicity symptoms if grown in clopyralid contaminated compost. It was suggested, however, that part of this issue may have been due to a lack of consideration given to the pesticide labelling and proper use (Blewett *et al*. 2005; Marin Municipal Water District 2010).

A number of studies have concentrated on AOPs rather than adsorption as a removal method for clopyralid (Momcilovic *et al*., 2014). However chitosan coated montmorillonite clay (Celis *et al*., 2012) and carbon cryogel (Momcilovic *et al*., 2014) are two adsorbents that have been studied for the removal of clopyralid. The maximum adsorption capacity seen for carbon cryogel was 16 mg g^{-1} which was found in acidic solutions when the clopyralid molecule was in its dissociated anionic form. This was shown to form an electrostatic attraction with the positive surface of the carbon cryogel (Momcilovic *et al*., 2014). Similarly, chitosan-montmorillonite was better able to adsorb clopyralid under acidic conditions. Again this was due to clopyralid being in a negatively charged state and electrostatic interactions occurring with the positively charged surface of the medium (Celis *et al*., 2012). The authors suggest that chitosan-montmorillonite could be successful in removing other organic pollutants such as other pesticides, pharmaceuticals or personal care products from water so long as the pollutants were in an anionic form.

2.3.2 Metaldehyde

Metaldehyde is a molluscicide used for the protection of crop plants against slugs and snails (Zhang *et al*., 2011). When consumed, it causes mollusc pests to excrete excessive amounts of mucus, causing death by desiccation as the compound is broken down from metaldehyde to acetaldehyde (Castle *et al*., 2017). However death can be prevented under wet or humid conditions (Wilkinson, 2010). Metaldehyde is a tetramer of acetaldehyde (C_2H_4O) (Tomlin, 2009; Busquets *et al*., 2014). Metaldehyde has a fairly stable structure (Table 2.4) and is not easily degraded under anaerobic conditions. It is polar in nature meaning any interactions with suspended organic matter will be weak and so it will become easily desorbed (Busquets *et al*., 2014). The K_d and K_f values for metaldehyde are low indicating little adsorption to soils will occur and so the compound is likely to be mobile in the environment. The K_{oc} value and range suggest that some interaction with organic matter could occur although this is still not high enough to prevent the pesticide from being mobile in the environment as seen from the high number of compliance failures that this pesticide has caused (Figure 2.1).

Table 2.4– Metaldehyde pesticide properties

Coefficient parameter	Value	Range	Medium	Reference
Molecular mass	176.21	-	-	
Chemical formula	$C_8H_{16}O_4$	-	-	
Structure				(Advanced Chemistry Development Inc., 2015)
K_d	0.234 mL g^{-1}	0.103 – 0.436 mL g^{-1}	Soil	(Defra, 1996)
K_{oc}	240 mL g^{-1}	15-240 mL g^{-1}	Soil	Value: (PPDB, 2014) Range: (Defra, 1996)
K_f	0.69 mL g^{-1}	0.432 – 0.977 mL g^{-1}	Soil	(EFSA, 2009c; PPDB, 2014)
1/n	0.96	0.675 – 1.023	Soil	(EFSA, 2009c; PPDB, 2014)
Log K_{ow}	0.12	-	-	(EFSA, 2009c; PPDB, 2014)
Solubility in water	188 mg L^{-1}	188 - 196 mg L^{-1}	-	(EFSA, 2009c; PPDB, 2014)
pKa	n/a	-	-	(EFSA, 2009c; PPDB, 2014)

Metaldehyde as a problem in drinking water was first reported by Bristol Water in 2007. Prior to this, methods were not available to detect the pesticide below the threshold limit of 0.1 µg L^{-1}. Since its initial discovery by Bristol Water, metaldehyde has been found at levels exceeding the Drinking Water Directive limit by other water companies around the UK (Bristol Water, 2009; Wilkinson, 2010; Drinking Water Inspectorate, 2016). Due to the problems encountered with the removal of metaldehyde from drinking water by adsorption on to GAC, in addition to the high energy and cost inputs required for other treatment methods such as AOPs, catchment management has been the main method used to try and reduce the amounts of the pesticide entering water sources used for drinking water (Marshall, 2013). Schemes such as Severn Trent Water's product substitution plan have been trialled to encourage farmers to switch to less problematic molluscicides such as ferric phosphate (Severn Trent Water, 2014). There are also campaigns such as 'Get Pelletwise' promoted by the metaldehyde stewardship group (Metaldehyde Stewardship Group, 2015). These endorse best practise methods and advice for farmers working with metaldehyde.

Up until now, removal of metaldehyde from drinking water has proven difficult. A number of new adsorption media have emerged that appear to have some promise. One of these is phenolic carbon (Busquets *et al*., 2014). These are AC beads synthesised from phenolic resin. The benefits of using phenolic carbon are that they can be "tailored" by controlling surface charge and porosity in order to increase the chances of adsorption for specific compounds. Busquets *et al*. (2014) have developed phenolic resins with pore sizes in the nano-porous range (<2 nm). These nano-porous phenolic carbons have reported metaldehyde removal rates of 76 mg metaldehyde per g carbon which is much greater than conventional GAC which has removal rates of 13 mg metaldehyde per g carbon (Busquets *et al*., 2014). Saratech is a polymer derived AC similar to the phenolic resins. Experimental work has shown that the

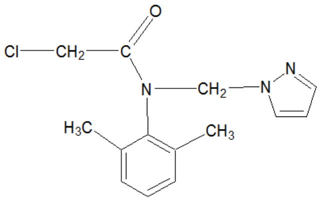
Saratech adsorbents show good removal of metaldehyde (>99.9%) exceeding the capacity of a commonly used AC (F400) which achieved around 90% removal (Jönsson *et al*., 2015).

Another medium reported to posess removal capabilities of metaldehyde is Osorb (ABS Materials, 2014). Osorb is an organo-sillica nanoparticle that swells upon contact with organic molecules. Its porous and hydrophobic surface makes it suitable for pesticide adsorption via hydrphobic interactions with some versions of the medium reported to have good removal of metaldehyde similar to the performance of standard GAC with removals around 90% (ABS Materials, 2014; Jönsson *et al*., 2015).

2.3.3 Metazachlor

Metazachlor is a synthetic residual herbicide used mainly for the protection of oilseed rape (Mohr *et al*., 2007; PPDB, 2014). It is an example of a chloroacetamide substance (Mohr *et al*., 2007; PPDB, 2014).The pesticide works by hindering the production of very long chain fatty acids, preventing metabolism and cell division during plant growth (Mohr *et al*., 2007). The low K_d, K_{oc} and K_f values all show that little interaction with soil or organic matter is likely to occur and therefore low levels of adsorption seen in the environment (EFSA, 2008). The K_d and K_{oc} values make metazachlor an intermediate/mobile pesticide according to the mobility categories previously defined (Table 2.1).

Table 2.5 – Metazachlor pesticide properties

Coefficient parameter	Value	Range	Medium	Reference
Molecular mass	277.75	-	-	
Chemical formula	$C_{14}H_{16}ClN_3O$	-	-	
Structure				(Advanced Chemistry Development Inc., 2015)
K_d	0.78 mL g^{-1}	0.37 - 1.659 mL g^{-1}	Soil	(EFSA, 2005b; PPDB, 2014)
K_{oc}	54 mL g^{-1}	29.2 - 73.1 mL g^{-1}	Soil	(EFSA, 2005b; PPDB, 2014)
K_f	1.02 mL g^{-1}	0.65 - 4.4 mL g^{-1}	Soil	(EFSA, 2005b; PPDB, 2014)
1/n	0.865	0.68 - 1.1	Soil	(EFSA, 2005b)
Log K_{ow}	2.49	-	-	(EFSA, 2005b; PPDB, 2014)
Solubility in water	450 mg L^{-1}	433 - 450 mg L^{-1}	-	(EFSA, 2005b; PPDB, 2014)
pKa	n/a	-	-	(EFSA, 2005b; PPDB, 2014)

Metazachlor undergoes microbial degradation in aerobic soil (Tomlin, 2009), although it is described by the European Chemicals Agency (2011) as not being readily biodegradable. It is also resistant to breakdown via hydrolysis or photolysis, with DT_{50} values of over one hundred days for a range of environmentally relevant temperature and pH values (European Chemicals Agency, 2011). In order to try and reduce the impact of metazachlor in water, a number of pesticide manufacturers have set-up a voluntary stewardship initiative. The aim is to try and encourage farmers to use best practice with suggested precautions to reduce the amount of pesticide getting into water sources. The stewardship group warns that if measures are not taken then metazachlor may end up becoming a restricted use pesticide and therefore impact crop protection for oilseed rape against blackgrass and broad-leaved weeds (BASF, 2015).

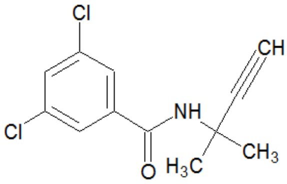
There have been few studies that have looked at the sorption of metazachlor, with most work concentrating on the indirect effects of metazachlor on macrophytes and soil microflora (Beulke and Malkomes, 2001; Mohr *et al*., 2007). Beulke and Malkomes (2001) found that more adsorption of metazachlor occurred with soils that had higher organic carbon content. However, the soils with higher organic carbon content also displayed less microbial degradation. Additionally, although the parent compound was not tested, the two main metabolites of metazachlor, metazachlor oxalic and metazachlor sulfonic acid, showed only weak adsorption to soil and adsorption was not significantly improved by the addition of biochar (Dechene *et al*., 2014).

2.3.4 Propyzamide

Propyzamide is a selective systematic herbicide that is used for the control of annual grasses, particularly black grass, on a range of crops but notably oilseed rape (Mersie and State, 1995; Tomlin, 2009; Tediosi *et al*., 2012; PPDB, 2014). It is an example of a benzamide chemical (Tomlin, 2009; PPDB, 2014). The K_d and K_{oc} values of propyzamide put it in the ‘low mobility’ category (Table 2.1) meaning that some interaction with soil and organic matter is likely to occur. The relatively high K_d, K_{oc} and K_{ow} values suggest that propyzamide will be easier to remove from water by adsorption compared to the other pesticides reviewed here.

The regular detection of propyzamide in drinking water has been in line with an increasing use of the pesticide alongside an increase in oilseed rape cropping (HGCA, 2009). Due to propyzamide being a key pesticide for blackgrass control in oilseed rape, it is another one of the pesticides that has been identified in the voluntary initiative scheme, where advice has been given on its use, reducing its presence in watercourses and to prevent it becoming restricted use which could cause problems for growers (Pendergrast, 2014).

Table 2.6- Propyzamide pesticide properties

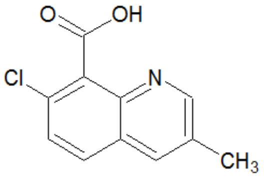
Coefficient parameter	Value	Range	Medium	Reference
Molecular mass	256.13	-	-	
Chemical formula	$C_{12}H_8ClNO_2$	-	-	
Structure				(Advanced Chemistry Development Inc., 2015)
K_d	5.5 mL g^{-1}	3.2 - 10 mL g^{-1}	Soil	(European Commission, 2003; PPDB, 2014)
K_{oc}	840 mL g^{-1}	548 - 1340 mL g^{-1}	Soil	(European Commission, 2003; PPDB, 2014)
K_f	5.8 mL g^{-1}	3.15 - 10.10 mL g^{-1}	Soil	(Orrick, 2007)
1/n	1.09	1.00 - 1.22	Soil	(Orrick, 2007)
Log K_{ow}	3.3	3 - 3.3	-	(European Commission, 2003; Orrick, 2007; PPDB, 2014)
Solubility in water	9 mg L^{-1}	8.5 - 15 mg L^{-1} (20 - 25°C, pH range 4 - 9.6)	-	(European Commission, 2003; Orrick, 2007; PPDB, 2014)
pKa	n/a	-	-	(European Commission, 2003; PPDB, 2014)

Propyzamide is most effectively degraded chemically through the cyclisation of the parent compound to inactive intermediate products (Walker and Thompson, 1977). Results from Zandvoort *et al*. (1979) suggest that improved adsorption of propyzamide occurs on soils with a higher organic carbon content. There was no indication in this study that the clay portion of the soil had any impact on adsorption. This is supported by Fenoll *et al*. (2011) who found better propyzamide adsorption to occurred in soils amended with either spent coffee grounds or composted sheep manure due to high levels of linnocellulosic biomass providing additional adsorption sites. Cantier *et al*. (1986) relate propyzamide adsorption to hydrophobic parameters and suggest that chemical degradation occurs when the pesticide is adsorbed.

2.3.5 Quinmerac

Quinmerac is another synthetic auxin-type herbicide (Despotović *et al*., 2012). It is a selective herbicide primarily used to control weeds such as cleavers (*Galiumaparine*) in sugar beet, oilseed rape and wheat (Deechauer and Kogel-Knabner, 1990; Despotović *et al*., 2012). It is acidic in nature and has a quinoline-carboxylic acid structure (Table 2.7) (Schwandt *et al*., 1992; Despotović *et al*., 2012). Quinmerac is often used in combination with metazachlor to improve crop protection (Clarke, 2014). The environmental pH has a large impact on the solubility of quinmerac in water, with a solubility ranging from 210 mg L^{-1} at pH 4.2 to 107,000 mg L^{-1} at pH 7 (Schwandt *et al*., 1992; EFSA, 2007a).

Table 2.7– Quinmerac pesticide properties

Coefficient parameter	Value	Range	Medium	Reference
Molecular mass	221.6	-	-	
Chemical formula	$C_{11}H_8ClNO_2$	-	-	
Structure				(Advanced Chemistry Development Inc., 2015)
K_d	0.84 mL g^{-1}	0.03 - 12 mL g^{-1}	Soil	(Deechauer and Kogel-Knabner, 1990; Schwandt *et al*., 1992; EFSA, 2007b)
K_{oc}	86 mL g^{-1}	19.2 - 184.8 mL g^{-1}	Soil	(EFSA, 2007b; PPDB, 2014)
K_f	0.59 mL g^{-1}	0.06 - 1.20 mL g^{-1}	Soil	(EFSA, 2007b; PPDB, 2014)
1/n	0.88	0.75 - 0.96	Soil	(EFSA, 2007b; PPDB, 2014)
Log K_{ow}	-1.41	1.17 - -4.41 (pH range 4 - 10)	-	(EFSA, 2007b; PPDB, 2014)
Solubility in water	107,000 mg L^{-1}	210 mg/L - 107000 mg L^{-1}	-	(Deechauer and Kogel-Knabner, 1990; Schwandt *et al*., 1992; EFSA, 2007b; PPDB, 2014;)
pKa	4.31	2.9 - 5.2	-	(Schwandt *et al*., 1992; EFSA, 2007b; PPDB, 2014;)

The K_d range for quinmerac spans the entire mobility spectrum from immobile to very mobile with the K_{oc} values ranging between very mobile to intermediate mobility depending on the pH of the soil. The K_{oc} value of 86 mL g^{-1} comes from an average of the K_{oc}s found for the four soils used in the study with pHs ranging from 6 to 7.7 (Defra, 1998). These factors all lead to the conclusion that the removal of quinmerac from water will be greatly dependent upon the surrounding environmental conditions.

Adsorption of quinmerac is highly dependent upon pH, due to the partial negative charge of the quinmerac molecule interacting with multivalent cations such as Ca^{2+} (Deechauer and Kogel-Knabner, 1990). The cation acts as a bridge between the negative surface charge of the soil and the partial negative charge of the quinmerac molecule. This mechanism occurs when the pH is above 5.5, while hydrophobic interactions are the main sorption mechanism below this pH (Deechauer and Kogel-Knabner, 1990; Schwandt *et al*., 1992). Ochreous sludge and synthetic ferrihydrite have been suggested as materials which could remove quinmerac by adsorption due to their high surface area and the electrostatic interactions which may occur between anionic quinmerac and the positively charged surface of the Fe based media under acidic conditions (Schwandt *et al*., 1992; Dudeney *et al*., 2004).

The main degradation pathway of quinmerac seems to be photodegradation as quinmerac is resistant to hydrolysis, while microbial breakdown was not shown to be a major contributory factor in its degradation (Defra, 1998). Photodegradation was shown to occur quickly under direct UV exposure, using xenon lamps with average intensities of 78,400 lux (Defra, 1998). However, under normal environmental illumination, degradation would be much slower due to lower light intensities (normally between 20,000 lux on a cloudy day, up to 70,000 lux on a sunny day (Defra, 1998)). Despotović *et al*. (2012) showed successful degradation of quinmerac using UV and TiO_2 treatment. However, the rate of degradation was much decreased when testing with raw water as organic matter present at much higher concentrations than the pesticide can consume the OH radicals produced and thus lower the rate at which it is able to react with the quinmerac molecule and break it down.

2.4 Comparison of removal of pesticides by adsorption

The pesticide properties focused on in this review have been compared with other commonly applied pesticides in Europe with respect to their polar and mobility properties (Figure 2.8). The majority of the pesticides reviewed fall into the polar mobile category as described previously. Only propyzamide falls into the immobile category as described previously (Figure 2.8) with a log K_{oc} of 2.9. It is therefore expected that propyzamide detection in run-off will be comparatively lower than the other pesticides.

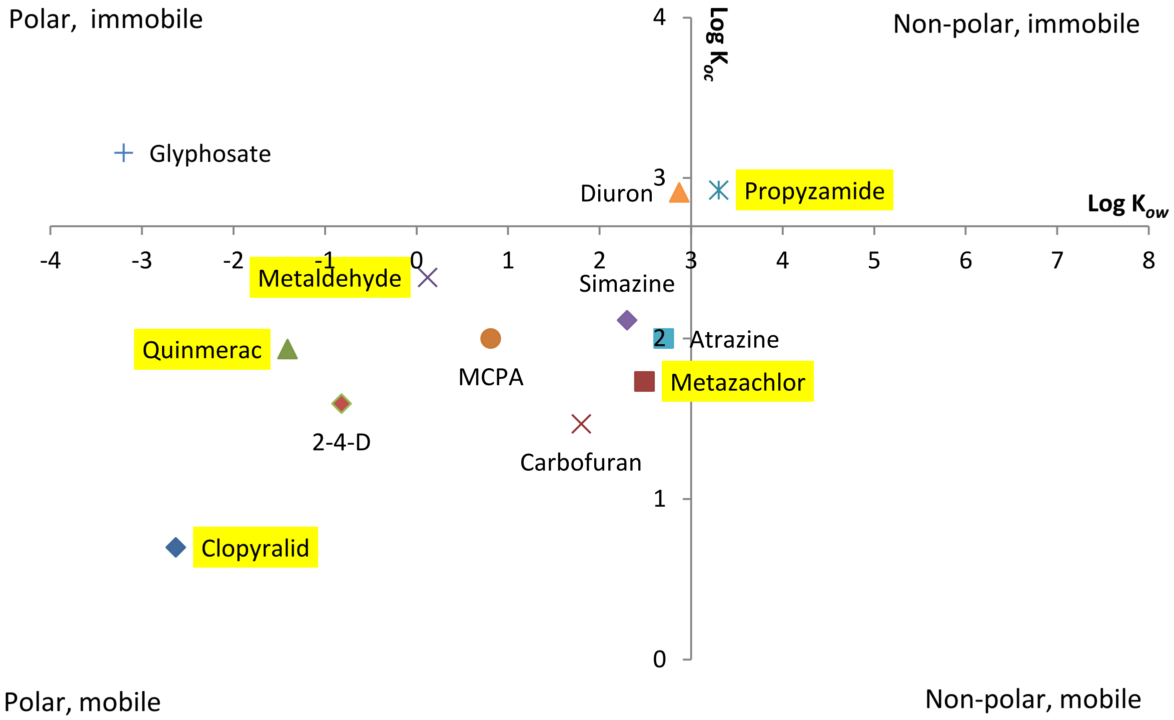


Figure 2.8 - Pesticide properties in terms of their polarity (Log K_{ow}) against their mobility (Log K_{oc}) adapted from (De Smedt *et al.*, 2015). All pesticides are those mentioned throughout the pesticide section of this review. Highlighted pesticides are the five identified pesticides focused on.

Pesticides with a log K_{ow} value below 3 are considered to be hydrophilic and thus are an indication of being polar (PPDB, 2014). A log K_{ow} above 3 is an indication of a substance being hydrophobic and therefore these compounds have the potential to bioaccumulate as there is a preference for these compounds to bind to organic matter and lipids in plants and animals (Stuart and Lapworth, 2011; Lymer and Jones, 2014; De Smedt *et al.*, 2015). Most pesticides have a log K_{ow} below 3 which is the reason why many pesticides persist in water sources (Lymer and Jones 2014). Quinmerac and clopyralid are both very polar compounds, with log K_{ow} values of -1.41 and -2.63 respectively and so are expected to be some of the most pesticides difficult to remove from water by adsoprtion. Media that have charged surfaces are likely to be more successful for the removal of these compounds by electrostatic attraction due to their more polar nature. In principle, metaldehyde should be easier to remove by adsorption compared to clopyralid and quinmerac due to its relatively higher log K_{oc} (2.38) and log K_{ow} (0.12) values. However, this has not been the case as seen by the high frequency of compliance failures it has caused. This may be because of metaldehyde's stable ring structure or because metaldehyde has only single bonds, it can change conformation (3D structure) and so its polarity, and therefore its adsorption, is not constant (Anet, 1974). The development of new phenolic based ACs with high surface areas may help to capture metaldehyde. Metazachlor has a lower log K_{ow} value of 2.49 so is less polar than metaldehyde, clopyralid and quinmerac which all have lower K_{ow} values and so should be relatively easier to remove from water. It does, however, have a low K_{oc} value (1.73) that is in a similar range to other pesticides such as simazine and atrazine. Although metazachlor has not itself caused many compliance failures (only 2 which occurred in 2012) its K_{oc} and K_{ow} are similar to other pesticides known to have been problematic in the past including atrazine, carbofuran (Figure 2.8). This may be due to factors such as lower application rates or a shorter DT_{50} in the soil (typically 8.6 days, PPDB, 2014).

The five pesticides considered in detail in this review can be seen to be representative of the different K_{oc} and K_{ow} properties of the majority of pesticides used in Europe and the UK. The groupings indicate that polarity and mobility are important factors in designing an effective herbicide that is able to move within its environment in order to be taken up by the target weeds. Conversely, this also means that the majority of herbicides have physico-chemical properties that inherently make them a threat to water quality.

2.5 Adsorption media

The most common place for adsorption processes to be applied for removal of pesticides is at the WTW. However, a number of studies have explored the possibility of utilising adsorption media as soil amendments (Cabrera *et al*., 2014; Shou *et al*., 2016) or in constructed wetlands (Dordio *et al*., 2007; Dordio and Carvalho, 2013) to prevent pesticides moving into water courses. The main pathway by which pesticides enter into water courses occurs following heavy rain events. During storm events, pesticide concentrations in streams can increase by up to 20 times that which can occur at base flow (Spalding and Snow, 1989; Laabs and Amelung, 2002). It is these pesticide peaks that cause problems for drinking water quality if abstraction for drinking water occurs downstream of where the contaminated run-off joins a larger water source. During storm events, pesticides are transported into larger water bodies very quickly preventing natural degradation or mineralisation processes from taking place. Evidence suggests that in rural sustainable drainage systems (RSuDS), soluble contaminants are only likely to be effectively removed if high retentions times (days) are present (Avery, 2012).

As adsorption processes can occur more quickly when compared to natural degradation in water (seconds/minutes compared to hours/days) (Gevao *et al*., 2000), it may be possible to use an adsorption medium to attenuate pesticide run-off from agricultural environments. The idea of utilising adsorption media in wetland systems has been explored in a number of other studies. Most concentrate on the use of different media for the removal of P from treated wastewater (Brix *et al*., 2001; Bachand, 2003; Carr, 2012). Some studies have also investigated the removal of pesticides from agricultural wastewater across wetland systems (Dordio and Carvalho, 2013). The proposed principle here is that using an adsorption medium in constructed wetlands on agricultural land slows the flow of water into wider water courses while simultaneously removing the contaminants by adsorption, thus preventing concentration peaks appearing downstream. Ideally the pesticides will adsorb on to the medium and be retained so that microbial degradation can then occur. A number of different media may be suitable to for this role. The following section reviews a number of candidate materials that have been applied in the role of pesticide removal.

2.6 Materials made from carbon

2.6.1 Granular activated carbon

AC is produced through a series of heating steps involving the regulation of oxygen and steam to raw carbonaceous material such as coal, lignite and coconut shell. Out of these AC produced from coconut shell has been found to have the highest surface areas and can exceed 1000 m^2 g^{-1} (Parsons and Jefferson, 2006).

Granular activated carbon (GAC) is the standard means of removing pesticides from drinking water by adsorption at drinking WTW (Stuart *et al*., 2011). The large surface areas of typically 300 – 2500 m^2 g^{-1} and highly microporous structure of GAC make it an effective adsorbent for treatment of pesticide contaminated water (Jusoh *et al*., 2011). GAC particles are typically around 1 mm in diameter (Velten *et al*., 2011; Gibert *et al*., 2013). Powdered activated carbon (PAC) is also used in water treatment, this is the same material as GAC but has a smaller particle size distribution, typically around 0.1 mm (Parsons and Jefferson, 2006). PAC is generally added into stirred tanks in the treatment works during seasonal periods when pesticide presence is higher. This is because PAC only needs a short contact time as the rate of adsorption is much faster compared to an equivelent dosage of GAC (Faust and Aly, 1998; ADAS UK Ltd, 2011). GAC is usually used in contactors where water flows through a fixed bed of the media. GAC is the most well established adsorbent in water treatment and has been shown to adsorb a number of different pesticides such as atrazine and chlorpyrifos, dependent on the physico-chemical properties of the pesticide (Snyder *et al*., 2007; Jusoh *et al*., 2013; Pham *et al*., 2013; Sophia and Lima, 2018). GAC could be applied within the agricultural environment in the form of an amendment to a constructed wetland.

2.6.2 Biochar

Biochar is charcoal-like carbon based material produced by the heating of waste biomass in a low oxygen atmosphere (Sophia and Lima, 2018). The properties of the biochar depend on the feedstock and methods by which it was produced as the biochar will keep the pore structure of the original feedstock (Mohanty *et al*., 2018). Biochar lacks the activation steps used to produce active carbon and so has a lower overall surface area. For example biochar produced from hickory chips had a specific surface area (SSA) of 12.9 m^2 g^{-1} and 15.3 m^2

g^{-1} SSA for biochar produced from bagasse (Xu *et al*., 2016; Mohanty *et al*., 2018) while AC is typically >1000 m^2 g^{-1} (Parsons and Jefferson, 2006). The lower energy input needed to produce biochar compared to AC makes it a potential cost effective alternative, however it does not have as high a removal capacity for organic pollutants compared to ACs in most instances (Inyang and Dickenson, 2015; Mohanty *et al*., 2018). Biochar has been found to be an effective adsorbent for relatively mobile pesticides such as MCPA (2-methyl-4-chlorophenoxyacetic acid) and diuron with leaching reduced by 30 to 90% but was less effective for glyphosate and chlorpyrifos with leaching reduced by 1 to 20%. However, adsorption was improved when the biochar was applied as a distinct layer in the adsorption column as opposed to mixed in with the substrate which, in the case of this study, was sand (Cederlund *et al*., 2017). Therefore biochar would best be used as a medium within a constructed wetland. Biochar has been shown to outperform AC for the removal of mercury from wastewater, this has been attributed to the higher number of C=O and C=C binding sites on biochar compared to AC (Xu *et al*., 2016).

2.6.3 Phenolic resins

Phenolic resin-derived ACs appear to be a promising medium for removal of pesticides, particularly those compounds that have been shown to be poorly removed by conventional AC. This includes pesticides such as metaldehyde and clopyralid (Busquets *et al*., 2014; Jönsson *et al*., 2015). Custom made AC beads manufactured from porous phenolic resin have been proven to be effective for removal of pesticides, with the most effective formed from cross-linked resins and ethylene glycol at a proportion of 10:25 (Busquets *et al*., 2014). The beads are manufactured by placing them in an ethylene glycol solution to help form the pores, followed by heating in an inert mineral oil at 160°C. A further heating step follows in order to carbonise the beads. The beads contain nano- (<2 nm) through to meso-pores (2-50 nm), in the size range of 125-250 µm (Busquets *et al*., 2014). Busquets *et al*. (2014) found that the smaller the pore size, the faster the uptake of metaldehyde occurred and so the faster equilibrium was reached. Medium with a bead size <45 µm reached adsorption equilibrium within 10 minutes, while the optimum time for the most effective uptake of metaldehyde was 30 minutes for the 125 -250 µm sized beads. All of the bead sizes had similar surface areas, (derived from Brunauer-Emmett-Teller (BET) N adsorption - desorption) in the range of 1166-1188 m^2 g^{-1}. It was thus concluded that the narrower pore size distribution and a shorter diffusion pathway located on the smaller beads contributed to higher metaldehyde uptake. Additionally, medium with a high point of zero charge (PZC) had a higher uptake of metaldehyde due to the positive surface charge on the medium at a wider range of pHs due to the presence of protonated carboxylic acids and basic functional groups. The PZC is the pH at which a surface has no detectable charge. At pH below the PZC, a surface will be positively charged and at pH above the PZC a surface will be negatively charged (Mcelroy, 2005; University of Texas, 2009). Busquets *et al*. (2014) state that the data appears to show the phenolic resin-derived carbons do not clog under conditions of high levels of organic matter in column tests using raw water. This could make it ideal for use infield conditions. However, as these carbons have been tailored for metaldehyde removal, their use in removing other pesticides may be limited.

A similar commercially available phenolic derived AC (Saratech), has been produced in a similar way to that described above in a number of different forms (Blucher, 2015) including a spherical bead variety similar to that described by Busquets *et al*. (2014). These beads are porous and hydrophobic, both properties that help to promote adsorption of hydrophobic compounds (Thrasher *et al*., 2004). Batch experiments have shown that Saratech showed superior adsorption of metaldehyde compared to conventional AC, with concentrations around 100 times lower than that found with an equivalent mass of GAC (Jönsson *et al*., 2015).

2.6.4 Organic matter

Materials with high organic matter content generally adsorb pesticides well, as shown by the higher adsorption rates of acid herbicides in soils with high organic matter content (Deechauer and Kogel-Knabner, 1990; Kuo and Regan, 1999). This is because the humin, the insoluble portion of soil organic matter, has surfaces with a high proportion of reactive functional groups such as hydroxyls and carboxylic acids, which are able to act as cation binding sites suitable for the adsorption of anionic pesticides (Kadlec *et al*., 2006; Drori *et al*., 2008). Kuo and Regan (1999) found that spent mushroom compost containing high amounts of organic matter (around 20% by mass) displayed better adsorption (up to 130 mg g^{-1} removal of carbaryl) for both single and multiple pesticide mixes compared to a number of different naturally occurring soil types (40 mg g^{-1} for silt to 100 mg g^{-1} for silty clay loam). Banana peel was found to be a successful adsorbent for the removal of the pesticide atrazine, with up to 98% removal from treated water, although this was reduced to 39 - 57% when tested with river water. It was postulated that adsorption occurred due to the presence of pectin in the banana peel, which has a high number of hydroxyl groups that provide suitable binding sites (Silva *et al*., 2013). Additionally, improved adsorption of propyzamide has been seen in soils amended with spent coffee grounds due to the increased number of binding sites present in the high lignocellulostic (lignin, cellulose and hemicellulose) biomass content resulting in reduced leaching (50% to <1%) (Fenoll *et al*., 2011). The use of lignocellulostic material as an effective sorbent for pesticides is supported by Boudesocque *et al*. (2008) who state that it had a similar adsorption capacity to AC although not as effective as some synthetic resins.

Organic matter for the purpose of reducing pesticide movement could be applied as a soil amendment in order to provide more binding sites in the soil to retain pesticides. Furthermore, the addition of plants to constructed wetlands would, over time, accumulate a layer of humin which can help to trap pesticides.

2.7 Clays and other mineral based media

2.7.1 Montmorillonite clay

Montmorillonite clays have been of interest as adsorbent materials due to their high surface area in the range of 600 – 760 m^2 g^{-1} (Helmy *et al*., 1999). The surface charge properties of montmorillonite clay enable it to adsorb some pesticides. Polati *et al*. (2006) found that a number of pesticides including simazine, atrazine and diuron were retained on Na-montmorrillionite as compared to an alternative clay (kaolinite) where they were not retained at all, with neutral molecules being better retained compared to ionic ones. The removal rates for simazine, atrazine and diuron were between 0.015 to 0.035 mg g^{-1}. However, the ability of natural montmorillonite clay to adsorb hydrophobic organic pollutants was reduced due to its hydrophilic aluminosilicate structure (Saha *et al*., 2013). In order to improve the capacity of clays for removal of organic compounds by adsorption, some inorganic components of the clay can be substituted with organic cations to form modified organo clays (Lemke *et al*., 1998; Saha *et al*., 2013). Saha *et al*. (2013) found that montmorillonite modified with octadecylamine and aminopropyltriethoxysilane, had the highest pesticide adsorption capabilities of the modified montmorillonite clays tested with removal capacities ranging between 0.17 – 0.52 mg g^{-1} for eight pesticides tested (alachlor, metolachlor, chlorpyriphos, fipronil, a-endosulfan, b-endo- sulfan, p,p0-DDT). This compared favourably with a montmorillonite clay modified with only octadecylamine. Increased removal (5-29%) of the eight pesticides was associated with higher proportions of carbon in the modified montmorillonite clays. Similarly, Celis *et al*. (2012) found improved removal of clopyralid using montmorillonite-chitosan nanocomposites. Chitosan can be produced from chitin, natural polysaccharides found in the shells of crustaceans for example (Pillai *et al*., 2009). The nanocomposites were successful in improving the adsorption of clopyralid from 5-38% to 15-55% but only where the pH of the soil solution was under slightly acidic conditions (pH ~5) (Celis *et al*., 2012). Montmorillonite clay would likely best be used as a soil amendment in order to enhance the sorption capabilities of the clay fraction of the soil (Polati *et al*., 2006; Celis *et al*., 2012)

2.7.2 Light Expanded Clay Aggregates (LECA)

LECA are lightweight ceramic pebbles produced by super-heating natural clay (Dordio *et al*., 2007). This causes the clay to expand to four to five times its original size, which in turn increases the inner surface area of the pellets giving it a “cellular” structure (Leca UK, 2014). LECA is mainly used in the construction industry to make masonry walls but it has a wide variety of other applications and is noted for its use in drainage due to its porous nature (Leca UK, 2014). This makes it an ideal candidate in terms of practicality for a sub-surface filter medium in a wetland where flow needs to occur. Dordio *et al*. (2007) and Dordio and Carvalho (2013) have shown LECA, particularly the smaller pellet sizes of 2 to 4 mm (sizes range up to 20 mm), to be effective in the removal of anionic organic compounds, specifically the herbicide MCPA, through adsorption. Using the medium alone, MCPA removal was between 40 to 96.7% dependent upon initial concentration and contact time. Increased removal of 66.2 to 99.1% was seen when the medium was planted with the reed plant *Phragmites*. The mobility (K_{oc}) of MCPA is highly dependent on soil type (Hiller *et al*., 2008) and pH is also a factor that affects the extent of MCPA adsorption. Using the K_{oc} values obtained by Hiller *et al*. (2008) for the non-amended soils, MCPA falls into a similar mobility range to metazachlor and quinmerac (Figure 2.8) so may be expected to adsorb some of these pesticides. Additionally as MCPA is negatively charged under most environmentally relevant conditions (Hiller et al., 2008), LECA should be able to adsorb polar compounds. Adsorption of compounds onto LECA is primarily driven by the charged surface of the LECA. LECA is positively charged around neutral pH and below due to its high PZC of (pH 8.5 – 9) (Dordio *et al*., 2007). The low density of the leca material of between 250 and 450 kg m^{-3} could be an issue if it was applied by itself without having some means of preventing its movement. However the structure and surface properties of LECA seem ideal for its use as an adsorption medium within a vegetated constructed wetland where the roots of the vegetation can keep the low density material in place as occurs with the stabilization of soil by root structures naturally.

2.7.3 Vermiculite

Vermiculite is a clay mineral composed of magnesium-aluminium-iron silicates (Sánchez-Camazano and Sánchez-Martín, 1987; William Sinclair Horticulture Ltd, 2008). It is usually available in an expanded or “exfoliated” form. The exfoliated form is produced when the raw vermiculite is heated. This causes the vermiculite to expand into a number of interconnected layers in a concertina-like matrix (The Vermiculite Association, 2015). Particles typically range between 2 to 8 mm in size (Papadopoulos *et al*., 2008). Vermiculite has a particularly high cation exchange capacity of 85 meq 100 g^{-1} as compared to other clay soil minerals such as kaolinite that have a cation exchange capacity of 4 meq 100 g^{-1} (Ellis and Foth, 1997) and this is particularly high when vermiculite is in its exfoliated form (The Vermiculite Association, 2015). The adsorbance of some pesticides by different types of vermiculite was studied by Sánchez-Camazano and Sánchez-Martín (1987). They found that the best adsorbance was obtained using Ca-vermiculite (vermiculite where the interlayer space contains hydrated calcium ions) compared to Na or Mg modified clays, however this is the least common type found in nature (Ellis and Foth, 1997).

Gregoire *et al*. (2008) found that the pesticides diuron and glyphosate (properties shown in Figure 2.8) did not adsorb well (<25%) to vermiculite as compared to organic media such as beet pulp and maize cob. Brix *et al*. (2001) found that it was not a particularly effective adsorbent for phosphorous adsorbing <1 mg g^{-1} dw P compared to calcite which achieved 25 mg g^{-1} dw P removal. Vermiculite could be either added as a soil amendment or as a filtering layer within a constructed wetland if applied into the agricultural environment (Baskaran *et al*., 1996; Bachand, 2003).

2.7.4 Osorb

Osorb is a commercially available medium and is an example of a swellable organo-silica nanoparticle that is hydrophobic and swells due to the disruption of noncovalent bonds when in contact with organic molecules (Burkett *et al*., 2008; Edmiston and Underwood, 2009; Edmiston, 2010). Osorb is still a relatively new material so there is little literature beyond the studies that have been carried out by those involved in its discovery and manufacture. Its selective capacity for organic molecules in an aqueous environment could be ideal for use within a wetland context. The manufacturers of Osorb claim that metaldehyde and clopyralid can be removed using this medium (ABSMaterials, Inc., 2014). In principle, these adsorbents should be effective for the removal of the other pesticides due to their organic nature although it is more effective at adsorbing more non-polar molecules (Edmiston and Underwood, 2009). A concern may come from the particle size, as these particles are small ranging between 180 to 500 µm in diameter. Osorb Biomax is a variant of the medium containing a blend of Osorb and iron particles through the addition of nanoscale zero valent iron to the osorb matrix to create a composite material. (Dahal *et al*., 2011). Osorb Biomax is, however, a very fine medium (0.25-0.5 mm) that is intended for use as a soil amendment. The use of Osorb Biomax within vegetation strips could be explored to treat initial field run-off at the field boundaries and capture organic pollutants. The claims of Osorb's ability to outperform GAC in the adsorption on both polar and non-polar pesticides (Edmiston and Underwood, 2009) make it a potentially valuable medium for reducing the movement of a range of pesticides within the agricultural environment.

2.7.5 pHlocrite

Phlocrite is a synthetic calcinated dolomitic limestone. It is produced in different grades, dependent upon the calcium:magnesium ratio. Phlocrite typically contains 45% magnesium as MgO and 29% calcium as CaO (Phlocrite, 2015). The high PZC of MgO (12.4) enables the medium to retain a positive surface charge over a wide range of naturally occurring pH conditions (Farooq and Ramli, 2011). A high pH increases the chances of surface interactions between the positively charged surface of the pHlocrite and the negatively charged polarity of polar pesticides. Nanocrystalline MgO has been reported to be an effective adsorbent through chemisorption of contaminants (diazinon and fenitrothion) and has been shown to be able to adsorb pyridine compounds, of which clopyralid is an example (Koper *et al*., 1997; Armaghan and Amini, 2014). Dolomite has been explored as a substrate medium for phosphorous removal although it was shown not to be as effective as a sand bed medium (Pant *et al*., 2001). Prochaska and Zouboulis (2006) however found relatively increased removal of P when using a 10:1 sand:dolomite mixture in a small scale pilot study increasing P accumulation by 6.5 to 18%. A constructed wetland setting may be the way in which pHlocrite could best be applied to an agricultural setting.

2.8 Industrial by-products

Ochreous sludge is a by-product of mine water treatment plants and contains high amounts of $Fe(OH)_3$ and FeO.OH (Heal *et al*., 2003). Ochreous sludge has been shown to be a good adsorbent for P able to achieve removals >98% within 5 minutes of contact time (Heal *et al*., 2003) and could be a candidate for pesticide adsorption (Schwandt *et al*., 1992; Dudeney *et al*., 2004). However, it is unlikely to out-perform organic matter unless under acidic (below pH 5.5) conditions because the main mechanism for adsorption is cation bridging. This was not very effective for removal of the herbicide quinmerac which was preferentially removed by hydrophobic interactions which occur at pHs >5.5 (Schwandt *et al*., 1992). Research has also been undertaken investigating alum sludge as an adsorbent. Alum sludge is a by-product of water treatment. During treatment, aluminium sulphate is used as a coagulant and waste alum sludge is produced. This sludge could be used as an adsorbent substrate in constructed wetlands (Babatunde and Zhao, 2007). Similar to ochreous sludge, alum has been shown to be a more effective adsorbent for P removal at lower pH (Yang *et al*., 2006; Zhao *et al*., 2009). Yang *et al*. (2006) found that organic matter competed for adsorption space with phosphate, so this could imply a reduced capacity of alum sludge for pesticide molecules in the presence of both P and background natural organic matter in the run-off.

The recycling of alum sludge is beneficial as it allows the reuse of a waste product. However Thuy *et al.*, (2008) found less than 50% removal of spiked pesticides (aldrin, dieldrin, atrazine and bentazon) even with high alum doses. Additionally, if aluminium sulphate and Fe coagulants are not able to remove pesticides at the water treatment stage then it is unlikely that the alum sludge will be an effective adsorbent for pesticide removal under field conditions. This may be of particular concern if the presence of potentially competing adsorbates, such as phosphorous, is considered.

By-products from steel manufacturing are another industrial by-product being considered in water treatment. Shilton *et al*. (2006) monitored a wastewater treatment plant for phosphorous removal over a 10 year period where steel slag was used as a medium in a filter column. It was found that the steel slag provided good P removal for the first 5 years removing 77% of the TP until the retention limit of 1.23 kg of TP per tonne of steel slag was reached. After reaching this limit, phosphorous removal was much reduced. Steel industry wastes have also been researched with regards to the adsorption of some pesticides. Gupta *et al*. (2006) looked at the removal of 2,4-D and carbofuran (properties shown in Figure 2.8) from aqueous solutions using steel industry by-products as adsorption medium. The best result was obtained using blast furnace slag. However, the pesticide removal was less than 10% of that achieved using standard AC. This suggests that steel industry wastes may not be an effective adsorbent for pesticides. In addition, at present these products are not readily available for implementation.

Each of the described media have advantages and disadvantages in terms of their potential to be used within an agricultural environment. The key features of each medium described has been summarised in Table 2.8. The table includes the particle size of each medium, the best means of its application within an agricultural landscape and the advantages and disadvantages that would be associated with its use. Practical applicability alongside the ability of each to adsorb the problematic pesticides described earlier in the review are important factors that must be taken in to account during media selection.

Table 2.8 – Summary of the characteristics of the described adsorption media.

Medium	**Size**	**How applied**	**Advantages**	**Disadvantages**	**Removal example**
GAC	1 mm	Constructed wetland	Large surface area, proven pesticide removal capabilities	Expensive compared to other media	13 mg g^{-1} metaldehyde removal (Busquets *et al*., 2014)
Biochar	~1 mm but depends on size of feedstock	Constructed wetland	Lower energy requirement and cost for production compared to GAC	Lower surface area compared to GAC	74 μg g removal of MCPA (Cederlund *et al*., 2017)
Phenolic resins	<45 - 250 μm	Constructed wetland	Very high surface areas	Due to polymer/resin nature, use in agricultural environment would need to be carefully controlled	76 mg g^{-1} metaldehyde removal (Busquets *et al*., 2014)

Organic matter	Dependant but generally <1 mm	Soil amendment	Low cost and low environmental impact	Reliant upon cation binding which has been seen to be less effective for some pesticides compared to hydrophobic interactions	35.8 µg g^{-1} atrazine removal (Silva *et al*., 2013)
Montmorrillionite clay	<1 mm	Soil amendment	Low environmental impact, reasonably high surface area	Dependent upon pH	Up to 0.52 mg g^{-1} DDT removal (Saha *et al*., 2013)
Leca	2-20 mm	Constructed wetland	Good porosity for higher flow rates	Low density so could be prone to movement out of application area	Up to 0.97 µg mL^{-1} removal of MCPA(Dordio and Carvalho, 2013)
Vermiculite	2-8 mm	Constructed wetland or soil amendment	High cation exchange capacity	Research so far has not shown good removal of pesticides	Up to 153 µg g^{-1} removal of phosdron (Sánchez-Camazano and Sánchez-Martín, 1987)
Osorb	180-500 µm	Soil amendment	Selective capacity for organic molecules	Little data available	0.1 mg g^{-1} metaldehyde removal (Jonsson *et al*., 2015)
pHlocrite	<5 mm	Constructed wetland	Positive surface charge under wide range of pH	Not previously tested for pesticide removal	n/a

Industrial by-products	10-20 mm (steel slag) <0.002-5 mm (Ochreous sludge) <0.063 mm (alum sludge)	Constructed wetland	Low cost due to use of recycled waste materials	Low removal of pesticides compared to AC	0.39 mg g^{-1} quinmerac removal (Schwandt et al., 1992)

2.9 Conclusions of review

In conclusion, compliance failures of pesticides in drinking water are dominated by herbicides and a single molluscicide, metaldehyde. The polar and mobile nature of these compounds is a major factor in contributing to their increased presence in run-off under storm conditions. A number of adsorption media that have the potential to be combined with constructed wetlands in order to reduce pesticide concentrations in run-off within the agricultural environment have been identified. However, there is no ‘universal’ medium identified in the literature which may be effective against all of the problematic pesticides identified in the review. One thing that does seem to link all the media is the presence of a high number of reactive –OH groups on their surfaces. It may be that a combination of different media may be needed in order to treat the different individual pesticides. Additionally the size of the media should be considered in order to ensure removal efficiency can be balanced with hydraulic conductivity to ensure the ongoing treatment of water and to prevent the system from being overrun through reducing retention times.

2.10 References

ABS Materials Inc. (2014) *Treating Atrazine*. Available at: http://www.absmaterials.com/stormwater/biomix-osorb/treating-atrazine (Accessed: 29 November 2014).

ADAS UK Ltd (2011) *Understanding the changes in pesticide usage to inform water company risk assessments*. Wolverhampton.

Advanced Chemistry Development Inc. (2015) *ChemSketch* (C10E41)[computer program]. ACD/Labs.

AHDB (2016) *Planting Survey History* AHDB-HGCA, Coventry

Anet, F.A.L. (1974) ‘Dynamics of Eight-Membered Rings in the Cyclooctane Class’, *Dynamic Chemistry*, 45, pp. 169–220.

Armaghan, M. and Amini, M.M. (2014) ‘Adsorption of diazinon and fenitrothion on nanocrystalline magnesium oxides’, *Arabian Journal of Chemistry*, 10(1), pp.91-99.

Assalin, M.R., de Moraes, S.G., Queiroz, S.C.N., Ferracini, V.L. and Duran, N. (2010) ‘Studies on degradation of glyphosate by several oxidative chemical processes: Ozonation, photolysis and heterogeneous photocatalysis’, *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, 45(1), pp. 89–94.

Avery, L.M. (2012) *Rural Sustainable Drainage Systems (RSuDS).*

Ayranci, E. and Hoda, N. (2004) ‘Studies on removal of metribuzin, bromacil, 2,4-D and atrazine from water by adsorption on high area carbon cloth’, *Journal of Hazardous Materials*, 112(1–2), pp. 163–168.

Babatunde, A.O. and Zhao, Y.Q. (2007) ‘A novel alum-sludge based Constructed Wetland system to reduce pollution effects of agricultural run-off: first results’, *International Journal of Water*, 3(3), pp. 207-213.

Bachand, P.A.M. (2003) *Literature Review Potential Application of Adsorptive Media to Enhance Phosphorus Uptake in Stormwater Basins and Wetlands at Lake Tahoe*. University of California.

BASF (2015) *Metazachlor stewardship*. Available at: http://www.agricentre.basf.co.uk/agroportal/uk/en/about_us_3/water_stewardship/metazachlor/metazachlor_faq.html (Accessed: 20 April 2015).

Baskaran, S., Bolan, N.S., Rahman, A. and Tillman, R.W. (1996) 'Pesticide sorption by allophanic and non-allophanic soils of New Zealand', *New Zealand Journal of Agricultural Research*, 39(2), pp. 297–310.

Beulke, S. and Malkomes, H.-P. (2001) 'Effects of the herbicides metazachlor and dinoterb on the soil microflora and the degradation and sorption of metazachlor under different environmental conditions', *Biology and Fertility of Soils*, 33(6), pp. 467–471.

Bingham, S. (2007) *Environmental facts and figures: Pesticides in rivers and groundwater.* Available at: http://webarchive.nationalarchives.gov.uk/20070114093545/http://www.environment-agency.gov.uk/yourenv/eff/1190084/business_industry/agri/pests/915588/?version=1&lang=_e (Accessed: 20 April 2018).

Blewett, T.C., Roberts, D.W. and Brinton, W.F. (2005) 'Phytotoxicity factors and herbicide contamination in relation to compost quality management practices', *Renewable Agriculture and Food Systems*, 20(02), pp. 67–72.

Blucher (2015) *Saratech: spherical high-performance adsorbants*. Available at: http://www.bluecher.com/en/brands/saratech/filtration-of-liquids/spherical-high-performance-adsorbents/ (Accessed: 6 May 2015).

Boudesocque, S., Guillon, E., Aplincourt, M., Martel, F. and Noël, S. (2008) 'Use of a Low-Cost Biosorbent to Remove Pesticides from Wastewater', *Journal of Environment Quality*, 37(2), pp. 631-638.

Bristol Water (2009) *Water : Achieving a Balance*. Bristol.

Brix, H., Arias, C.A. and Del Bubba, M. (2001) ‘Media selection for sustainable phosphorus removal in subsurface flow constructed wetlands’, *Water Science and Technology*, 44, pp. 47–54.

Burkett, C.M., Underwood, L.A., Volzer, R.S., Baughman, J.A. and Edmiston, P.L. (2008) ‘Organic-inorganic hybrid materials that rapidly swell in non-polar liquids: Nanoscale morphology and swelling mechanism’, *Chemistry of Materials*, 20(4), pp. 1312–1321.

Busquets, R., Kozynchenko, O.P., Whitby, R.L.D., Tennison, S.R. and Cundy, A.B. (2014) ‘Phenolic carbon tailored for the removal of polar organic contaminants from water: a solution to the metaldehyde problem?’, *Water Research*, 61(0), pp. 46–56.

Cabrera, A., Cox, L., Spokas, K., Hermosín, M.C., Cornejo, J. and Koskinen, W.C. (2014) ‘Influence of biochar amendments on the sorption-desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil’, *Science of the Total Environment*, 470–471, pp. 438–443.

Cantier, J.M., Bastide, J. and Coste, C. (1986) ‘Structure-degradability realationships for propyzamide analogues in soils’, *Pesticide Science*, 17(4), pp. 235–241.

Carr, S. (2012) *An Investigation into Phosphorus Removal by Iron Ochre for the Potential Treatment of Aquatic Phosphorus Pollution*. The University of Edinburgh.

Carvalho, F.P. (2006) ‘Agriculture, pesticides, food security and food safety’, *Environmental Science and Policy*, 9(7–8), pp. 685–692.

Castle, G.D., Mills, G.A., Gravell, A., Jones, L., Townsend, I., Cameron, D.G. and Fones, G.R. (2017) ‘Review of the molluscicide metaldehyde in the environment’, *Environmental Science: Water Research & Technology*, 3(3), pp. 415–428.

Cederlund, H., Börjesson, E. and Stenström, J. (2017) ‘Effects of a wood-based biochar on the leaching of pesticides chlorpyrifos, diuron, glyphosate and MCPA’, *Journal of Environmental Management*, 191, pp. 28–34.

Celis, R., Adelino, M.A., Hermosín, M.C. and Cornejo, J. (2012) ‘Montmorillonite-chitosan bionanocomposites as adsorbents of the herbicide clopyralid in aqueous solution and soil/water suspensions.’, *Journal of Hazardous Materials*, 209–210, pp. 67–76.

Chemicals Regulation Directorate (2012) *Data requirements handbook V2.2*. York.

Chen, W., Hertl, P., Chen, S. and Tierney, D. (2002) ‘A pesticide surface water mobility index and its relationship with concentrations in agricultural drainage watersheds.’, *Environmental Toxicology and Chemistry / SETAC*, 21(2), pp. 298–308.

Clarke, A. (2014) Campaign aims to save key oilseed rape herbicides, *Farmers Weekly*.

Clayden, J., Greeves, N., Warren, S. and Wothers, P. (2001) *Organic Chemistry*. Oxford: Oxford University Press.

Council of the European Union (1998) ‘Drinking Water Directive 98/83/EC’, *Official Journal of the European Communities.*

Crittenden, J.C., Rhodes Trussell, R., Hand, D.W., Howe, K.J. and Tchobanoglous, G. (2012) ‘Adsorption’, in *MWH’s water treatment: principles and design*. 3rd ed. John Wiley & Sons, Inc, pp. 1117–1262.

Dahal, G., Holcomb, J. and Socci, D. (2011) ‘Surfactant-Oxidation Co-Application for soil and groundwater Remediation’, *Remediation Journal*, 26(2), pp. 101–108.

Dechene, A., Rosendahl, I., Laabs, V. and Amelung, W. (2014) ‘Sorption of polar herbicides and herbicide metabolites by biochar-amended soil.’, *Chemosphere*, 109, pp. 180–186.

Deechauer, H. and Kogel-Knabner, I. (1990) ‘Sorption behaviour of a new acidic herbicide in soils’, *Chemosphere*, 21(12), pp. 1397–1410.

Defra (1996) *Evaluation on: Metaldehyde*. York.

Defra (1998) *Evaluation on Quinmerac*. York.

Despotović, V.N.V.N., Abramović, B.F.B.F., Šojić, D.V.D.V., Kler, S.J.S.J., Dalmacija, M.B.M.B., Bjelica, L.J.L.J. and Orčić, D.Z.D.Z. (2012) ‘Photocatalytic degradation of herbicide quinmerac in various types of natural water’, *Water, Air, and Soil Pollution*, 223(6), pp. 3009–3020.

Dordio, A. and Carvalho, A.J.P. (2013) ‘Constructed wetlands with light expanded clay aggregates for agricultural wastewater treatment.’, *The Science of the Total Environment*, 463–464, pp. 454–61.

Dordio, A. V, Teimão, J., Ramalho, I., Carvalho, A.J.P. and Candeias, A.J.E. (2007) ‘Selection of a support matrix for the removal of some phenoxyacetic compounds in constructed wetlands systems.’, *The Science of the Total Environment*, 380(1–3), pp. 237–246.

Drinking Water Inspectorate (2016) *Annual Report., DWI Annual Report* Available at: http://www.dwi.gov.uk/about/annual-report/index.htm (Accessed: 13 June 2016).

Drori, Y., Aizenshtat, Z. and Chefetz, B. (2008) ‘Sorption of organic compounds to humin from soils irrigated with reclaimed wastewater’, *Geoderma*, 145(1–2), pp. 98–106.

Dudeney, A.W.L., Neville, K.J., Tarasova, I., Heath, A.O.D. and Smith, S.R. (2004) ‘Utilisation of Ochreous Sludge as a Soil Amendment’,*International Mine Water Association Symposium* Newcastle: University of Newcastle, pp. 31–39.

Edmiston, P.L. (2010) *Pilot Scale Testing of Swellable Organo- Silica-Nanoparticle Composite Materials for the in-situ and ex-situ remediation of groundwater contaminated with chlorinated organics*. Wooster.

Edmiston, P.L. and Underwood, L.A. (2009) ‘Absorption of dissolved organic species from water using organically modified silica that swells’, *Separation and Purification Technology*, 66(3), pp. 532–540.

EFSA (2008) *Conclusion regarding the peer review of the pesticide risk assessment of the active substance metazachlor*. United Kingdom.

EFSA (2006a) *Draft Assessment Report (DAR) Asulam*. United Kingdom.

EFSA (2009a) *Draft Re-Assessment Report Carbendazim*. Germany.

EFSA (2006b) *Draft Assessment Report (DAR) Carbetamide*. France.

EFSA (2007a) *Draft Assessment Report (DAR) Dicamba*. Denmark.

EFSA (2009b) *Assessment report Fluroxypyr*. Ireland.

EFSA (2014) *Renewal Assessment Report: Isoproturon*. Germany.

EFSA (1997) *Initial risk assessment provided by the rapporteur Member State Finland for the existing active substance Clopyralid*. Finland.

EFSA (2005a) *Initial risk assessment provided by the rapporteur Member State Finland for the existing active substance Clopyralid*. Helsinki.

EFSA (2009c) *Metaldehyde*. Vienna.

EFSA (2005b) *Metazachlor - Environmental Fate and Behaviour*. United Kingdom.

EFSA (2007b) *Initial risk assessment provided by the rapporteur Member State United Kingdom for the existing active substance Quinmerac*. United Kingdom.

Ellis, B. and Foth, H. (1997) *Soil fertility*. 2nd ed. Florida: CRC Press LLC.

Environment Protection Agency (2000) Adsorption - Desorption Using a Batch Equilibrium Method.

Environmental Protection Agency (1996) *Product properties test guidelines: OPPTS 830.7370 Dissociation constants in water*. Washington D.C.

European Chemicals Agency (2011) *Annex 1 Background Document to RAC opinion on metazachlor*. United Kingdom.

European Commission (2003) *Review report for the active substance propyzamide*. Sweden

Evans, H., Bauer, M., Luckman, I. and Page, M. (2003) 'An Assessment of the Benefits Afforded by the Continuous Versus Intermittent Operation of Ozone for Drinking Water Treatment', *Ozone: Science and Engineering*, 25(5), pp. 417–430.

Farooq, M. and Ramli, A. (2011) 'The determination of point zero charge (PZC) of Al2O-MgO mixed oxides', *2011 National Postgraduate Conference*, pp. 1–5.

Faust, S.D. and Aly, O.M. (1998) *Chemistry of Water Treatment*. 2nd ed. Florida: CRC Press LLC.

Fenoll, J., Ruiz, E., Flores, P., Vela, N., Hellín, P. and Navarro, S. (2011) 'Use of farming and agro-industrial wastes as versatile barriers in reducing pesticide leaching through soil columns.', *Journal of Hazardous Materials*, 187(1–3), pp. 206–212.

FERA (2018) Pesticide usage statistics.

Finch, S., Samuel, A. and Lane, G. P. (eds.) (2014) *Lockhart & Wiseman's Crop Husbandry Including Grassland.* 9th ed. Cambridge: Elsevier Ltd.

Finizio, A., Vighi, M. and Sandroni, D. (1997) 'Determination of n-octanol/water partition coefficient (K_{ow}) of pesticide critical review and comparison of methods', *Chemosphere*, 34(1), pp. 131–161.

Gevao, B., Semple, K. and Jones, K. (2000) 'Bound pesticide residues in soils: a review', *Environmental Pollution*, 108, pp. 3–14.

Ghafoor, A., Jarvis, N.J. and Stenström, J. (2013) 'Modelling pesticide sorption in the surface and subsurface soils of an agricultural catchment.', *Pest Management Science,* 69(8), pp. 919–29.

Gibert, O., Lefèvre, B., Fernández, M., Bernat, X., Paraira, M. and Pons, M. (2013) ‘Fractionation and removal of dissolved organic carbon in a full-scale granular activated carbon filter used for drinking water production’, *Water Research*, 47(8), pp. 2821–2829.

Giribaldi, C. (2013) *Adsorption of metaldehyde in water using resins*. MSc, Cranfield University.

Gregoire, C., Elsaesser, D., Huguenot, D., Lange, J., Lebeau, T., Merli, A., Mose, R., Passeport, E., Payraudeau, S., Schütz, T., Schulz, R., Tapia-Padilla, G., Tournebize, J., Trevisan, M. and Wanko, A. (2008) ‘Mitigation of agricultural nonpoint-source pesticide pollution in artificial wetland ecosystems’, *Environmental Chemistry Letters*, 7(3), pp. 205–231.

Gu, B., Meldrum, B., McCabe, T. and Phillips, S. (2011) ‘Enhancing concentration and mass sensitivities for liquid chromatography trace analysis of clopyralid in drinking water.’, *Journal of Separation Science*, 35(2), pp. 185–192.

Guertin, J., Herron, C. and Jacobs, J.A. (eds.) (2001) *Mtbe: Effects on Soil and Groundwater Resources*. Florida: CRC Press LLC.

Gupta, V.K., Ali, I., Suhas and Saini, V.K. (2006) ‘Adsorption of 2,4-D and carbofuran pesticides using fertilizer and steel industry wastes’, *Journal of Colloid and Interface Science*, 299(2), pp. 556–563.

Harrison, R.M. (ed.) (2007) *Principles of Environmental Chemistry*. Cambridge: The Royal Society of Chemistry.

Heal, K., Younger, P.L., Smith, K., Glendinning, S., Quinn, P. and Dobbie, K. (2003) ‘Novel use of ochre from mine water treatment plants to reduce point and diffuse phosphorus pollution’, *Land Contamination & Reclamation*, 11(2), pp. 145–152.

Helmy, A.K., Ferreiro, E.A. and De Bussetti, S.G. (1999) ‘Surface area evaluation of montmorillonite’, *Journal of Colloid and Interface Science*, 210(1), pp. 167–171.

Hemond, H.F. and Fechner, E.J. (2015) *Chemical Fate and Transport in the Environment.* 3rd ed. San Diego: Elsevier.

HGCA (2009) *Oilseed rape herbicides and water protection* HGCA, Warwickshire

Hiller, E., Bartaľ, M., Milička, J. and Čerňanský, S. (2008) 'Environmental Fate of the Herbicide MCPA in Two Soils as Affected by the Presence of Wheat Ash', *Water, Air, and Soil Pollution*, 197(1–4), pp. 395–402.

Howard, P.H. (1993) *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*. 4th ed. Michigan: Lewis Publishers.

Inyang, M. and Dickenson, E. (2015) 'The potential role of biochar in the removal of organic and microbial contaminants from potable and reuse water: A review', *Chemosphere*, 134, pp. 232–240.

Jönsson, J., Clementson, A. and O'Donoghue, N. (2015) *Evaluation of emergent adsorbent based processes for removal of metaldehyde and other problem organic micropollutants [Draft].*Swindon.

Jusoh, A., Hartini, W.J.H., Ali, N. and Endut, A. (2011) 'Study on the removal of pesticide in agricultural run off by granular activated carbon', *Bioresource Technology*, 102(9), pp. 5312–5318.

Jusoh, A., Lam, S.S., Hartini, W.J.H. and Ali, N. (2013) 'Removal of pesticide in agricultural runoff using granular-activated carbon: a simulation study using a fixed-bed column approach', *Desalination and Water Treatment*, 52(4–6), pp. 861–866.

Kadlec, R.H., Knight, R.L., Vymazal, J., Brix, H., Cooper, P. and Haberl, R. (2006) *Constructed Wetlands for Pollution Control: processes, performance, design and operation*. London: IWA Publishing.

Kay, P. and Grayson, R. (2014) 'Using water industry data to assess the metaldehyde pollution problem', *Water and Environment Journal*, 28, pp. 410–417.

Kegley, S.E., Hill, B.R., Orme, S. and Choi, A.H. (2016) *PAN Pesticide Database., Pesticide Action Network* Available at: http://www.pesticideinfo.org (Accessed: 20 February 2017).

Khan, M.A. and Brown, C.D. (2017) ‘Influence of commercial formulation on the sorption and leaching behaviour of propyzamide in soil’, *Science of the Total Environment*, 578, pp. 158–166.

Koper, O.B., Lagadic, I., Volodin, A. and Klabunde, K.J. (1997) ‘Alkaline-Earth Oxide Nanoparticles Obtained by Aerogel Methods. Characterization and Rational for Unexpectedly High Surface Chemical Reactivities’, *Chemistry of Materials*, 9(11), pp. 2468–2480.

Kuo, W.S. and Regan, R.W. (1999) ‘Removal of pesticides from rinsate by adsorption using agricultural residuals as medium’, *Journal of Environmental Science and Health, Part B*, 34(3), pp. 431–447.

Laabs, V. and Amelung, W. (2002) ‘Pesticides in surface water, sediment, and rainfall of the northeastern Pantanal basin, Brazil’, *Journal of Environmental Quality*, 31(5), pp. 1636–1648.

Leca UK (2014) *Leca., Lightening the load for civil engineering and geotechnical applications.* Chester.

Lemke, S.L., Grant, P.G. and Phillips, T.D. (1998) ‘Adsorption of Zearalenone by Organophilic Montmorillonite Clay’, *Journal of Agricultural and Food Chemistry*, 46(9), pp. 3789–3796.

Lewis, R. and Evans, W. (2006) *Chemistry*. 3rd ed. Hampshire: Macmillan Publishers Limited.

Linde, C.D. (1994) *Physico-Chemical Properties and Environmental Fate of Pesticides*. Sacramento.

Lu, Q., Whitehead, P.G., Bussi, G., Futter, M.N. and Nizzetto, L. (2017), 'Modelling metaldehyde in catchments: a River Thames case-study', *Environmental Science Processes & Impacts,* 19, pp. 586–595.

Lymer, J. and Jones, K. (2014) *Organic chemistry and toxicology of contaminants in the ground*. London.

Maillard, E., Payraudeau, S., Faivre, E., Grégoire, C., Gangloff, S. and Imfeld, G. (2011) ‘Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment.’, *The Science of the Total Environment*, 409(11), pp. 2317–24.

Malone, R.W., Shipitalo, M.J., Wauchope, R.D. and Sumner, H. (2004) ‘Residual and contact herbicide transport through field lysimeters via preferential flow.’, *Journal of Environmental Quality*, 33(6), pp. 2141–2148.

Margoum, C., Malessard, C. and Gouy, V. (2006) ‘Investigation of various physicochemical and environmental parameter influence on pesticide sorption to ditch bed substratum by means of experimental design’, *Chemosphere*, 63(11), pp. 1835–1841.

Marin Municipal Water District (2010) *Marin Municipal Water District Vegetation Management Plan Herbicide Risk Assessment: Chapter 5 – Clopyralid* Marin Municipal Water District, California

Marshall, J. (2013) *Briefing paper on metaldehyde*. United Kingdom

Mcelroy, J.A. (2005) *Adsorption of substituted aromatic compounds by activated carbon : a mechanistic approach to quantitative structure*. University of Florida.

Mersie, W. and State, V. (1995) ‘Absorption, translocation, and fate of propyzamide in witloof chicory (Cichorium intybus L .) and common amaranth (Amaranthus retroflexus L .)’, *Weed Research*, 35(192), pp. 15–19.

Met Office (2011) *Climate observations and projections*. Exeter

Met Office (2015) *UK and regional series.* Available at: http://www.metoffice.gov.uk/climate/uk/summaries/datasets (Accessed 3 June 2016)

Metaldehyde Stewardship Group (2015) *Get Pelletwise*. Available at: http://www.getpelletwise.co.uk/ (Accessed: 16 April 2015).

Mohanty, S.K., Valenca, R., Berger, A.W., Yu, I.K.M., Xiong, X., Saunders, T.M. and Tsang, D.C.W. (2018) ‘Plenty of room for carbon on the ground: Potential applications of biochar for stormwater treatment’, *Science of the Total Environment,* 625, pp. 1644–1658.

Mohr, S., Berghahn, R., Feibicke, M., Meinecke, S., Ottenströer, T., Schmiedling, I., Schmiediche, R. and Schmidt, R. (2007) ‘Effects of the herbicide metazachlor on macrophytes and ecosystem function in freshwater pond and stream mesocosms.’, *Aquatic Toxicology*, 82(2), pp. 73–84.

Molyneux, P. (2014) ‘Octanol/water partition coefficients K_{ow}: A critical examination of the value of the methylene group contribution to log K_{ow} for homologous series of organic compounds’, *Fluid Phase Equilibria*, 368, pp. 120–141.

Momcilovic, M., Randjelovic, M., Onjia, A., Zarubica, A., Babic, B. and Matovic, B. (2014) ‘Study on efficient removal of clopyralid from water using resorcinol-formaldehyde carbon cryogel’, *Journal of the Serbian Chemical Society*, 79(4), pp. 481–494.

Montgomery, J.H. (2007) *Groundwater Chemicals Desk Reference*. 4th ed. Florida: CRC Press LLC.

Müller, K., Magesan, G.N. and Bolan, N.S. (2007) ‘A critical review of the influence of effluent irrigation on the fate of pesticides in soil’, *Agriculture, Ecosystems & Environment*, 120(2–4), pp. 93–116.

NFU (2016) *Farming in East Anglia.* Available at: https://www.nfuonline.com/about-us/our-offices/east-anglia/east-anglia-key-content/farming-in-east-anglia/ (Accessed 18 March 2016)

OECD (1995) ‘Test N° 105: Water Solubility’, *OECD Guideline for the Testing of Chemicals*, (July), pp. 1–7.

Orrick, G. (2007) *Propyzamide new uses*. Washington D.C.

Pant, H.K., Reddy, K.R. and Lemon, E. (2001) ‘Phosphorus retention capacity of root bed media of sub-surface flow constructed wetlands’, *Ecological Engineering*, 17(4), pp. 345–355.

Papadopoulos, A.P., Bar-Tal, A., Silber, A., Saha, U.K. and Raviv, M. (2008) ‘Inorganic and synthetic organic components of soilless culture and potting mixes’, *Soilless Culture*, pp. 505–543.

Parsons, S.A. and Jefferson, B. (2006) *Potable water treatment processes*. Oxford: Blackwell Publishing Ltd.

Paszko, T. (2014) ‘Adsorption, degradation and mobility of carbendazim in profiles of Polish mineral soils’, *Geoderma*, 226–227, pp. 160–169.

Pendergrast, D. (2014) *Update on pesticides of concern in water NFU Briefing* National Farmers Union, United Kingdom.

Pérez, D.J., Okada, E., De Gerónimo, E., Menone, M.L., Aparicio, V.C. and Costa, J.L. (2017) ‘Spatial and temporal trends and flow dynamics of glyphosate and other pesticides within an agricultural watershed in Argentina’, *Environmental Toxicology and Chemistry*, 36(12), pp. 3206–3216.

Pham, T.T., Nguyen, V.A. and Bruggen, B. Van Der (2013) ‘Pilot-Scale Evaluation of GAC Adsorption Using Low-Cost , High-Performance Materials for Removal of Pesticides and Organic Matter in Drinking Water Production’, *Journal of Environmental Engineering*, 139(7), pp. 958–965.

Phlocrite (2015) *pHlocrite - synthetic semi-calcined dolomitic limestone*. Available at: http://www.phlocrite.co.uk/ (Accessed: 17 March 2015).

Pillai, C.K.S., Paul, W. and Sharma, C.P. (2009) ‘Chitin and chitosan polymers: Chemistry, solubility and fiber formation’, *Progress in Polymer Science*, 34(7), pp. 641–678.

Polati, S., Angioi, S., Gianotti, V., Gosetti, F. and Gennaro, M.C. (2006) ‘Sorption of pesticides on kaolinite and montmorillonite as a function of hydrophilicity.', *Journal of Environmental Science and Health. Part. B, Pesticides, Food Contaminants, and Agricultural Wastes*, 41(4), pp. 333–44.

PPDB (2014) *University of Hertfordshire Pesticide Properties Database*. Available at: http://sitem.herts.ac.uk/aeru/ppdb/en/ (Accessed: 17 November 2014).

Prochaska, C.A. and Zouboulis, A.I. (2006) 'Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate', *Ecological Engineering*, 26(3), pp. 293–303.

Rakness, K.L. (2005) *Ozone in drinking water treatment: Process design, operation and optimization*. Denver: American Water Works Association.

Rowell, D. (1994) *Soil Science: Methods and Applications*. Essex: Routledge.

Saha, A., Shabeer, A.T.P., Gajbhiye, V.T., Gupta, S. and Kumar, R. (2013) 'Removal of mixed pesticides from aqueous solutions using organoclays: evaluation of equilibrium and kinetic model.', *Bulletin of Environmental Contamination and Toxicology*, 91(1), pp. 111–6.

Sánchez-Camazano, M. and Sánchez-Martín, M.J. (1987) 'Interaction of some organophosphorus pesticides with vermiculite', *Applied Clay Science*, 2(2), pp. 155–165.

Schumacher, B.A. (2002) *Methods for the Determination of Total Organic Carbon in Soils and Sediments*. Las Vegas.

Schütz, S., Vedder, H., Düring, R.A., Weissbecker, B. and Hummel, H.E. (1996) 'Analysis of the herbicide clopyralid in cultivated soils', *Journal of Chromatography A*, 754(1–2), pp. 265–271.

Schwandt, H., Ksgel-knabner, I., Stanjek, H. and Totsche, K. (1992) 'Sorption of an acidic herbicide on synthetic iron oxides and soils: sorption isotherms', *The Science of the Total Environment*, 124(1), pp. 121–131.

Severn Trent Water (2014) *Final Water Resources Management Plan 2014*. Coventry.

Shilton, A.N., Elmetri, I., Drizo, A., Pratt, S., Haverkamp, R.G. and Bilby, S.C. (2006) ‘Phosphorus removal by an “active” slag filter-a decade of full scale experience’, *Water Research*, 40(1), pp. 113–118.

Shipitalo, M.J., Malone, R.W. and Owens, L.B. (2008) ‘Impact of Glyphosate-Tolerant Soybean and Glufosinate-Tolerant Corn Production on Herbicide Losses in Surface Runoff’, *Journal of Environment Quality*, 37(2), pp. 401–-408.

Shou, J., Dong, H., Li, J., Zhong, J., Li, S., LÃ J. and Li, Y. (2016) ‘Influence of Al-oxide on pesticide sorption to woody biochars with different surface areas’, Environmental Science and Pollution Research, 23(19) *Environmental Science and Pollution Research*, pp. 19156–19163.

Silva, C.R., Gomes, T.F., Andrade, G.C.R.M., Monteiro, S.H., Dias, A.C.R., Zagatto, E.A.G. and Tornisielo, V.L. (2013) ‘Banana peel as an adsorbent for removing atrazine and ametryne from waters.’, *Journal of Agricultural and Food Chemistry*, 61(10), pp. 2358–63.

De Smedt, C., Spanoghe, P., Biswas, S., Leus, K. and Van Der Voort, P. (2015) ‘Comparison of different solid adsorbents for the removal of mobile pesticides from aqueous solutions’, *Adsorption*, 21(3), pp. 243–254.

Snyder, S.A., Adham, S., Redding, A.M., Cannon, F.S., DeCarolis, J., Oppenheimer, J., Wert, E.C. and Yoon, Y. (2007) ‘Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals’, *Desalination*, 202(1–3), pp. 156–181.

Šojić, D.V., Anderluh, V.B., Orčić, D.Z. and Abramović, B.F. (2009) ‘Photodegradation of clopyralid in TiO2 suspensions: Identification of intermediates and reaction pathways’, *Journal of Hazardous Materials*, 168, pp. 94–101.

Sophia, C.A. and Lima, E.C. (2018) ‘Removal of emerging contaminants from the environment by adsorption’, *Ecotoxicology and Environmental Safety*, 150, pp. 1–17.

Spalding, R.F. and Snow, D.D. (1989) ‘Stream levels of agrichemicals during a spring discharge event’, Chemosphere, 19(8–9), pp. 1129–1140.

Strawn, D.G., Bohn, H.L. and O’Connor, G.A. (2015) *Soil Chemistry*. Chichester: John Wiley & Sons, Ltd.

Stuart, M. and Lapworth, D. (2011) *Emerging contaminants in groundwater: occurrence and risk assessment* NERC, Swindon

Stuart, M.E., Manamsa, K., Talbot, J.C. and Crane, E.J. (2011) *Emerging contaminants in groundwater*. Nottingham.

Tan, K.H. (2011) *Principles of soil chemistry*. 4th ed. Florida: CRC Press LLC.

Tao, B. and Fletcher, A.A.J. (2013) ‘Metaldehyde removal from aqueous solution by adsorption and ion exchange mechanisms onto activated carbon and polymeric sorbents’, *Journal of Hazardous Materials*, 244–5(1), pp. 240–250.

Tediosi, A., Whelan, M.J., Rushton, K.R., Thompson, T.R.E., Gandolfi, C. and Pullan, S.P. (2012) ‘Measurement and conceptual modelling of herbicide transport to field drains in a heavy clay soil with implications for catchment-scale water quality management.’, *The Science of the Total Environment*, 438, pp. 103–12.

The Vermiculite Association (2015) *What is vermiculite?*. Available at: http://www.vermiculite.org/resources/vermiculite (Accessed: 12 May 2015).

Schumacher, B.A. (2002) *Methods for the Determination of Total Organic Carbon in Soils and Sediments*. Las Vegas.

Thrasher, J., Morgan, P. and Buss, S.R. (2004) *Attenuation of mecoprop in the subsurface*. Bristol.

Thuy, P.T., Moons, K., Van Dijk, J.C., Viet Anh, N. and Van Der Bruggen, B. (2008) ‘To what extent are pesticides removed from surface water during coagulation-flocculation?’, *Water and Environment Journal*, 22(3), pp. 217–223.

Tomlin, C.D.S. (2009) *The Pesticide Manual*. 15th ed. Hampshire: BCPC.

Tran, V.S., Hao, H., Guo, W., Zhang, J., Liang, S. and Ton-That, C. (2015) 'Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water', *Bioresource Technology*, 182, pp. 353–363.

Trautmann, N.M., Porter, K.S. and Wagenet, R.J. (2012) *Pesticides and Groundwater: A Guide for the Pesticide User*., Cornell University Available at: http://psep.cce.cornell.edu/facts-slides-self/facts/pest-gr-gud-grw89.aspx (Accessed: 17 January 2015).

Trenberth, K.E. (2011) 'Changes in precipitation with climate change', *Climate Research*, 47(1–2), pp. 123–138.

Twining, S., Clarke, J., Harris, D., Wynn, S. and Peers, D. (2009) *Future of UK winter oilseed rape production*. United Kingdom.

Ulrich, U., Dietrich, A. and Fohrer, N. (2013) 'Herbicide transport via surface runoff during intermittent artificial rainfall: A laboratory plot scale study', *Catena*, 101, pp. 38–49.

University of Texas (2009) *Surface Chemistry and Ion Exchange* University of Texas, Texas

Vallée, R., Dousset, S., Billet, D. and Benoit, M. (2014) 'Sorption of selected pesticides on soils, sediment and straw from a constructed agricultural drainage ditch or pond.', *Environmental Science and Pollution Research International*, 21(7), pp. 4895–905.

Velten, S., Knappe, D.R.U., Traber, J., Kaiser, H.-P., von Gunten, U., Boller, M. and Meylan, S. (2011) 'Characterization of natural organic matter adsorption in granular activated carbon adsorbers', *Water Research*, 45(13), pp. 3951–3959.

Walker, A. and Thompson, J.A. (1977) 'The degradation of simazine, linuron and propyzamide in different soils', *Weed Research*, 17(6), pp. 399–405.

Washington State Department of Ecology (2015) *Cleanup Levels and Risk Calculation (CLARC)*. Available at: https://fortress.wa.gov/# (Accessed: 27 June 2017).

White, R.E. (1997) *Principles and practice of soil science*. 3rd ed. Oxford: Blackwell Science Ltd.

Wilkinson, P.G. (2010) *Characterisation of the bacterial flora associated with the grey field slug Deroceras reticulatum and assessment of its suitability as a target for biological control*. University of Edinburgh.

William Sinclair Horticulture Ltd (2008) *Vermiculite material data safety sheet* Lincolnshire

Worch, E. (2012) *Adsorption Technology in Water Treatment*. Berlin: De Gruyter.

Xu, X., Schierz, A., Xu, N. and Cao, X. (2016) 'Comparison of the characteristics and mechanisms of Hg(II) sorption by biochars and activated carbon', *Journal of Colloid and Interface Science*, 463, pp. 55–60.

Yang, Y., Zhao, Y., Babatunde, A, Wang, L., Ren, Y. and Han, Y. (2006) 'Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge', *Separation and Purification Technology*, 51(2), pp. 193–200.

Zandvoort, R., Dord, D.C., Leistra, M. and Verlaat, J.G. (1979) 'The decline of propyzamide in soil under field conditions in the Netherlands', *Weed Research*, 19(3), pp. 157–164.

Zhang, H.-Y., Wang, C., Lu, H.-Z., Guan, W.-B. and Ma, Y.-Q. (2011) 'Residues and dissipation dynamics of molluscicide metaldehyde in cabbage and soil.', *Ecotoxicology and Environmental Safety*, 74(6), pp. 1653–1658.

Zhao, Y.Q., Babatunde, A.O., Zhao, X.H. and Li, W.C. (2009) 'Development of alum sludge-based constructed wetland: An innovative and cost effective system for wastewater treatment', *Journal of Environmental Science and Health, Part A*, 44(8), pp. 827–832.

From this point onwards, the research in the thesis concentrates on three pesticides of interest: propyzamide, metazachlor and metaldehyde. Only the parent compounds have been considered. The reasons for this include difficulties experienced in developing an analytical method for metabolites and the other pesticides described in chapter 2. Additionally, the field site described in chapter 3 only used the herbicides metazachlor and propyzamide during the monintoring period within the catchment studied.

3 Monitoring pesticides in field leachate using rain dependent sampling

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3.1 Abstract

Pesticides are widely used in agriculture. Some of these compounds, particularly those associated with the crop oilseed rape, can have a detrimental impact on water quality. Rainfall and storm events are known to be an important factor in causing run-off and leaching which moves pesticides away from their application area through the solublisation of the pesticides in to the water phase. This in turn causes contamination of water courses which can affect aquatic organisms and cause the pollution of potable water sources. Sampling run-off water is important for providing data which can be applied to models in order to be able to predict run-off risk. Most previous studies of pesticide run-off have used flow dependant or timed sampling. This research introduces a new novel method of sampling according to the relationship between rainfall and pesticide concentrations. The development of this new sampling method provides a lower cost but highly balanced sampling regime which considers sampling over a wide range of rainfall conditions. This enables the identification of the point at which pesticide concentrations increase in field run-off. This study found the highest risk of increased pesticide concentrations in run-off to occur

when rainfall was >10 mm within a 24 h time period, an intensity of approximately 0.4 mm h^{-1} .

3.2 Introduction

The use of pesticides in agriculture is a key element of modern intensive crop production. However, a balance needs to be struck between ensuring food security and preventing pollution of the environment and water bodies through the addition of chemicals. Over time, pests targeted by pesticides can develop resistance to these chemicals, an effect that has been exacerbated by the overuse of pesticides in the past (Carvalho, 2006; Pesticides Forum, 2014; Liang *et al*., 2016). Often, to counteract resistance, even higher doses of pesticide then need to be used (Bloomfield *et al*., 2006). Another way to treat pests that have developed resistance is to change the active ingredient used in the pesticide. For example isoproturon was withdrawn from the UK market in 2009 due to increasing blackgrass resistance in addition to concerns about its affect on aquatic organisms. Following this withdrawal, an increase in the use of alternative products such as chlorotoluron was seen. This pesticide has a slightly higher water solubility at 74 mg L^{-1} compared to 70.2 mg L^{-1} for isoproturon (ADAS UK Ltd, 2011; PPDB, 2014). The replacement of existing products with ones that have higher water solubility has been shown to result in higher pesticide concentrations being seen in run-off following storm events. This continuous change in the type, concentration and combination of pesticides used means that water quality is dynamically changing. This is a challenge, particularly where contaminated water bodies are used as sources for drinking water. The presence of pesticides in run-off has been shown to have negative impacts on some aquatic organisms for example crustaceans and insect larvae can be particularly sensitive to chlorpyriphos (Sherrard, 2004) and chloro-2-methylphenol (4-CMP), a degradation product of mecoprop is highly toxic to aquatic organisms (Thrasher *et al*., 2004). In addition to this, pesticides can have potentially negative effects on human health and financially impact water companies (Kreuger, 1998; Stuart *et al*., 2011; Destandau *et al*., 2013).

Pesticide contamination of water courses is often attributed to run-off that occurs during storm events whereby the soluble pesticides are diluted into the water phase and are mobilised in surface run-off and leached into wider water courses (Larson *et al*., 1997; Franco and Matamoros, 2016). The monitoring of pesticide run-off is important as contaminants can have detrimental effects on potable water sources in addition to the wider environment (Stuart *et al*., 2011). The sampling for pesticides in run-off is usually carried out using automatic samplers. The most common sampling regimes used are timed sampling, flow sampling, and grab sampling. Timed sampling is where samples are taken at set time intervals using automatic samplers, regardless of other environmental factors such as rain, temperature and flow rates (Kreuger, 1998; Shipitalo *et al*., 2008; Rabiet *et al.*, 2010). Typically these use automatic samplers on a timed programme. Flow dependent sampling is where samples are taken at increasing frequency as flow rates increase (Kjær *et al*., 2011; Passeport *et al*., 2013). Flow dependant sampling utilises automatic samplers coupled to a flow meter. Depending on the flow measuring device, and its intended location, it may also require the installation of a weir into the flow stream. Grab samples are those samples taken to substantiate samples gathered by other automatic means, and are carried out manually by the researcher as and when they are in the right place (Rabiet *et al*., 2010; Xu *et al*., 2015). This method of sampling requires someone to take the sample and a receptacle to hold it. Each of these methods have disadvantages with respect to measuring pesticides in run-off. If timed samples are taken too often, the sampling will not be efficient, leaving the researcher with excess samples that can be expensive to analyse and may add little to the overall result. Similarly, too few samples and events may be missed or the results may not be representative of the true concentrations experienced (Johnes, 2007; Rabiet *et al*., 2010). Flow dependant sampling is more representative of the dynamic conditions throughout a storm event and therefore will more accurately reflect the changing concentrations (Rabiet *et al*., 2010). However, if flow dependant sampling is carried out later in the year when flows are higher, this efficiency may decrease as run-off durations, and therefore sample triggering, increase. In addition, flow meters are expensive apparatus so if sampling is to be carried out at multiple locations then this will significantly increase the cost of a study. Manual or grab samples are the least efficient way of sampling and are highly dependent on chance, as they require a high labour input in terms of time and are dependent upon someone being in the right place at the right time. Although they are the least expensive option in terms of equipment, grab samples require a human resource to be at the sampling location for the duration of a storm in order to get samples representative of fluxes throughout the storm. As a result they are expensive with respect to human resources. Furthermore, sampling may not be feasible if, for example, a storm occurred in the middle of the night or the sampling location is in an isolated location. In addition there are also passive methods of sampling such as Chemcatcher and Polar Organic Chemical Integrative Sampler (POCIS) (Castle *et al*., 2017; Fauvelle *et al*., 2017). These passive sampling technologies work by sequestration of pesticides using membrane technology which is later analysed in the laboratory. The amount of pesticides captured is then calibrated to give a time averaged estimation of pesticide concentration dependent upon the timescale for which the passive sampler was deployed (Castle *et al*., 2017). As these methods use average estimations, and due to the fact that pesticide run-off is strongly linked to storm events, there is a high risk of underestimation of peak concentrations (Rabiet *et al*., 2010; Kay and Grayson, 2014; Castle *et al*., 2018a, 2018b). This underestimation may be particularly problematic when considering the issue of shock loads to water treatment facilities, as the peak concentrations and length of time for which elevated levels of pesticides are present are unknown.

In this work, a new method of sampling is proposed that is proportional to rainfall (mm) that occurs during storm events. This is important because climate change models predict the occurrence of increased rainfall intensity alongside longer event durations (Osborn and Hulme, 2002; Ekström *et al*., 2005; Trenberth, 2011). It is therefore expected that this will lead to an increase in run-off events and therefore increased frequency of the contamination of potable water sources. It would consequently be useful to be able to develop a link between rainfall duration and intensity and run-off risk. Detailed rainfall data is more readily accessible to the public and researchers through agencies such as the UK Meteorological Office compared to data available on water flow rates. This is particularly the case for small drainage ditches associated with field run-off and leaching, where pesticides will first enter into these water channels. With this localised information pertaining to rainfall characteristics and pesticide concentrations in drainage ditches, it should therefore be possible to develop a link between local rainfall conditions and pesticides in run-off to inform water companies when shock loads containing high pesticide concentrations will occur. Ultimately these data could be fed into models (e.g. Asfaw *et al*., 2016) which could incorporate factors such as the pesticides which have been used and the local topography of the landscape. Furthermore, increased knowledge of localised rainfall and run-off relationships would help to identify when a temporary application of adsorption media could be most effectively utilised. For example, a temporary application of in-field treatment at key times into drainage systems could help to trap and remove pesticides from the farm channels and prevent their further movement into wider water courses from which abstraction occurs. The main focus of this research was to look at the initial feasibility of gathering data on pesticide run-off by using rainfall data.

Rain dependent sampling uses rainfall detection as the primary indicator of storm run-off events, with flow rate being a secondary indicator thereby increasing sampling efficiency. The method also includes additional timed samples triggered by rainfall in order to give information on how pesticide concentrations change following a storm event. Additionally, this approach uses less expensive equipment as compared to flow dependant sampling therefore reducing sampling costs. The monitoring of pesticides according to rainfall has become increasingly relevant due to the predicted effects of global warming. The expectation is for rainfall events to increase in intensity with longer dry periods in between. These are the conditions when high amounts of run-off occur (Trenberth, 2011). To the authors knowledge there have been no studies that use rain dependent sampling to monitor pesticide run-off at the agricultural field scale.

The aim of this work was to determine whether rain dependent sampling could be an accurate and efficient way of monitoring pesticide run-off within agricultural catchments under storm conditions. The research developed a proof of concept system in order to determine if sampling by rainfall according to detection via a rain gauge could give data that could be used in conjunction with a catchment management approach. This would enable better control and monitoring of the pesticides in run-off by targeting sampling to periods of 'high risk' for contamination to potable water sources.

3.3 Materials & Methods

3.3.1 Field Site

Sampling was carried out on a conventional arable farm in Wolverhampton in the West Midlands region of England (Figure 3.1). The farm catchment studied was 110 ha in area and was comprised of nine fields ranging between 3.1 to 14.5 ha in area. Oilseed rape was grown in fields 4, 6, 7 and 8 during the study period, the remaining fields were cropped with winter wheat. The soil was comprised of slowly permeable fine to coarse loamy soil with some deep reddish fine loamy soils in fields 1-4 (Figure 3.2). The farm soils had a pH of 6±0.8 and a soil organic carbon content of 2.7±2.1% (National Soil

Resources Institute, 2019). Slowly permeable soils typically have permeability rates of 0.13-0.3 cm h^{-1} although average permeability rates for loamy soils is 1.3 cm h^{-1} which is classified as moderately slow (FAO, 2019). The average slope across the farm catchment was 1° (Figure 3.2). Field drains were approximately 1 m below the soil surface. Two pesticides of interest were being used on the farm during the eight month sampling period from September 2015 to May 2016: metazachlor and propyzamide. Metazachlor application occurred on the 26th September 2015 with pesticide application at 1.5 L ha^{-1} containing 50% metazachlor active ingredient. Application of propyzamide occurred on the 21st January 2016 with an application rate of 1.5 L ha^{-1} containing 50% propyzamide active ingredient. Both of these pesticides were used on the oilseed rape crop. Water samples were also tested for metaldehyde as it is the pesticide that causes the highest number of water quality issues in the UK (Drinking Water Inspectorate, 2016). Although in this case, metaldehyde was not used during the sampling period and had not been used in the study catchment for the previous two years.

Sampling equipment was set up at the inlet (PI) and outlet (PO) of a typical farm pond with an area of 255 m^2. The pond was ovoid shaped and located approximately two thirds of the way along the distance of the drainage ditch across the farm catchment. The distance between the inlet and outlet of the pond was 16.9 m and the pond had a maximum depth of 1 m. The pond for the most part was unvegetated but had some Sedge *Carex spp*. around the edges. The inlet to the pond contained water run-off from field drains and drainage ditches that ran through the farm. Additional sample points were located at the beginning and end of the main drainage route through the farm at the end of February 2016 referenced as the farm inlet (FI) and outlet (FO). This enabled pesticide inputs and outputs to be established across the entire farm catchment. The FI sample point was located at the top of the farm catchment next to a road across from which was further farmland. The purpose of the FI sample point was to verify whether any pesticide run-off entering the farm catchment was from adjacent farmland.

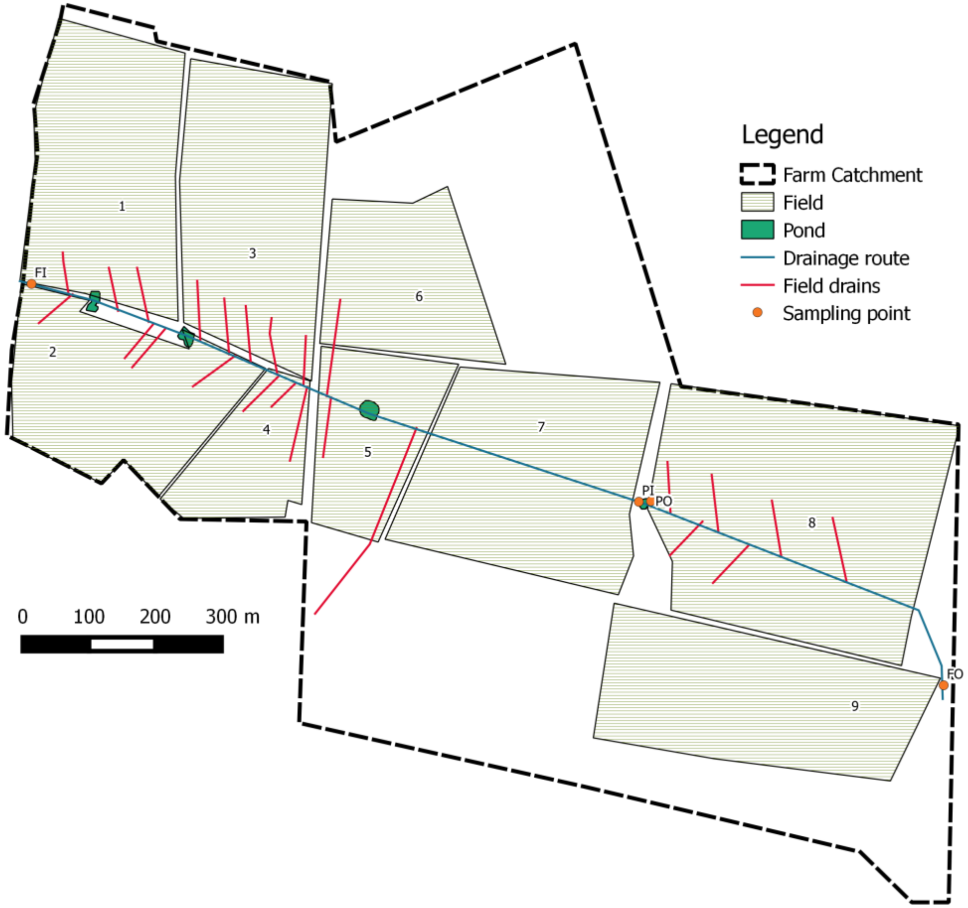

Figure 3.1– Plan of the farm catchment, the fields identified are those that drain into the main drainage ditch running through the identified catchment. Sampling points identified are FI: Farm inlet, PI: Pond inlet, PO: Pond outlet and FO: Farm outlet.

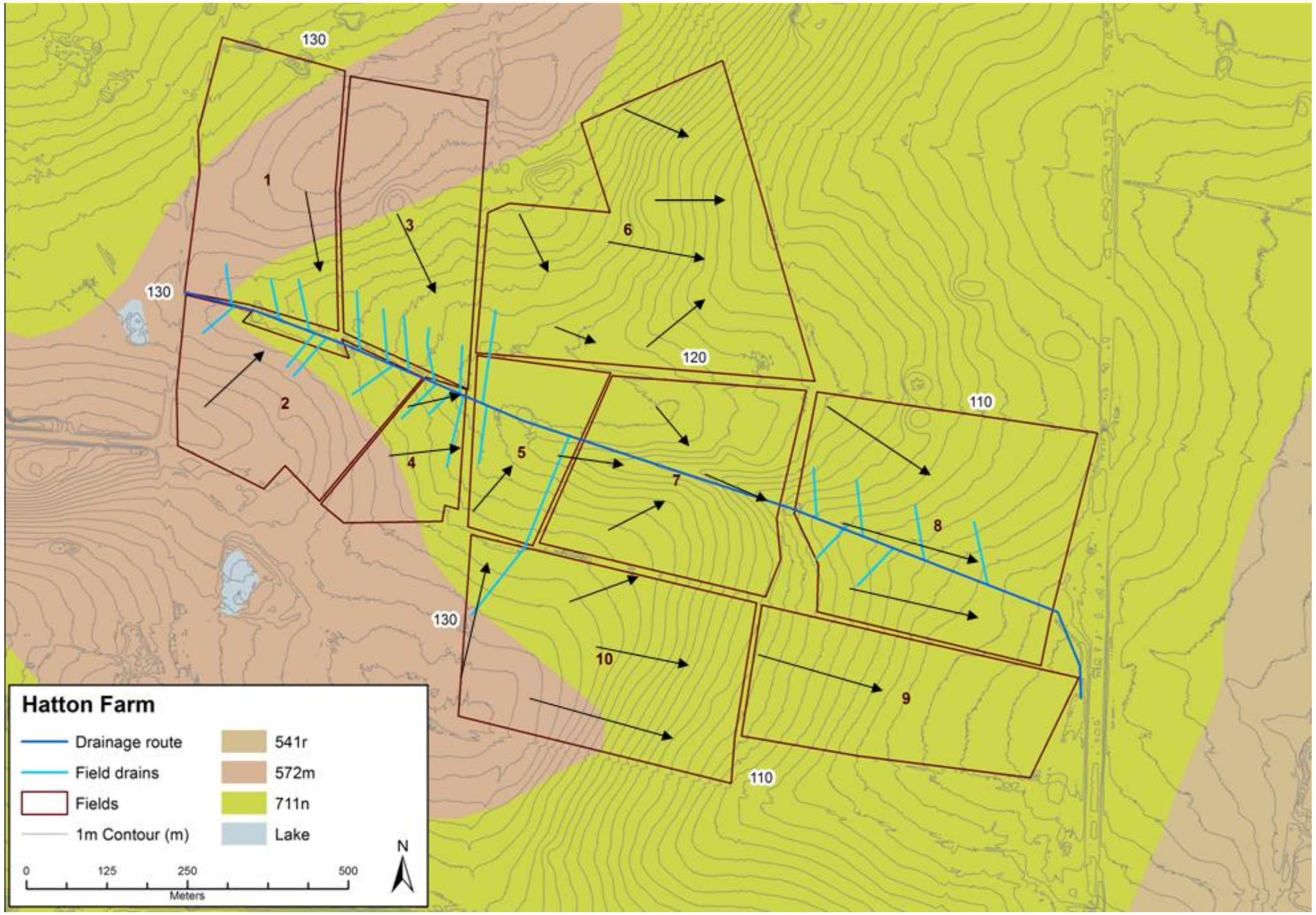

Figure 3.2 - Soil and contour map of farm. Black arrows show preferential flow paths according to slope. 541r = Wick 1 - 'Deep well drained coarse loamy and sandy soils locally over gravel'; 572m = Salwick - 'Deep reddish fine loamy soils with slowly permeable subsoils and slight seasonal waterlogging'; 711n = Clifton - 'Slowly permeable seasonally waterlogged reddish fine and coarse loamy soils and similar soils with slight seasonal waterlogging'.

3.3.2 Equipment and sampling methodology

Sampling equipment at each location comprised of a Young model tipping bucket rain gauge that had a catchment area of 200 cm^2 and tipped for every 0.1 mm of rainfall captured. Teledyne Isco bubbler flow meters (model 4230 and signature model) were set up at the inlet and outlet of the farm pond. These were used to gather additional data for flow rates ($L\ s^{-1}$), volumes (m^3) and water height (m) to help understand the flow conditions and volumes of water experienced during storm conditions for the pond studied and to be able to calculate the pesticide loads. As such, while they were used here to gather additional data in this study, they would not be necessary for rain dependent sampling as a means of identifying peak concentrations. The flow meters used inserts with a round orifice which were attached in the inlet and outlet pipes of the wetland pond to monitor the flow. Bubbler flow meters were calibrated prior to being installed in the field, where the calibration was rechecked as per equipment instructions. Isco 3700 autosamplers were used with glass bottles to ensure no pesticide adsorption occurred. The sample volume collected for each sample was 300 mL. Each piece of monitoring equipment was connected to an Intel® Edison board used as a small computer to collect data and control sampling (Figure 3.3). These retail in the UK for around £100 compared to the flow meters which cost >£2000 each. The computer logged rainfall data and collected data from the flow meter (flow rate ($L\ s^{-1}$), water level (m), volume of water passed (m^3)). Data was uploaded to cloud storage through an internet connection, where it could be accessed remotely. Originally, mobile devices with 3G network access were used to upload data and allow remote access to the computer. However these were later changed to 3G dongles to improve the strength and reliability of the data connection.

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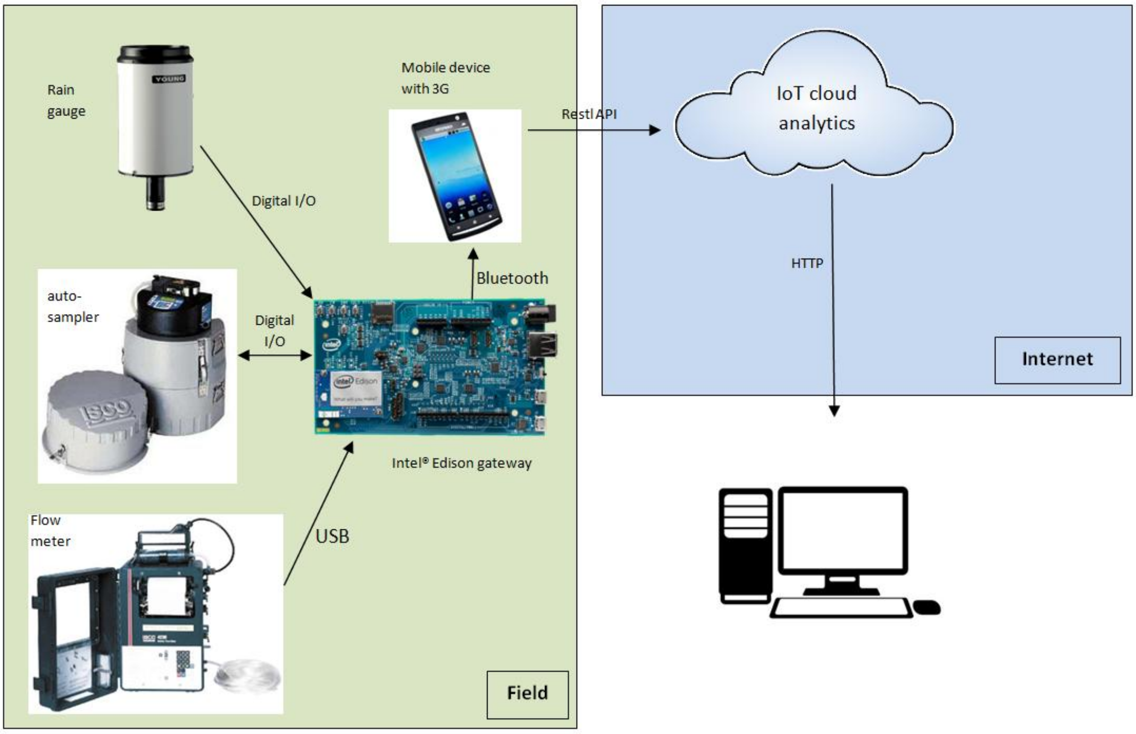

Figure 3.3 – Conceptual model of data transfer between components of rainfall dependent sampling solution

A sampling event was triggered based on rainfall. Data was recorded for each incremental increase of 0.1 mm of rainfall and every 15 minutes for the flow meter data. The computer also controlled the signal to the autosampler where it was originally programmed to take a water sample for every 2.5 mm of rainfall detected by the rain gauge. Increments of 2.5 mm of rainfall were chosen as this was the 75th percentile volume of rainfall for the area in which the sampling took place, this was calculated from data provided by the Met office (Ball, 2015). The 75th percentile was used as it was representative of a rainfall event where the volume of rain falling was within the top 25% for the local area, but still enabled a sample to be taken at relatively low rainfall rates. Rainfall of 2.5 mm was thought to be an efficient starting sampling unit with regards to local historical weather. This was in order to collect water samples at relatively low rainfall volumes and to get sampling reflective of rainfall conditions and pesticide concentrations throughout an event but not so low as to fill the auto-sampler before the end of an event or to require a high frequency of site visits to collect samples (>once a week). The local historical weather data was acquired from the Met office library and archive (Ball, 2015) using rainfall data gathered from rain gaugesas close to the farm's location as possible (approximately 20 miles away). However, after initial sampling it was felt that the data gathered using 2.5 mm units was too intermittent. Therefore sampling was decreased to 2 mm on 29th October 2015 in order to increase the number of data points gathered to provide better definition of pesticide concentrations throughout rainfall events. This allowed monitoring of concentration changes without producing excess samples and causing the samplers to fill up before the end of a rainfall event. The sampling was originally carried out by daily rainfall (i.e. the rainfall count would reset at midnight) in order to concentrate on storm events. A rainfall event was deemed to have ceased if no rainfall was detected within one hour of the last tip of the rain gauge. Sampling was changed to each 2 mm increase in cumulative rainfall to account for rainfall events that occurred over several days and to prevent missed samples when 2 mm would otherwise be reached past the midnight hour. Equipment installed at additional sampling points only included rain gauges and autosamplers, with the computer used to control when samples were taken (Figure 3.4). The timed part of the method occurred when 6 mm of rainfall was observed over a rolling 24 h period, this was considered as an indication of the start of increased pesticide concentrations being detected due to this pattern being seen during early events. This then triggered timed samples to be taken at 8 h intervals for the following 3 days in order to monitor how the concentration of the pesticides changed following the storm event regardless of the rainfall in that period. This was judged according to patterns detected during early events before the additional timed sampling was added. The timed sampling was added to the methodology on 4th March 2016. The timed sampling was introduced to act as a 'safety net' so that the decline in concentrations could continue to be monitored even if no rainfall was present. Sampling based on rainfall continued whilst timed samples were triggered.

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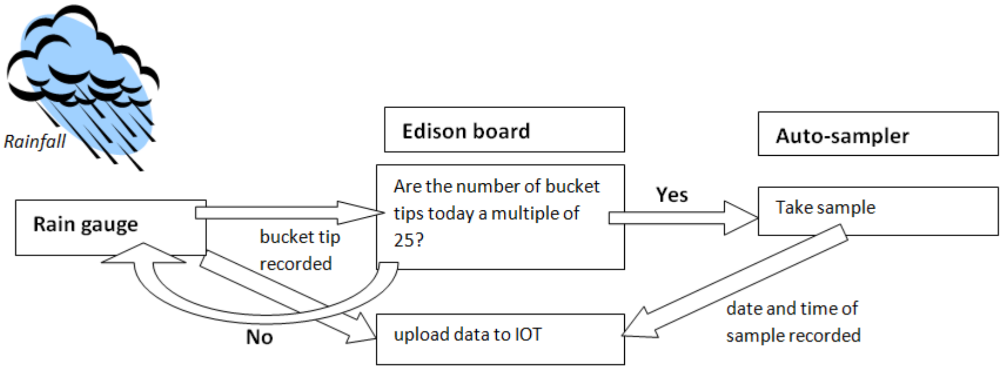

Figure 3.4 – Data communication between key components leading to sampling in the case of a rainfall event

Water quality samples were filtered using 0.2 µm filters and frozen prior to analysis. The analysis of the water samples was carried out using direct injection to a Waters Alliance 2695 liquid chromatography coupled to Quattro premier XE tandem quadrapole mass spectrometry (LCMS-MS/MS) using a method described previously (Ramos *et al*., 2017). Samples were analysed in duplicate. Pesticides used in the preparation of standards were acquired from QMX Laboratories. Prepared samples for calibration were: 0.1, 0.2, 0.5, 1, 2, 5, 8 and 10 µg L^{-1}.

3.4 Results and Discussion

Metazachlor and propyzamide were both detected at the PI and PO locations, with the highest concentrations occurring during rainfall events shortly after application of propyzamide (21st January 2016). Elevated pesticide concentrations were seen during particularly heavy rainfall events which exceeded 10 mm d^{-1} for both pesticides (Figure 3.4). The maximum concentration of propyzamide was 15.6 µg L^{-1} seen at the pond outlet shortly after application. This was higher than previous studies monitoring propyzamide run off in Southern Spain where the maximum concentration seen was 0.37 µg L^{-1} (Moreno-González *et al*., 2013). The maximum propyzamide concentration detected at the PI was 12.6 µg L^{-1} and occurred during the first heavy rainfall event following application.

The propyzamide concentrations found were much higher than those found for metazachlor, where the maximum concentration seen was 1.4 µg L^{-1} at the PI and 0.9 µg L^{-1} at the PO. The metazachlor spike detected at the PI occurred during a particularly heavy rainfall event that saw 15.2 mm of rain within 24 h. This was the second heaviest rainfall event observed during the sampling period, the heaviest rainfall event occurred on the 23rd March, where 18.2 mm of rainfall fell in a single day. The largest metazachlor spike at the PO was detected during the first rainfall event which exceeded 10 mm over 24 h that occurred following propyzamide application. This suggests that competition between pesticides for adsorption on the sediments in the pond has an impact on pesticide detection at the PO. Subsequent rainfall events following application saw gradually declining concentration spikes of propyzamide. Similar trends were seen for metazachlor although this pesticide was more affected by the amount and intensity of rain fallen (mm) and the subsequent application of propyzamide. However this may have been due to the missing of metazachlor peaks directly after the metazachlor had been applied. At the time the sampling methodology was still being developed during the early stages of sampling when metazachlor application occurred.

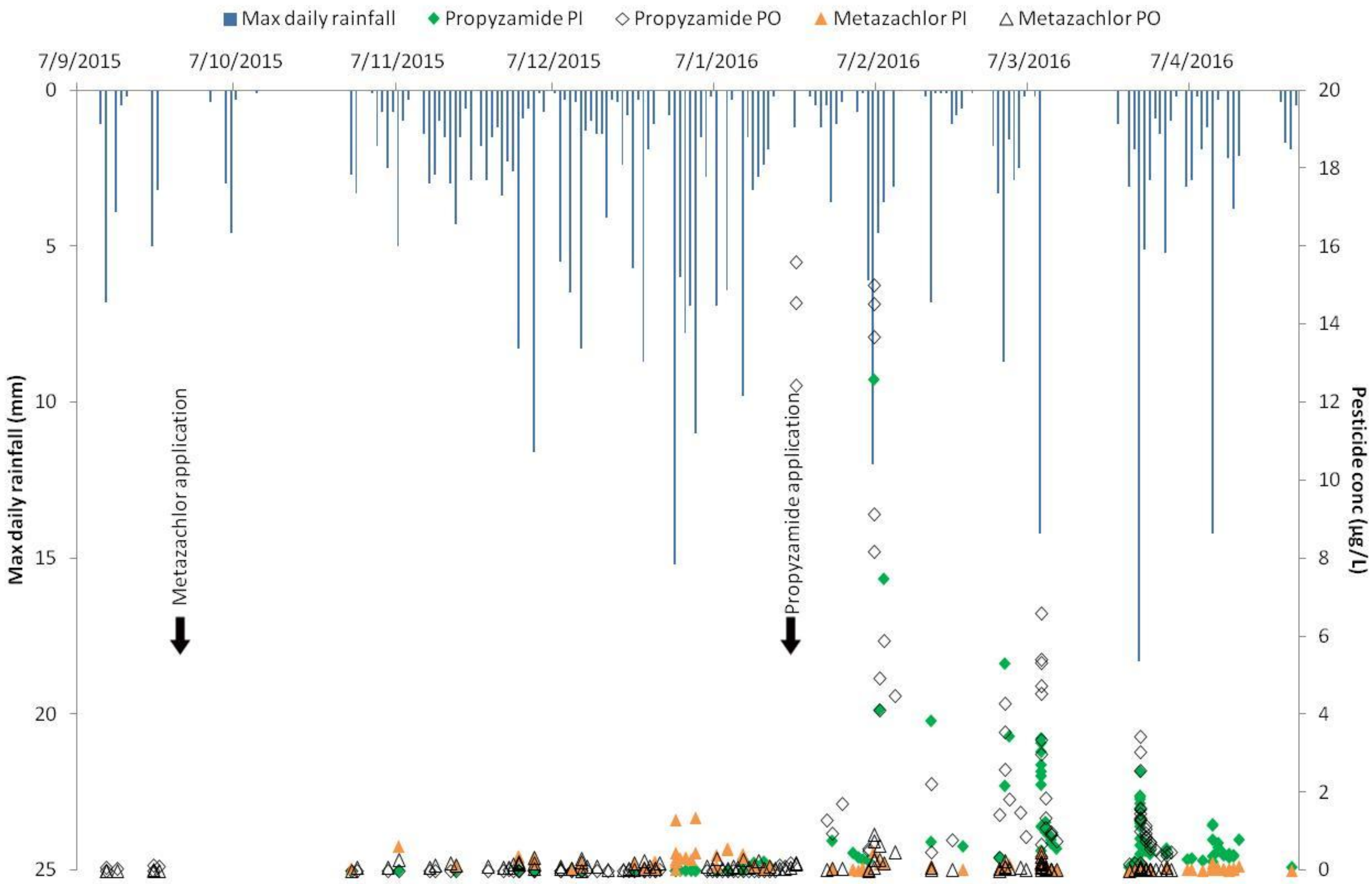

Figure 3.5 – Metazachlor and propyzamide applications and concentrations detected in the farm pond inlet and outlet locations against rainfall over the eight month sampling period. Samples were triggered for every 2 mm of rainfall from October onwards with occasional timed and manual samples.

The majority of samples were taken according to rainfall, however intermittently, alternative sampling methods needed to be used (Figure 3.6). Timed samples were used in early January due to damage to a data cable connecting the computer to the autosampler that could not be fixed in the field. Manual samples were then used to test the equipment was working correctly. This coincided with the day after propyzamide was applied. A representative reflection of changes in pesticide concentration was observed during rainfall events using the rain dependant sampling while the rainfall triggered timed samples proved useful in showing the concentration decline following a rainfall event. Increased concentrations of the pesticides metazachlor and propyzamide were found when there were high amounts of rainfall (>10 mm over a 24 h period). Rainfall <10 mm within a 24 h period did not result in significant concentrations of pesticides in leachate being detected. This is in agreement with other studies that have found rainfall intensity to be an important factor in the occurrence of run-off/leachate (Gouy *et al*., 1999; Zhao *et al*., 2014). This was due to the fact that low amounts of rainfall, even over an extended period, did not exceed the infiltration rate of the soil and so significant movement of pesticides out of the field was not seen (Macary *et al*., 2014). The infiltration rate is the rate at which the water from rainfall is able to penetrate through the soil. If the rate of rainfall exceeds the infiltration rate of the soil, then overland flow will occur (Malone *et al*., 2004).

Automatic timed samples were triggered three times at the pond location between March 2016 and April 2016 (Figure 3.6). Both the PI and PO locations were in agreement with one another as to the timing of the triggered samples.

Two additional timed samples were triggered at the FI and FO at the beginning of April and beginning of May 2016. This may have been due to the location of the rain gauges at these sampling points as they were susceptible to strong wind gusts from a westerly direction. Strong wind caused movement of the rain gauge resulting in subsequent tipping of the bucket mechanism and thus increased 'rainfall' detection. This issue was not seen at the pond location as trees on either side of the pond provided shelter from the wind but were not so overgrown as to affect the collection of rainfall. This issue could be overcome in future use by employing a wind guard around the lower part of the rain gauge. Other than the additional timed samples, good conformity was seen between the timing of the triggered samples. The timed samples helped to give improved insight in to the steady reduction in pesticide concentrations following a large storm event. This was particularly evident following the events that occurred on the 9th March and 11th April (Figure 3.6). A drawback of the rainfall dependent sampling method was that it did not account for the time period immediately after pesticide application unless rainfall was present. However the pesticide loads lost (g) from the catchment were much smaller as seen by comparison of the pesticide mass leaving the farm pond following application compared directly to that lost following the first rainfall event. The propyzamide load lost was calculated using Equation 3.1 for the immediate aftermath of propyzamide application (21 - 28 January 2016) against the propyzamide load lost during the first large rainfall event following application (5 - 17 February 2016). The propyzamide spike detected at the pond outlet immediately after application was calculated to contain 4.69 g of propyzamide whereas the load following the first major rainfall event consisted of 27.18 g of propyzamide (Table 3.1). This suggests that although high pesticide concentrations can be reached post application through drift or infiltration, pesticide losses through rainfall events are much more important for impacting on water quality.

Table 0.1- Calculated loads for each event of elevated pesticides according to Figure 3.9 at the inlet and outlet of the farm pond between 20th December 2015 and 14th April 2016. Pond outlet samples became contaminated during events 1 and 2 due to flooding and so could not be analysed.

Event no.	Load (g) Pond inlet			Load (g) Pond outlet			Load removal (g)		
	Metaldehyde	Metazachlor	Propyzamide	Metaldehyde	Metazachlor	Propyzamide	Metaldehyde	Metazachlor	Propyzamide
1	0.48	2.12	0.01	n/a	n/a	n/a	n/a	n/a	n/a
2	0.40	1.54	0.00	n/a	n/a	n/a	n/a	n/a	n/a
3	0.26	0.25	1.35	0.04	0.09	4.69	0.22	0.16	-3.34
4	0.13	1.60	49.79	0.28	1.45	27.18	-0.15	0.15	22.61
5	0.07	0.22	4.26	0.07	0.21	5.44	0.00	0.01	-1.18
6	0.04	0.53	6.67	0.02	0.49	10.12	0.02	0.04	-3.45
7	0.02	0.09	1.98	0.21	0.19	6.11	-0.19	-0.1	-4.13
8	0.05	0.11	1.40	0.02	0.11	1.52	0.03	0.00	-0.12

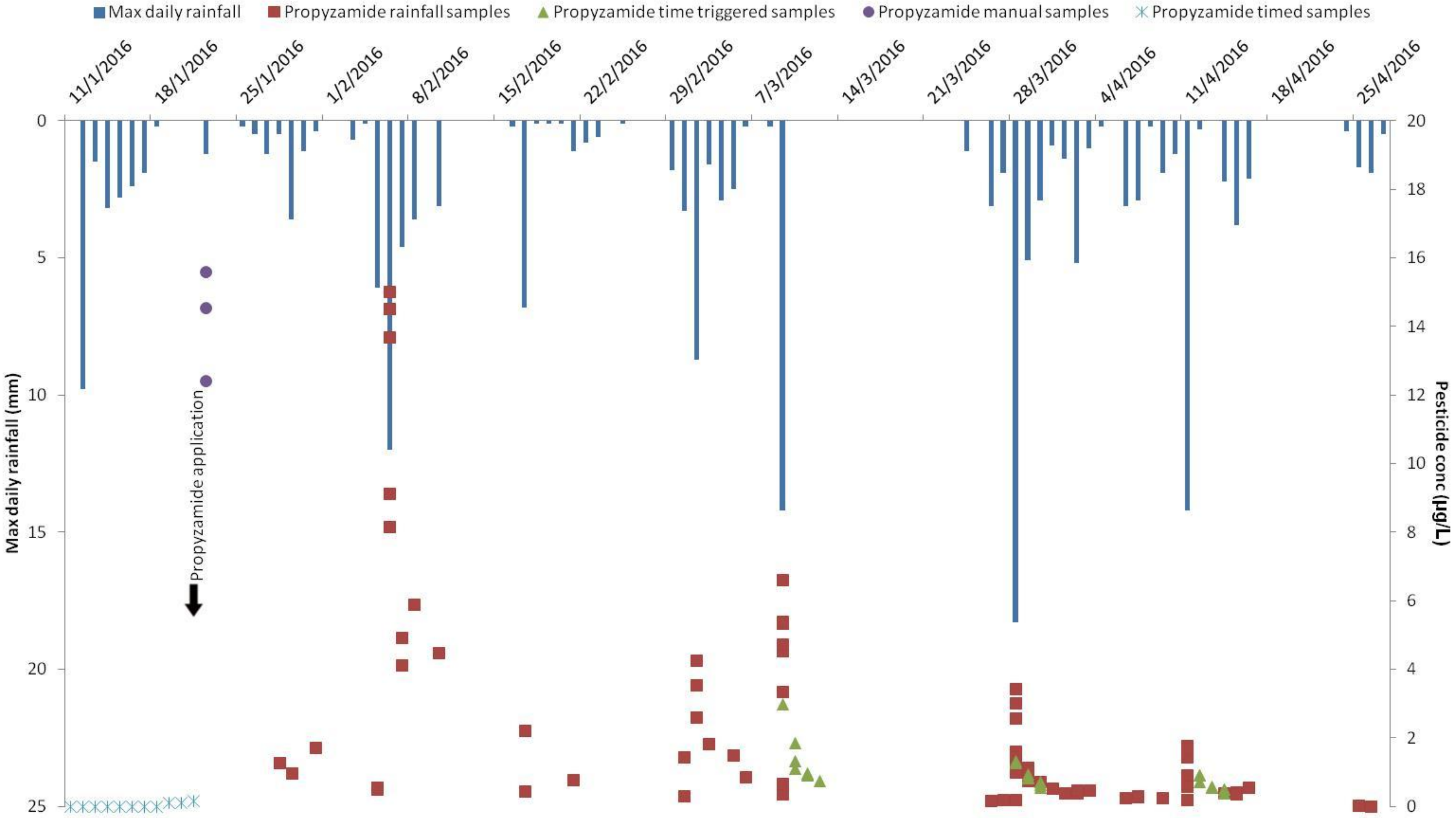

Figure 3.6 – Propyzamide detection in the PO according to sampling method against rainfall for January to April 2016

$$L = CQ\Delta t$$ **Equation 0.1**

L = Load (g)

C= pesticide concentration (g)

Q = flow rate (L/s)

Δt = time difference (s)

It took just over 24 h for the concentration at the PO to increase from 0.5 µg L^{-1} to 15 µg L^{-1} during the first major rainfall event following propyzamide application. This can in part be explained by the slowly permeable nature of the soil. However it would take approximately 3 days for the rainfall to reach the field drains according to the typical hydraulic conductivity for loamy soil of 1.3 cm h^{-1}. This explains the slow decline in pesticide concentrations following an event but suggests that once propyzamide has been dissolved into the water phase, it moves through the soil water much quicker than the permeation rate water. The shallow slope across the farm of approximately 1° was also likely to have been a factor that affected the initial lag time as movement rate would likely be reduced, particularly under low intensity conditions. However the increase in concentration from 9 µg L^{-1} to 15 µg L^{-1} took only 5 h 40 min, a rate of increase in concentration of 1.07 µg L^{-1} per h. The rate of rainfall during the 25.6 h period for the increase in concentration to the peak was 0.4 mm h^{-1} with a total rainfall of 10.1 mm. During the increase in concentration from 9 µg L^{-1} to 15 µg L^{-1}, the rate of rainfall was 1.4 mm per h with 7.6 mm total falling during this shorter time period (5 h 40 min). Subsequent concentration peaks occurred during periods of rainfall >10 mm and there was relationship between the amount of rainfall and the increase in pesticide concentration detected (Figures 3.5, 3.6). This was particularly the case when rainfall >10 mm occurred within a 24 h period. These findings are in agreement with previous studies which have found increased pesticide concentrations in runoff during periods of intensive rainfall. However, the amounts of rainfall in these previous studies was much higher (18-36 mm h^{-1}) than the maximum seen during this study (Sigua *et al*., 1995; Gouy, 1999; Beulke *et al*., 2002).

Of the 155 samples taken according to rainfall at the PO, the majority of samples occurred either within 3 h, or more than 24 h of the previous sample (Figure 3.7). This indicates that dynamic sampling is needed to give the most accurate representation of pesticide changes throughout storm events. It also suggests that timed samples taken in between events produce excessive and unnecessary samples over extended periods of application. These extra samples add to cost and time in terms of handling, processing and analysis. Sampling took place over 279 days meaning that if timed sampling had been used and if sampling had occurred once a day, this would have resulted in 124 extra samples with much lower definition of events.

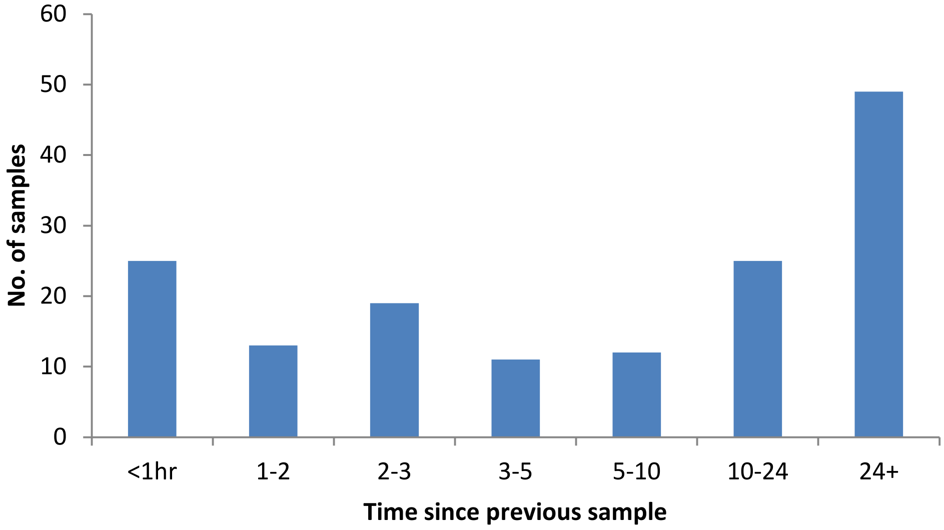

Figure 3.7- The number of samples according to the time since the previous sample was taken for rainfall dependent samples at PO.

The following section discusses in more detail the findings and data trends found from the use of this rain dependent sampling methodology.

A regularly recurring trend in the sampling data was the detection of higher concentrations of pesticides at the PO than those found at the PI. This phenomena was seen for metazachlor in February 2016 and for propyzamide in February and March 2016 (Figure 3.5). A plausible explanation for this may be that the pesticides were getting washed into the pond during storm events and adsorbing to sediment particles in the pond. Subsequent desorption of pesticides may then occur during storm events when other pesticides or natural organic matter from the environment are washed into the pond and compete for adsorption spaces on the pond sediments. This then causes desorption of the previously adsorbed pesticides and results in a higher concentration of the pesticide to be found at the PO compared to the PI. Similar instances of competitive adsorption and drawn out periods of desorption has been seen in previous research which looked at pesticide adsorption/desorption to sediments in a pond in southern Germany (Gao *et al*., 1998a, 1998b). This research included analysis of the pesticide atrazine which has similar physico-chemical properties to metazachlor (Figure 2.8). It is possible that some pesticide detection in the pond was due to infiltration from the soil surrounding the pond, however this was only relevant to a small area of field 7 so was not expected to be a significant contributor of pesticides into the pond. The sides of the pond were flanked by wooded areas and field 8 was sloped away from the pond and separated by a small ditch. Therefore the vast majority of the pesticide contaminated water entering into the pond was expected to have entered as throughflow through field drains and the main drainage system that runs through the farm catchment.

The pattern of declining concentration peaks for metazachlor in the pond can be seen with spikes coinciding with the heavier periods of rainfall >10 mm (Figure 3.5). During an exceptionally high period of rainfall between the 30th December and 3rd of January (where 46.9 mm of rain fell) there were two events that saw rainfall exceeding 10 mm in 24 h. The metazachlor concentration increased to 1.4 mg L^{-1} above the previous maximum concentration of 0.6 mg L^{-1} at the PI in November. This further supports the view that heavy rainfall mobilizes the pesticide and that the amount of rainfall controls the extent to which this mobilisation occurs. It is likely that the DT_{50} for propyzamide (typical: 50.5 d) and metazachlor (typical: 8.6 d) explained the pattern of declining peaks and why it took longer for propyzamide (approx 4 months) compared to metazachlor (approx 3 months) to consistantly fall below

1 µg L^{-1}. The short DT_{50} of metazachlor in comparison to propyzamide would also explain why rainfall events >10 mm in the period between metazachlor and propyzamide application saw relatively low increases in metazachlor concentration as compared to that seen for propyzamide following its application. Weather data from the closest weather station to the study area (Birmingham) was used to develop an intensity-duration-frequency (IDF) curve with which to compare the maximum rainfall seen at the study area. The IDF curve calculated for the study area shows that the maximum rainfall intensity experienced during the study period was below the calculated extreme values for the local area (Figure 3.8). The return period for 10 mm of rainfall within 24 hours was calculated to be <1 year.

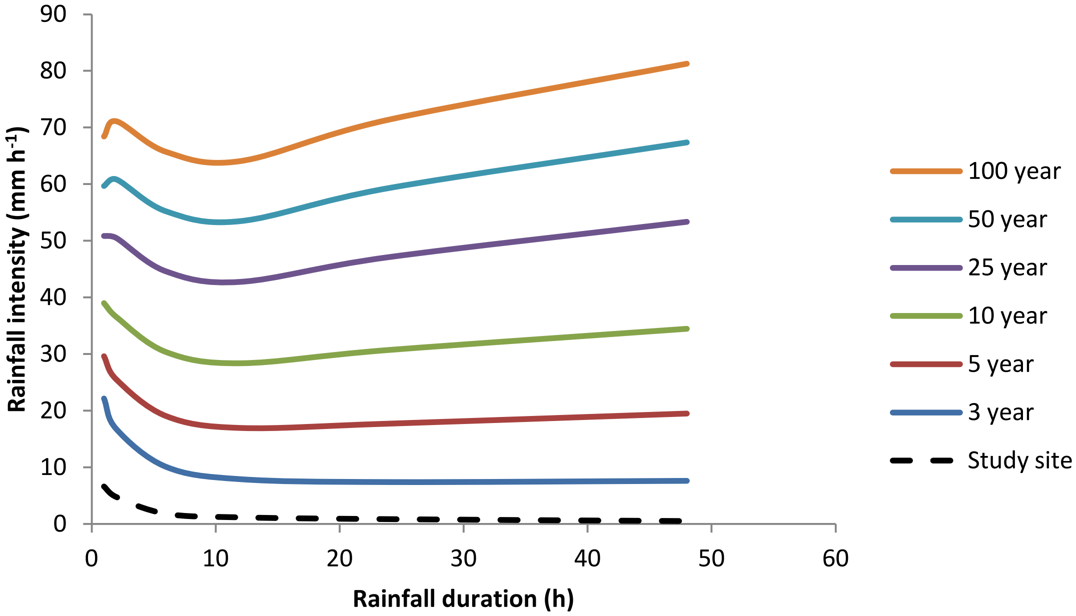

Figure 3.8 - IDF curve for study site compared to historical data for the local area (Met office, 2018). Each line shows the predicted frequency over which an event of a certain intensity and duration will occur.

The mechanism of pesticide mobilisation likely occurs as pesticides adsorb onto dissolved organic carbon (DOC) in the pore water of the soil matrix. Subsequent erosion of the soil during heavy rainfall then moves the pesticides via leachate and throughflow into the pond (Gao *et al.*, 1998a; Johnson *et al*., 1999; Bloomfield *et al.*, 2006). The higher concentrations of metazachlor found at the PI relative to the PO suggest that there was some retention or removal of metazachlor occurring in the pond. During a rainfall event at the beginning of February 2016, the concentration of metazachlor detected at the pond outlet exceeded that in the pond inlet, where it increased from 0.08 to 0.92 µg L^{-1}. This was concurrent with the high spike in propyzamide of 15 µg L^{-1} also detected at the PO. This release of metazachlor from the pond suggests that there was a competition effect occurring between the pesticides for adsorption sites within the pond. Propyzamide would likely outcompete metazachlor for adsorption sites due to its higher K_{oc} and log K_{ow} values of 840 mL g^{-1} and log 3.3 respectively compared to 54 mL g^{-1} and log 2.49 for metazachlor. This means that propyzamide, relative to metazachlor, has a higher preference to be in the adsorbed phase due to its higher affinity for adsorption onto organic carbon and its more hydrophobic nature (PPDB, 2014). This finding is in agreement with previous research that has shown that film diffusion and adsorption capacity are factors affected by the physico-chemical properties of the studied pesticides (Rojas *et al.*, 2015).

The major rainfall events where increased pesticide concentrations were observed throughout the sampling period were numbered (Figure 3.12) and the intensity-duration for each event and for the periods inbetween each event were plotted (Figure 3.9). This allows for comparison between the events themselves and between any smaller rainfall events where no increases in pesticide concentrations were detected. The rainfall intensity at 24 h during events exceeded the rainfall intensity experienced during the periods between events following propyzamide application (Figure 3.9). The exception to this was event 3, where elevated propyzamide concentrations in samples was thought to have been caused by drift following propyzamide application rather than run-off or leaching. Figure 3.9 indicates that both intensity and duration of rainfall, particularly over a 24 hour period with intensities exceeding 0.4 mm h^{-1}, were major contributing factors to elevated pecticide concentrations in leachate.

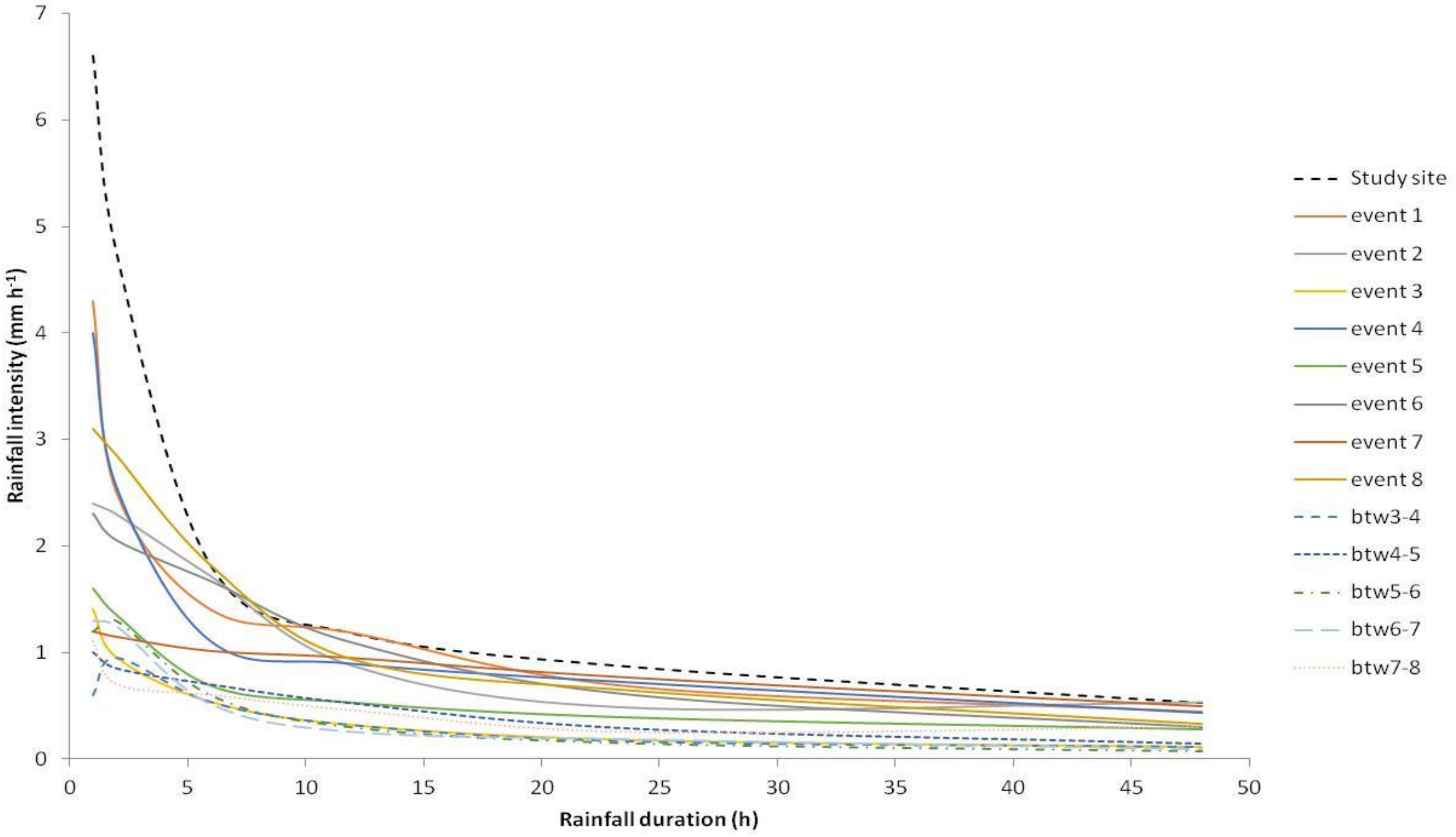

Figure 3.9 - Graph of the maximum rainfall intensity to duration for each event where increased pesticide concentrations were seen in comparision to the maximum rainfall intensity and duration between events. Solid lines consider rainfall during events where increased pesticide concentrations were observed (1-8), dashed lines show periods between events where no increase in pesticide concentrations was observed (btw 3-8) and these are only considered for the period following propyzamide application. The study site line is that shown in Figure 3.8.

The concentrations of metazachlor found were much lower than that seen for propyzamide. This could have been because the sampling was not carried out at a point in time close to the application of metazachlor. It took approximately three months from pesticide application for the propyzamide concentration to not exceed 1 µg L^{-1} during storm events. For metazachlor, although the run-off data concerning the time period immediately following application was not collected, it took approximately four months following application for concentrations not exceeding 1 µg L^{-1} to be detected during rainfall events. However, it was also found that only rainfall events >10 mm in 24 h caused increases in metazachlor detection from 2.5 months following the most recent application. Furthermore, the application of other pesticides such as propyzamide that have physico-chemical properties that make them more prone to adsorption compared to metazachlor during this time period can result in increased concentrations of metazachlor detected during rainfall events.

The concentration of metaldehyde was also measured during the monitoring period because of its association with historic water quality concerns (chapter 2). However metaldehyde had not been used on the farm for approximately three years. Even so, during a period of heavy rainfall at the end of March 2016 metaldehyde concentrations reached 0.65 µg L^{-1} (Figure 3.10).

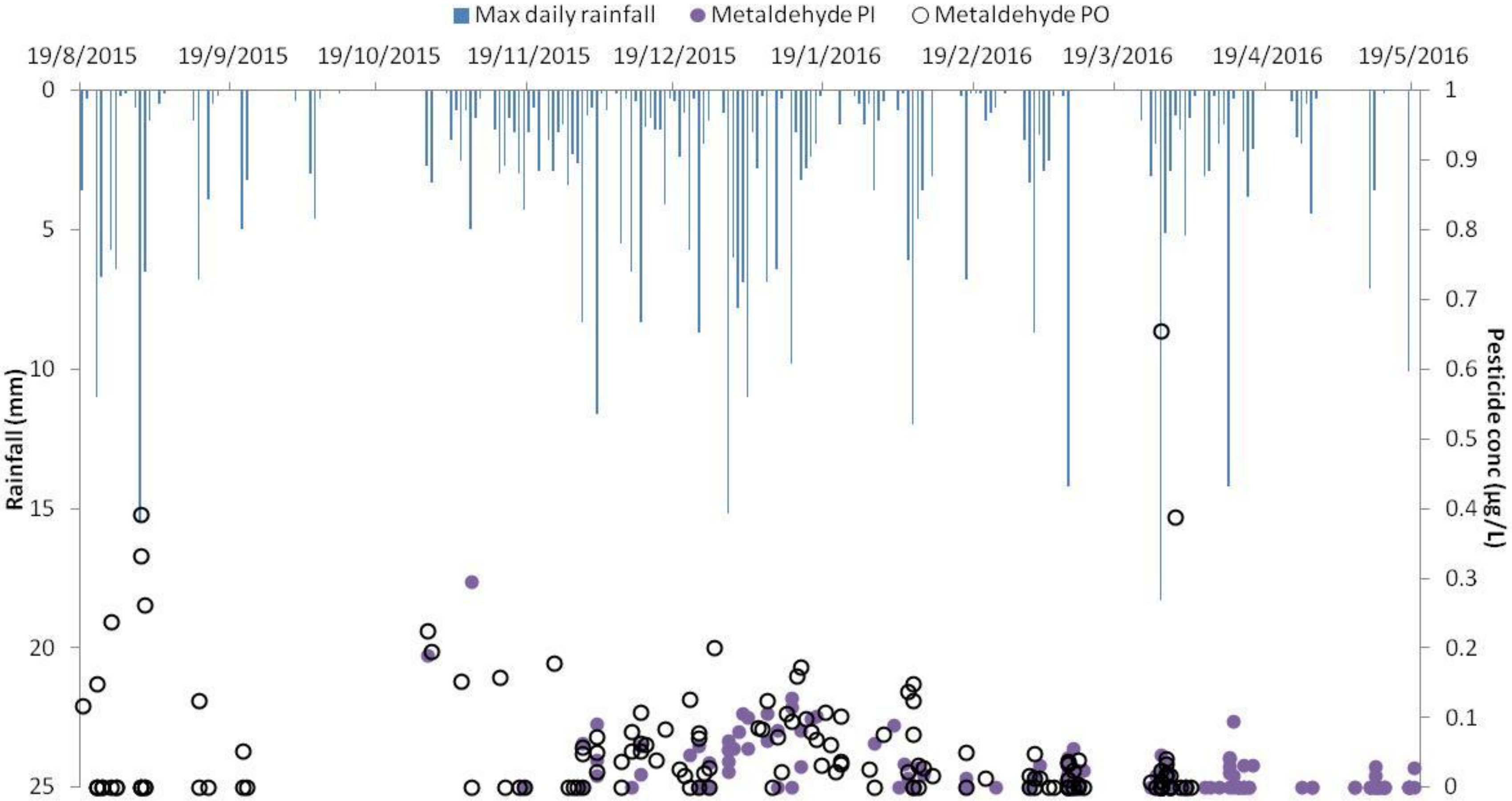

Figure 3.10 – Concentrations of metaldehyde detected at the PI and PO as monitored by rain dependent sampling for the period between August 2015 and May 2016.

Metaldehyde can be rapidly degraded under aerobic conditions (EFSA, 2009; Thomas *et al*., 2017). The reported half life (DT_{50}) value for metaldehyde undergoing aerobic degradation in soil is 5.1 days, with the DT_{50} in the water phase being only 11.5 d and 12.2 d for the water-sediment phase, although it is also noted that metaldehyde is stable to photolysis and hydrolysis (PPDB, 2014). These results suggest that metaldehyde should be degraded relatively quickly in soil and water. However this does not align with the observations seen here which show significant persistence of metaldehyde in the environment. EFSA (2009) note that metaldehyde was found to be near stable under anaerobic conditions. If metaldehyde had been washed into the pond during previous storm events and then trapped under anaerobic conditions within the sediment, this may explain how the detection of the pesticide at the farm pond three years after metaldehyde was last used on the farm was possible. Anecdotal evidence of increased sediment presence in samples during and shortly after rainfall events supports a theory of disturbance and remobilisation of sediment in the pond during storm events and thus explains increased metaldehyde detection during these periods. Since the concentrations of metaldehyde observed were all below 1 µg L^{-1}, the impacts on the environment and water quality would be low due to the high dilution factors that would occur once the pesticides reached larger water bodies.

Additional sampling points were set up at the FI and FO in February 2016 and monitored until May 2016. Sampling at the FI was carried out in order to establish whether any pesticides were entering the monitored catchment from adjacent farmland. Sampling at the outlet of the farm took place to understand whether any changes in concentration occurred between the PO and the FO. All pesticide concentrations detected at the FI sampling location were below 0.1 µg/L (Figure 3.11). This means there was little to no movement of pesticides from the adjacent farmland into the trial catchment area.

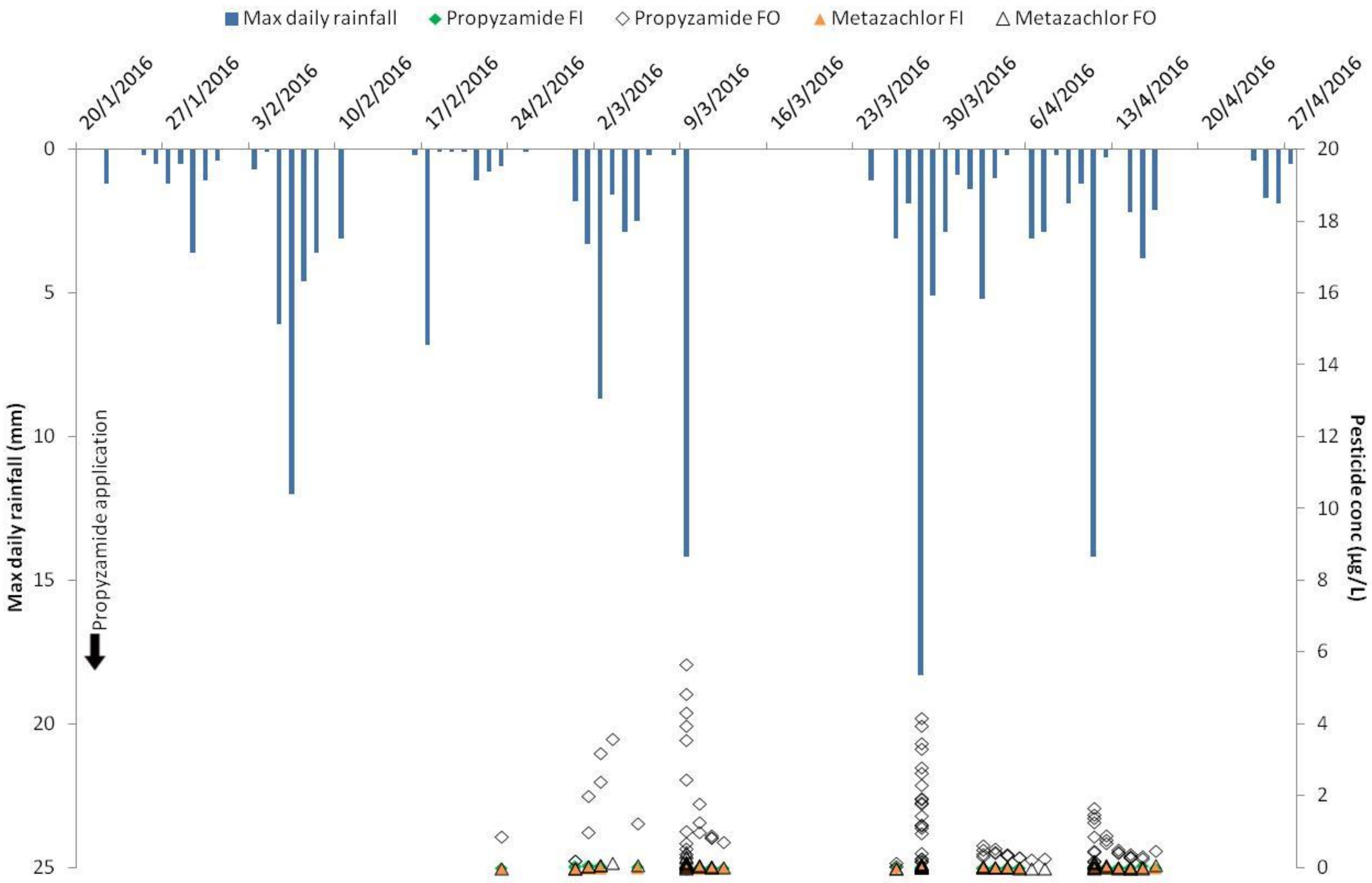

Figure 3.11- Metazachlor and propyzamide concentrations detected in the FI and FO locations against rainfall between February and April 2016. All metaldehyde concentrations were below 0.1 µg L^{-1} at the FI and reached a maximum of 0.4 µg L^{-1} at the FO and so are not shown.

The highest concentration peak for propyzamide was recorded at the FO on the 9th March was 5.67 µg L^{-1}, 1 µg L^{-1} less than the maximum concentration found at the PO on the same day (6.61 µg L^{-1}). The third peak concentration of propyzamide detected at the FO during the 18.3 mm event was 4.19 µg L^{-1} and so exceeded the concentration from the PO which was 3.42 µg L^{-1}. The final peak detected for propyzamide at the FO (1.49 µg L^{-1}) resulted in similar values being observed to those at the PO (1.79 µg L^{-1}). This may be explained by an initial dilution of pesticides as run-off from other fields and adjacent non-cropped areas entering the drainage system. In addition, the farming practices being undertaken in the catchment such as horizontal furrows across the slope when ploughing and a wider buffer zone (approx 5 m) at the FO sampling location (compared to smaller buffer zones in other field of 1-2 m) coupled with the shallow slope of field 8 may have caused a delay in the movement of propyzamide. This would account for peak concentrations at the FO not exceeding those seen at the PO in the initial rainfall events. Subsequent heavy rainfall events then resulted in the mobilisation of pesticides via field drains from field 8, downstream of the pond. The following section discusses the pesticide loads during rainfall events at the PI and PO locations.

Pesticide loads were calculated for the PI and PO using Equation 3.1. Total loads were calculated for the time period from when the PI monitoring equipment was installed, 29th October 2015, to 19th May 2016 (Table 3.2). Eight elevated pesticide events (>1 µg L^{-1}) were identified throughout the sampling period (Figure 3.12) and the pesticide loads were calculated for each event (Table 3.1). The highest loads were detected for propyzamide at the PI during the first major rainfall event following application (event 4) and was calculated to be 49.79 g of pesticide.

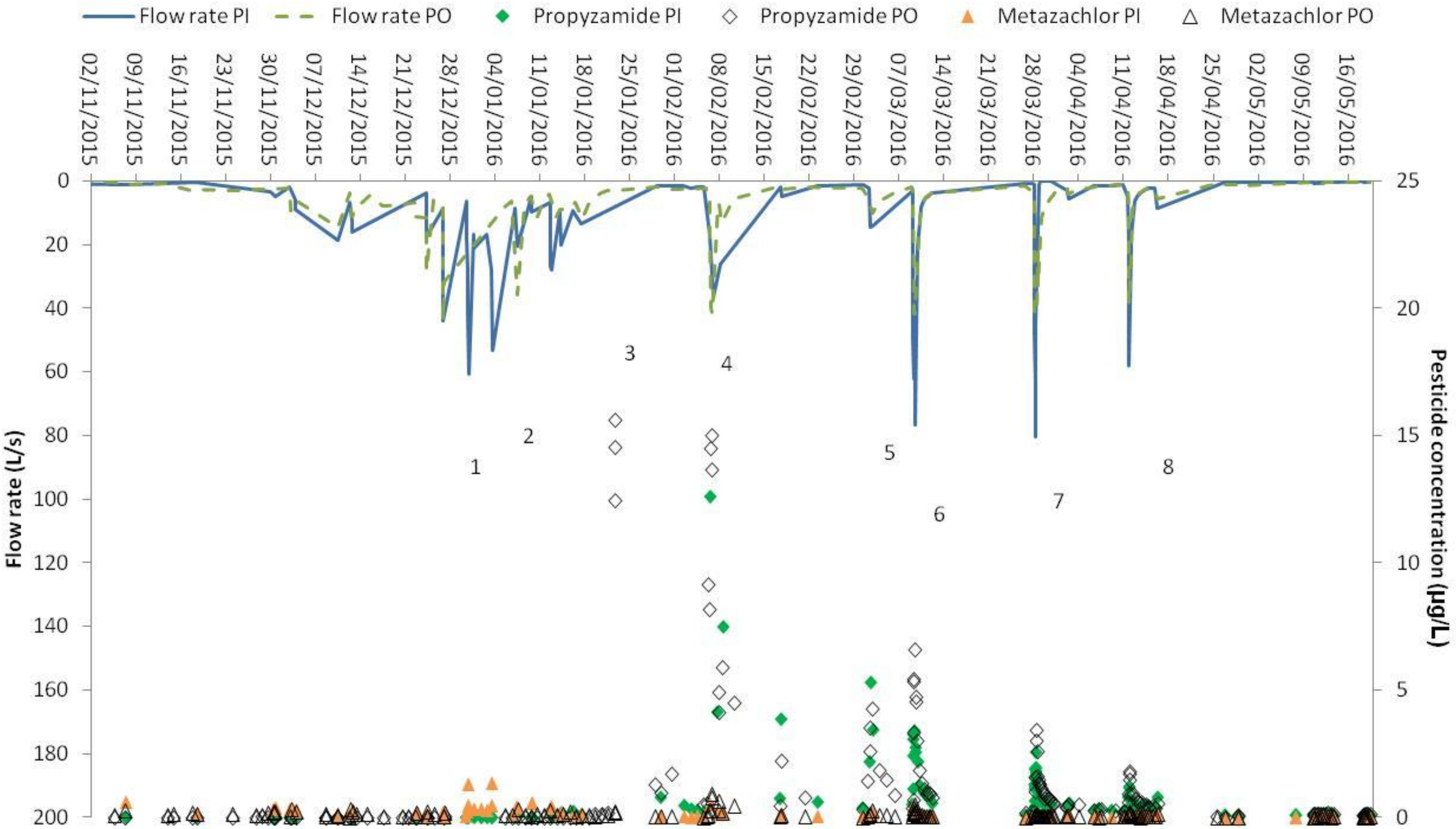

Figure 3.12- Flow rates into and out of the farm pond between November 2015 and May 2016. Each number denotes an event where elevated pesticide peaks were detected. Metaldehyde concentrations are not shown due to all detections being below 1µg/L.

There was evidence that the pond had some impact on pesticide retention for propyzamide and metazachlor, with overall removals of 10.6 g and 6.47 g respectively (Table 3.2). The pond also provided retention of propyzamide during event 4, removing 22.61 g of pesticide during the largest pesticide load input into the pond. However, subsequent loadings show higher values of pesticide at the outlet as compared to the inlet, suggesting that the pond only has a buffering capacity during the first rainfall event after application. Subsequent events caused desorption and resulted in higher loads being found at the PO. For metaldehyde, the pond appeared to act as a sink that slowly releases the pesticide resulting in a net loss of 0.66 g over the sampling period of December 2015 to April 2016. Net losses of metazachlor were seen during event numbers 4 and 7 (Table 3.1). Event 4 was the first major rainfall following propyzamide application and event 7 was the largest rainfall event that occurred over the entire sampling period. This further supports the conclusion that competition with other pesticides and the extent of rainfall are factors that negatively affect the adsorption of metazachlor in the farm pond. These results suggest that although ponds have the potential for pesticide removal in the first instance, they are prone to re-release of pesticides due to a mixture of resuspension of sediment and competition from other pesticides and natural organic matter that gets washed into the pond during subsequent storm events (Gao *et al*., 1998b; Budd *et al*., 2009; Guittonny-Philippe *et al*., 2014).

Table 0.2- Total pesticide loads for PI and PO with net removal for the sampling period 20th December 2015 and 14th April 2016

Pesticide	Load at PI (g)	Load at PO (g)	Load removal (g)
Propyzamide	68.52	57.92	10.6
Metazachlor	13.24	6.77	6.47
Metaldehyde	2.98	3.64	-0.66

This study showed that monitoring rainfall directly is a viable method that could be used to indicate the risk of pesticides in run-off. Additionally, rainfall dependent sampling has been shown to be useful to identify the amount of rainfall required to mobilise pesticides into run-off. In the case study here, this was shown to be rainfall events which exceeded 10 mm in a 24 h period.

3.5 Conclusions

This study developed a new method of sampling based on rainfall to determine the effects of storm events on pesticide run-off for two pesticides on a farm catchment in Wolverhampton. The effects of both rate and total amount of rainfall, especially within a 24 h period, were the main contributing factors to high concentrations of pesticides being detected in agricultural run-off. There was little evidence to suggest that biodegradation plays much of a part in pesticide removal once the pesticides enter the farm drainage system following the first storm events as seen by the negative removal rates in Table 3.1. In addition to this, the fact that metaldehyde was detected well beyond the period that it should have been degraded. The evidence supports adsorption as the main means of pesticide removal. The data also showed that pesticides already adsorbed onto pond sediment could be desorbed back into the water. The high flow rates observed when high concentrations of pesticides were seen in run-off limit the potential for pesticide removal processes to take place in farm pond systems due to their limited volume. This method of sampling could be used as a more targeted and cost effective means for catchment management in order to confirm high risk agricultural areas for pesticide run-off and so better utilise their resources. Further work should be targeted towards the use of rain dependent sampling at sites with different slopes, soils and pesticide use to determine how these factors affect the point at which enhanced run-off occurs. This is particularly the case for sites with steeper slopes and soils that are more conducive to higher rates of hydraulic conductivity in order to test whether there still exists a lag time/ intensity of rainfall required for pesticide contamination to appear in the farm drainage systems.

3.6 References

ADAS UK Ltd (2011) *Understanding the changes in pesticide usage to inform water company risk assessments*. Wolverhampton.

Ball, D. (2015) *Wolverhampton historic rainfall data* Met office library and archive.

Beulke, S., Brown, C.D., Fryer, C.J. and Walker, A. (2002) ‘Lysimeter study to investigate the effect of rainfall patterns on leaching of isoproturon’, *Pest Management Science*, 58(1), pp. 45–53.

Bloomfield, J.P., Williams, R.J., Gooddy, D.C., Cape, J.N. and Guha, P. (2006) ‘Impacts of climate change on the fate and behaviour of pesticides in surface and groundwater-a UK perspective’, *Science of the Total Environment*, 369(1–3), pp. 163–177.

Boivin, A., Cherrier, R. and Schiavon, M. (2005) ‘A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils.’, *Chemosphere*, 61(5), pp. 668–76.

Budd, R., O'Geen, A., Goh, K.S., Bondarenko, S. and Gan, J. (2009) ‘Efficacy of constructed wetlands in pesticide removal from tailwaters in the central valley, California’, *Environmental Science and Technology*, 43(8), pp. 2925–2930.

Carvalho, F.P. (2006) ‘Agriculture, pesticides, food security and food safety’, *Environmental Science and Policy*, 9(7–8), pp. 685–692.

Castle, G.D., Mills, G.A., Bakir, A., Gravell, A., Schumacher, M., Snow, K. and Fones, G.R. (2018a) ‘Measuring metaldehyde in surface waters in the UK using two monitoring approaches’, *Environmental Science: Processes and Impacts*, 20(8), pp. 1180–1190.

Castle, G.D., Mills, G.A., Bakir, A., Gravell, A., Schumacher, M., Townsend, I., Jones, L., Greenwood, R., Knott, S. and Fones, G.R. (2018b) ‘Calibration and field evaluation of the Chemcatcher® passive sampler for monitoring metaldehyde in surface water’, *Talanta*, 179, pp. 57–63.

Castle, G.D., Mills, G.A., Gravell, A., Jones, L., Townsend, I., Cameron, D.G. and Fones, G.R. (2017) ‘Review of the molluscicide metaldehyde in the environment’, *Environmental Science: Water Research & Technology*, 3(3), pp. 415–428.

Destandau, F., Imfeld, G. and Rozan, A. (2013) ‘Regulation of diffuse pesticide pollution: Combining point source reduction and mitigation in stormwater wetland (Rouffach, France)’, *Ecological Engineering*, 60, pp. 299–308.

Drinking Water Inspectorate (2016) *Annual Report., DWI Annual Report* Available at: http://www.dwi.gov.uk/about/annual-report/index.htm (Accessed:

13 June 2016).

EFSA (2009) *Metaldehyde*. Vienna.

Ekström, M., Fowler, H.J., Kilsby, C.G. and Jones, P.D. (2005) 'New estimates of future changes in extreme rainfall across the UK using regional climate model integrations. 2. Future estimates and use in impact studies', *Journal of Hydrology*, 300(1–4), pp. 234–251.

FAO (2019) *Soil Permeability* Available at: http://www.fao.org/tempref/FI/CDrom/FAO_Training/FAO_Training/General/x6706e/x6706e09.htm (Accessed 3 April 2019).

Fauvelle, V., Kaserzon, S.L., Montero, N., Lissalde, S., Allan, I.J., Mills, G., Mazzella, N., Mueller, J.F. and Booij, K. (2017) 'Dealing with Flow Effects on the Uptake of Polar Compounds by Passive Samplers', *Environmental Science and Technology*, 51(5), pp. 2536–2537.

Franco, J. and Matamoros, V. (2016) 'Mitigation of polar pesticides across a vegetative filter strip. A mesocosm study', *Environmental Science and Pollution Research*, 23(24), pp. 25402–25411.

Gao, J.P., Maguhn, J., Spitzauer, P. and Kettrup, A. (1998a) 'Sorption of pesticides in the sediment of the Teufelsweiher pond (Southern Germany). I: Equilibrium assessments, effect of organic carbon content and pH', *Water Research*, 32(5), pp. 1662–1672.

Gao, J.P., Maguhn, J., Spitzauer, P. and Kettrup, A. (1998b) 'Sorption of pesticides in the sediment of the Teufelsweiher pond (Southern Germany). II: Competitive adsorption, desorption of aged residues and effect of dissolved organic carbon', *Water Research*, 32(7), pp. 2089–2094.

Gouy, V., Dur, J., Calvet, R., Belamie, R. and Chaplain, V. (1999) 'Influence of adsorption – desorption phenomena on pesticide run-off from soil using simulated rainfall', *Pesticide Science*, 55, pp. 175–182.

Guittonny-Philippe, A., Masotti, V., Höhener, P., Boudenne, J.-L., Viglione, J.

and Laffont-Schwob, I. (2014) ‘Constructed wetlands to reduce metal pollution from industrial catchments in aquatic Mediterranean ecosystems: a review to overcome obstacles and suggest potential solutions.’, *Environment International*, 64, pp. 1–16.

Johnes, P.J. (2007) ‘Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation methodology, sampling frequency, baseflow index and catchment population density’, *Journal of Hydrology*, 332(1–2), pp. 241–258.

Johnson, A.C., Bettinson, R.J. and Williams, R.J. (1999) ‘Differentiating between physical and chemical constraints on pesticide and water movement into and out of soil aggregates’, *Pesticide Science*, 55(5), pp. 524–530.

Kay, P. and Grayson, R. (2014) ‘Using water industry data to assess the metaldehyde pollution problem’, *Water and Environment Journal*, 28, pp. 410–417.

Kjær, J., Ernsten, V., Jacobsen, O.H., Hansen, N., de Jonge, L.W. and Olsen, P. (2011) ‘Transport modes and pathways of the strongly sorbing pesticides glyphosate and pendimethalin through structured drained soils.’, *Chemosphere*, 84(4), pp. 471–479.

Kreuger, J. (1998) ‘Pesticides in stream water within an agriculture catchment in southern Sweden, 1990-1996’, *The Science of the Total Environment*, 216, pp. 227–251.

Larson, S.J., Capel, P.D. and Majewski, M. (1997) *Pesticides in Surface Waters: Distribution, Trends, and Governing Factors*. Florida: CRC Press.

Liang, J., Tang, S. and Cheke, R.A. (2016) ‘Pure Bt-crop and mixed seed sowing strategies for optimal economic profit in the face of pest resistance to pesticides and Bt-corn’, *Applied Mathematics and Computation*, 283, pp. 6–21.

Macary, F., Morin, S., Probst, J.-L. and Saudubray, F. (2014) ‘A multi-scale method to assess pesticide contamination risks in agricultural watersheds’, *Ecological Indicators*, 36(2014), pp. 624–639.

Malone, R.W., Weatherington-Rice, J., Shipitalo, M.J., Fausey, N., Ma, L., Ahuja, L.R., Wauchope, R.D. and Ma, Q. (2004) ‘Herbicide leaching as affected by macropore flow and within-storm rainfall intensity variation: A RZWQM simulation’, *Pest Management Science*, 60(3), pp. 277–285.

Met office (2018) Wimbourne rainfall.

Moreno-González, R., Campillo, J.A., García, V. and León, V.M. (2013) ‘Seasonal input of regulated and emerging organic pollutants through surface watercourses to a Mediterranean coastal lagoon’, *Chemosphere*, 92(3), pp. 247–257.

National Soil Resources Institute (2019) *Soils Site Report for location 388195E, 304490N, 5km x 5km*, National Soil Resources Institute, Cranfield University. Accessed via: https://www.landis.org.uk/sitereporter

Osborn, T.J. and Hulme, M. (2002) ‘Evidence for trends in heavy rainfall events over the UK.’, *Philosophical transactions. Series A, Mathematical, physical, and engineering sciences*, 360(1796), pp. 1313–1325.

Pappalardo, S.E., Otto, S., Gasparini, V., Zanin, G. and Borin, M. (2015) ‘Mitigation of herbicide runoff as an ecosystem service from a constructed surface flow wetland’, *Hydrobiologia*, 774(1), pp. 193–202.

Passeport, E., Tournebize, J., Chaumont, C., Guenne, A. and Coquet, Y. (2013) ‘Pesticide contamination interception strategy and removal efficiency in forest buffer and artificial wetland in a tile-drained agricultural watershed.’, *Chemosphere*, 91(9), pp. 1289–96.

Pesticides Forum (2014) *Pesticides in the UK*. York.

PPDB (2014) *University of Hertfordshire Pesticide Properties Database*. Available at: http://sitem.herts.ac.uk/aeru/ppdb/en/ (Accessed: 17 November 2014).

Rabiet, M., Margoum, C., Gouy, V., Carluer, N. and Coquery, M. (2010) ‘Assessing pesticide concentrations and fluxes in the stream of a small vineyard catchment--effect of sampling frequency.', *Environmental Pollution*, 158(3), pp. 737–48.

Ramos, A.M., Whelan, M.J., Cosgrove, S., Villa, R., Jefferson, B., Campo, P., Jarvis, P. and Guymer, I. (2017) 'A multi-component method to determine pesticides in surface water by liquid-chromatography tandem quadrupole mass spectrometry', *Water and Environment Journal*, 31(3), pp. 380–387.

Rojas, R., Morillo, J., Usero, J., Vanderlinden, E. and El Bakouri, H. (2015) 'Adsorption study of low-cost and locally available organic substances and a soil to remove pesticides from aqueous solutions', *Journal of Hydrology*, 520, pp. 461–472.

Sherrard, R. (2004) 'Feasibility of constructed wetlands for removing chlorothalonil and chlorpyrifos from aqueous mixtures', *Environmental Pollution*, 127(3), pp. 385–394.

Shipitalo, M.J., Malone, R.W. and Owens, L.B. (2008) 'Impact of Glyphosate-Tolerant Soybean and Glufosinate-Tolerant Corn Production on Herbicide Losses in Surface Runoff', *Journal of Environment Quality*, 37(2), p. 401.

Sigua, G.C., Isensee, A.R., Sadeghi, A.M. and Im, G.J. (1995) 'Distribution and transport of atrazine as influenced by surface cultivation, earthworm population and rainfall pattern', *Chemosphere*, 31(10), pp. 4237–4242.

Stuart, M.E., Manamsa, K., Talbot, J.C. and Crane, E.J. (2011) *Emerging contaminants in groundwater*. Nottingham.

Thomas, J.C., Helgason, T., Sinclair, C.J. and Moir, J.W.B. (2017) 'Isolation and characterization of metaldehyde-degrading bacteria from domestic soils', *Microbial Biotechnology*, 10(6), pp. 1824–1829.

Thrasher, J., Morgan, P. and Buss, S.R. (2004) *Attenuation of mecoprop in the subsurface*. Bristol.

Trenberth, K.E. (2011) 'Changes in precipitation with climate change', *Climate Research*, 47(1–2), pp. 123–138.

Xu, J., Lo, S.L. and Xu, L. (2015) ‘Removal of pollutants during storm and non-storm events by two wetlands’, *Desalination and Water Treatment*, 57(22) , pp. 1–12.

Zhao, N., Yu, F., Li, C., Wang, H., Liu, J. and Mu, W. (2014) ‘Investigation of rainfall-runoff processes and soil moisture dynamics in grassland plots under simulated rainfall conditions’, *Water*, 6(9), pp. 2671–2689.

4 Removal of three recalcitrant pesticides using different activated carbon based media

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4.1 Abstract

The performance of six different forms of AC (four spherical beads, one granular and one fabric medium) were analysed for their ability to remove the pesticides metaldehyde, metazachlor and propyzamide from deionised and raw water. Kinetic and isotherm adsorption experiments were carried out on solutions containing these pesticides to determine the speed of adsorption and their adsorption capacity. These tests were carried out to understand the properties of each medium that make them suitable for application in agricultural environments to adsorb pesticides from field run-off. The largest sized polymer derived AC bead (PDACB) (696 µm), PDACB-D had the highest uptake rate for metaldehyde within a 30 min contact time using the pseudo second order model, with a rate of 0.28 µg g^{-1} min^{-1}. However PDACB-D also had the lowest adsorption capacity as indicated by the Freundlich constant (K_f) in raw water of 14.9 (µg g^{-1})(µg L^{-1})$^{1/n}$. Although the smaller PDACB (452-459 µm) had a higher capacity for metaldehyde adsorption (2957-5421 (µg g^{-1})(µg L^{-1})$^{1/n}$ in deionised water; 436-1470 (µg g^{-1})(µg L^{-1})$^{1/n}$ in raw water), they also had the slowest uptakes of 0.02–0.1 µg g^{-1} min^{-1}. The headloss through media beds was calculated over a range of flow rates to determine the practicality of

applying adsorption media in the field under storm-flow conditions. Due to the small size of the beaded and granular forms of carbon (<1 mm), headlosses were high for these media with headlosses up to 15 m at flow rates of 50 L/s. As shown by the models used the similar capacity and kinetics observed for the fabric AC in comparison to the particulate media and the opportunity to orientate the fabric into low headloss configurations mean that the AC fabric would be the best medium for treating pesticide run-off under storm conditions within agricultural watersheds.

4.2 Introduction

Pesticides impact on water quality in many parts of the world where concentrations have been seen at levels high enough to cause concern to inland watersheds in Europe, North and South America, South Africa and India (Kreuger, 1998; Ferenczi *et al*., 2002; Mamta *et al*., 2015; Pérez *et al*., 2017; Gakuba *et al*., 2018). Even marine environments such as the great barrier reef in Australia have been affected by pesticide contamination (Smith *et al*., 2012). In the UK, as in other countries where crop growth is seasonal, the issue of pesticide pollution into water courses is amplified at certain times of the year, coincidental with the application of specific chemicals. This has implications for drinking water quality when pesticides enter water courses used for potable water abstraction. Pesticides can enter water through diffuse routes such as leaching, run-off, drain flow, spray drift and atmospheric deposition (Holvoet *et al*., 2007; Vymazal and Březinová, 2015) or point sources such as from spillages and cleaning of spray equipment (Holvoet *et al*., 2007; Tediosi *et al*., 2012). The allowable concentration of individual pesticides in drinking water is

0.1 µg L^{-1} and for total pesticides is 0.5 µg L^{-1}. The concentrations detected in the source water before they reach the WTW can reach levels of >5 µg L^{-1} for individual pesticides (Drinking Water Inspectorate, 2016). Concentrations in field run-off have been reported to reach up to 100 µg L^{-1} (Mohr *et al*., 2007; Silburn *et al*., 2013). There are a number of pesticides that are of particular concern for drinking water quality. Many are herbicides that, due to their mode of action, are highly mobile to promote their uptake by the target plants. This mobility means that, particularly during rain events after application, these pesticides can move in relatively high concentrations via leaching or surface run-off from their area of application into water courses and therefore provide a threat where abstraction for drinking water occurs. The molluscicide metaldehyde is also of particular concern in the UK due to its regular detection in drinking water above 0.1 µg L^{-1} (Drinking Water Inspectorate, 2016). Metaldehyde is polar with a log K_{ow} of 0.12 (PPDB, 2014) indicating that it has a preference to be in the water phase compared to being adsorbed.

A number of other pesticides that have caused significant issues for drinking water quality are associated with one particular crop, namely oilseed rape. These pesticides include metazachlor and propyzamide (HGCA, 2009; Twining *et al*., 2009; Clarke, 2014; Voluntary Initiative, 2015). Oilseed rape is a crop that needs a high input of pesticides in its early stages of growth in order to become established. This also means that when the pesticides are applied there is unlikely to be much plant growth to act as a physical barrier to help slow the pesticide movement via surface run-off.

At present, the main way by which pesticides are removed from drinking water sources is at the WTW. This is through processes such as ultraviolet (UV) light, adsorption, and oxidation processes such as ozone which is commonly combined with GAC (Crittenden *et al*., 2005; Shi *et al.*, 2012). However UV and oxidation processes are high in cost and/or energy input for example it would cost approximately £2.1 million to install a UV/H_2O_2 system) (Jonsson *et al*., 2016). In addition, removal of pesticides at WTW may not represent the most efficient position to target bulk removal of pesticides. If a low-energy, passive and low cost means of reducing pesticide concentrations could be utilised in the field environment, where the contamination occurs, this would help to reduce the pesticide load entering WTW and reduce the input of shock loads that many treatment works struggle to deal with. The use of adsorption media has been identified for application in agricultural watersheds as it is the most appropriate method for application where pesticide contaminated water is collected over a large area (>1 ha). In addition, such a system should be easy to install and maintain, as well as providing a passive means of treatment without external power requirements. It would also only need to treat relatively small volumes of water compared to WTW enabling smaller, temporary treatment systems to be installed.

The aim of this research was to determine the most practical and efficient adsorption medium for removal by adsorption of three pesticides with differing physico-chemical properties. Consideration was given to the capacity of removal, the kinetics of adsorption and the impact of the background matrix on adsorption processes. Different structural forms of ACs have been compared (granular, spherical beads and fabric based media) in order to consider different potential design configurations for the most appropriate and practical means of application in agricultural watersheds.

4.3 Materials and methods

Three pesticides were studied:

- Metaldehyde, a particularly problematic pesticide in the UK for numerous water companies due to its low adsorption partition coefficient (K_d) of 0.23 and low soil organic carbon/water partitioning coefficient (K_{oc}) of 240. These values indicate that it does not adsorb well and a low octanol water coefficient (log K_{ow}) of 0.12 indicates that it is polar and therefore has a preference to be in water rather than being adsorbed.
- Propyzamide, which has a low solubility in water (9 mg L^{-1}) alongside high K_d and K_{oc} values (5.5 and 840 respectively) and a high log K_{ow} showing it to be a non-polar compound and therefore a preference to be in the adsorbed phase.
- Metazachlor which has a high solubility in water (450 mg L^{-1}) and a low K_{oc} (54) but its K_d and log K_{ow} values (0.78 and 2.49 respectively) fall between those of metaldehyde and propyzamide (Table 4.1).

Analytical standards of these pesticides were obtained from Sigma-Aldrich (Darmstadt, Germany) which were used to make stock solutions which were made up in methanol at 1 g L^{-1}. Working solutions were prepared from the stock solution by adding the stock into deionised (DI) or raw water to give the required concentration range. The raw water was collected from a farm pond in Wolverhampton and a sample was tested for pesicide presence. No pesticides were detected in these samples. The proportion of methanol in the working solutions was ≤0.1% of the total volume and so was not expected to have an impact upon the adsorption processes in the batch tests (Saha *et al*., 2013).

Table 0.1– Properties of the three pesticides used in this study (PPDB, 2014)

Pesticide	Pesticide properties							
	Substance group	Molecular mass (g mol^{-1})	Chemical formula	Solubility in water (mg L^{-1})	pKa	K_d	K_{oc}	Log K_{ow}
Metazachlor	Chloroacetamide	277.75	$C_{14}H_{16}ClN_3O$	450	n/a	0.78	54	2.49
Metaldehyde	Cyclo-octane	176.21	$C_8H_{16}O_4$	188	n/a	0.23	240	0.12
Propyzamide	Benzamide	256.13	$C_{12}H_{11}Cl_2NO$	9	n/a	5.5	840	3.3

Polymer derived AC beads (PDACB) were obtained from Blucher (Erkrath, Germany) and varied in their surface properties with respect to the proportion of minimicro- (<1 nm), micro- (1-2 nm) and meso-pores (2-50 nm). Filtrasorb 400 (F400) granular activated carbon (GAC) and a fabric activated carbon (AC Fabric) were obtained from Calgon carbon (Tyne & Wear, UK). The F400 GAC was ground and sieved to a size range of 425 - 600 µm in order to ensure a similar particle size range to the PDACB. The fabric was made up of individual fibres of AC of approximately 10 to 15 µm in diameter. These fibres were twisted together to form strands of 0.5 mm diameter which were in turn woven with other strands to form the fabric sheets. The spaces in between the woven strands (approx 170 x 330 µm average) account for 17% of the total fabric area. The fabric sheets were cut up into approximately 2 x 2.5 cm squares and was dosed at equivalent masses as was used for the particulate carbons. Raw water was collected from a farm pond in Wolverhampton, containing field run-off and known to have pesticide contamination.

Table 0.2– Properties of adsorption media tested.

Medium	Medium Type	Typical Specific Surface Area (m^2 g^{-1})	Average particle size (µm)	Particle size range (µm)	Pore size distribution Minimicro- (<1 nm) (cm^3 g^{-1})	Pore size distribution Micro- (1-2 nm) (cm^3 g^{-1})	Pore size distribution Meso- (2-50 nm) (cm^3 g^{-1})	Reference
A	PDACB	Data not available	451.6	398 – 510	Data not available	Data not available	Data not available	Provided by manufacturer
B	PDACB	1486	458.6	413 – 499	0.29	0.22	0.48	Provided by manufacturer
C	PDACB	1920	451.7	374 – 558	0.32	0.16	0.13	Provided by manufacturer
D	PDACB	1412	695.7	552 – 995	0.27	0.13	0.11	Provided by manufacturer
E	F400 GAC	993	589.3	94 – 1550	0.26	0.37	0.28	(Lu and Sorial, 2004; Lian *et al.*, 2011; Golea, 2018)
F	Fabric	1200	na	na	Data not available	Data not available	Data not available	Provided by manufacturer

During batch adsorption tests, 100 mg of media was added to 100 mL of water in conical flasks giving a media concentration of 1 g L^{-1}. Each experimental condition was run in triplicate. The medium was pre-wetted in DI water overnight to remove any dust and particulates, and to saturate the medium with water. The excess water was then removed by sieving and air drying prior to experiments. 100 mL of DI water spiked with individual pesticides to a concentration of 10 µg L^{-1} was then added to the flask. Kinetics tests were carried out to inform on the time needed for adsorption to reach equilibrium and to determine the respective rate of adsorption for the different media. The test solution was mixed on an orbital shaker (Stuart SSL1) for 1, 5, 10, 20, 30, 60, 120 and 480 min. For isotherm experiments, solutions using pesticide concentrations of 10, 100, 500, 800 and 1000 µg L^{-1} for metazachlor and propyzamide and 10, 100, 500, 800, 1000, 2000, 3000, 4000, 5000 and 7000 µg L^{-1} for metaldehyde were prepared. Adsorbents were added to conical flasks at a concentration of 1 g L^{-1}. The conical flasks were then placed on an orbital shaker at 150 rpm for 24 h. For both kinetics and isotherm experiments, tests were run firstly using pesticides spiked into deionised water and secondly with pesticides spiked into raw water to understand the impact of the background matrix on adsorption. The raw water had a pH of 7.5 and a turbidity value of 38.2 NTU. The raw water had a total organic carbon (TOC) of 13.8 mg/L, inorganic carbon (IC) 22.5 mg L^{-1}, total carbon (TC) 36.2 mg L^{-1}, non-purgable organic carbon (NPOC) 9.3 mg L^{-1} and total nitrogen (TN) 15.8 mg L^{-1}. The same experiments were then repeated using mixtures of all three pesticides at concentrations between 10 - 1000 µg L^{-1}. After this period the flasks were removed from the shaker and filtered into glass vials using 0.2 µm filters and frozen at -4°C prior to analysis.

4.4 Analysis

Analysis was carried out using a Waters liquid chromatography-tandem mass spectrometer (LC-MS/MS), Aquity ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) and Sciex LC-MS/MS with direct injection of pre-filtered samples. The calibration concentrations used for pesticide determination were 0.1, 0.2, 0.5, 1, 2, 5, 8, 10 µg L^{-1}. Where working solutions contained concentrations greater than 10 µg L^{-1}, samples were diluted to within the calibration range. Calibrations were run at the beginning and end of each run alongside quality control (QC) and blank standards throughout to ensure accuracy. The concentration of samples was determined using a regression of the average area from the chromatograms obtained from the known standards.

4.4.1 Modelling

Isotherm and kinetics modelling was carried out in order to understand the capacity and dynamics of the adsorption process, determine which factors were dominant in the adsorption process and to compare the mechanisms of adsorption for each of the tested media.

Adsorption rates and capacities were determined for the kinetic (the notation q_e is replaced with q_t for kinetic datum not at equilibrium) and batch studies using Equation 4.1 to give the adsorption mass normalised to the mass of adsorbent (µg g^{-1}):

$$q_e = (C_0 - C_e)\frac{V}{m}$$ **Equation 0.1**

C_0 is the initial pesticide concentration (µg L^{-1}), C_e is the equilibrium concentration of pesticide (µg L^{-1}), V is volume of solution (L) and m is the mass of media used in grams (Jusoh *et al*., 2011).

The kinetics of adsorption was modelled using pseudo first order (Equation 4.2) and pseudo second order (Equation 4.3) expressions following protocols used by others (Nethaji *et al*., 2013; Saucier *et al*., 2015; Sanchez Lopez, 2017). These models were used in the linear forms alongside the intraparticle diffusion model (Equation 4.4) and the film diffusion model (Equation 4.5), to determine whether intraparticle or film diffusion was the rate limiting step in the adsorption process.

$$\mathrm{Ln}(qe - qt) = \ln qe - k_1 t$$ **Equation 0.2**

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$ **Equation 0.3**

$$q_t = k_i t^{\frac{1}{2}} + c$$ **Equation 0.4**

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -R^l t$$ **Equation 0.5**

k is the rate constant (k_1 min^{-1}; k_2 g µg^{-1} min^{-1}; k_i µg g^{-1} min$^{1/2}$) and t is time in minutes. C (µg g^{-1}) represents the intercept and can be used as an indication on the size of the boundary layer (Nethaji *et al*., 2013). R^{l} (min^{-1}) is the liquid film diffusion constant (Qiu *et al*., 2009).

The adsorption data from Equation 1 was fitted to the Freundlich model (Equation 4.6) which describes multilayer adsorption (Boudesocque *et al*., 2008).

$$q_e = K_f C^{(1/n)}$$ **Equation 0.6**

q_e is equilibrium adsorption capacity (µg g^{-1}), C is the chemical concentration in solution (µg L^{-1}). K_f is an empirical constant indicating the capacity of the adsorbent for the adsorbate at equilibrium (µg g^{-1})(µg L^{-1})$^{1/n}$, and 1/n is unitless and is also an empirical constant that indicates the intensity of adsorption (Crittenden *et al*., 2012; Njoku *et al*., 2015). The linear form of the Freundlich equation is:

$$\log q_e = \log Kf + \frac{1}{n}\log C$$ **Equation 0.7**

The data was also fitted to the Langmuir model (Equation 4.8) which describes monolayer adsorption (Boudesocque *et al*., 2008).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Equation 0.8

Where q_m is the maximum adsorption capacity and K_L is the Langmuir constant.

4.5 Results & discussion

4.5.1 Kinetics

The AC fabric showed the most rapid removal of metaldehyde from the water (Figure 4.1), with 8.5 µg g^{-1} (61%) removed after 5 minutes and 12.4 µg g^{-1} removal after 30 minutes (92%). This was followed closely by F400 GAC with 4.7 µg g^{-1} (44%) removed after 5 minutes and 10.1 µg g^{-1} removal after 30 minutes (89%). The PDACB took longer to adsorb the pesticide although all the media had the same degree of removal after 8 h of between 9.1 and 13.2 µg g^{-1}, close to the starting concentration. The slowest medium for adsorption of metaldehyde after 1 and 2 h was PDACB-D, with 8.1 and 9.6 µg g^{-1} removal respectively, this represents 66 and 81 % removal from the solution. PDACB–D was the largest of the AC beads tested, with an average particle size of 695.7 µm (Table 4.2). The uniformity of the bead sizing and shape shown by the particle size distribution (Figure A-11 in Appendix A) was likely to have implications in terms of the speed of uptake. For spherical particles such as the

PDACB, adsorption will occur more slowly due to the lower surface area to volume ratio when compared to the more irregular cloth and granular forms of AC. Irregular sized media therefore have larger available outer surface areas for diffusion and mass transfer across the boundary layer (Lowell *et al*., 2004). The datum for metaldehyde adsorption was best fitted to the pseudo-second order model (Figure A-1 in Appendix A) using the linear form of the equation (Equation 4.3) on a plot of $\frac{t}{q_t}$ vs *t*, with R^2 values ranging between 0.90 and 0.99 Table A-1 in Appendix A.

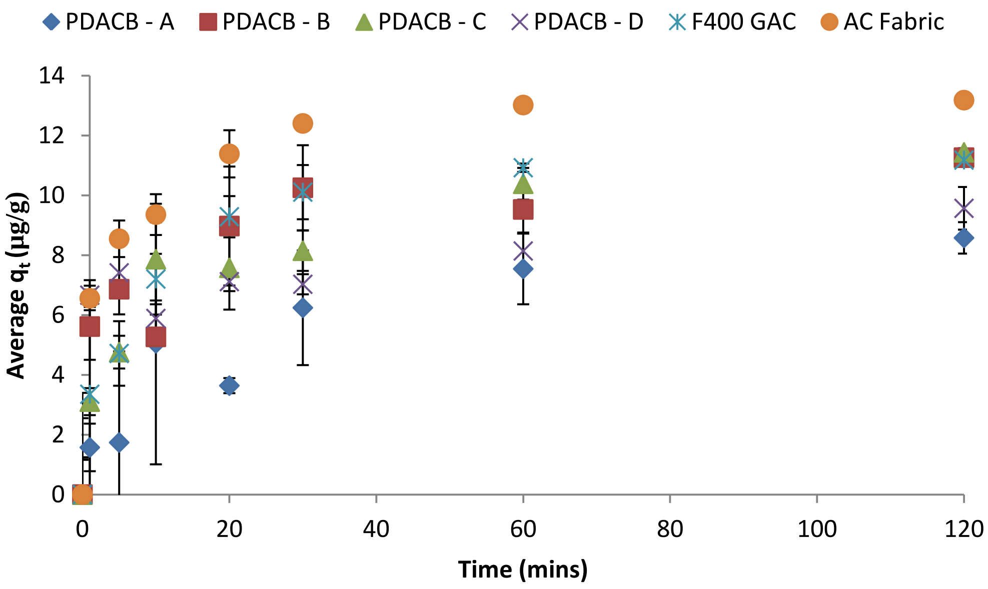

Figure 0.1– Metaldehyde removal from DI water over 120 minutes for the different AC media.

The F400 GAC had the fastest uptake of metazachlor with an average removal of 8.6 μg g^{-1} after 10 minutes compared to the other media which ranged from 2.3 μg g^{-1} after 10 minutes for PDACB–A to 4.6 μg g^{-1} for PDACB–

D (Figure 4.2). F400 GAC also had the highest removal after 120 min of 9.9 µg g^{-1} compared to 7.8 µg g^{-1} for PDACB–A and AC fabric to 8.9 µg g^{-1} for PDACB–C. The majority of the data for metazachlor was best fitted to the pseudo second order model with R^2 values ranging from 0.993 to 0.999 (Appendix A). There was one exception (PDACB–B) which fitted better to the pseudo first order model with R^2 values of 0.453 for the pseudo second order model and 0.647 for the pseudo first order model. However the data for PDACB-B was skewed by a high level of removal seen in one of the replicates at 30 minutes. As a result all comparisons have been made using kinetic data obtained using the pseudo second order model.

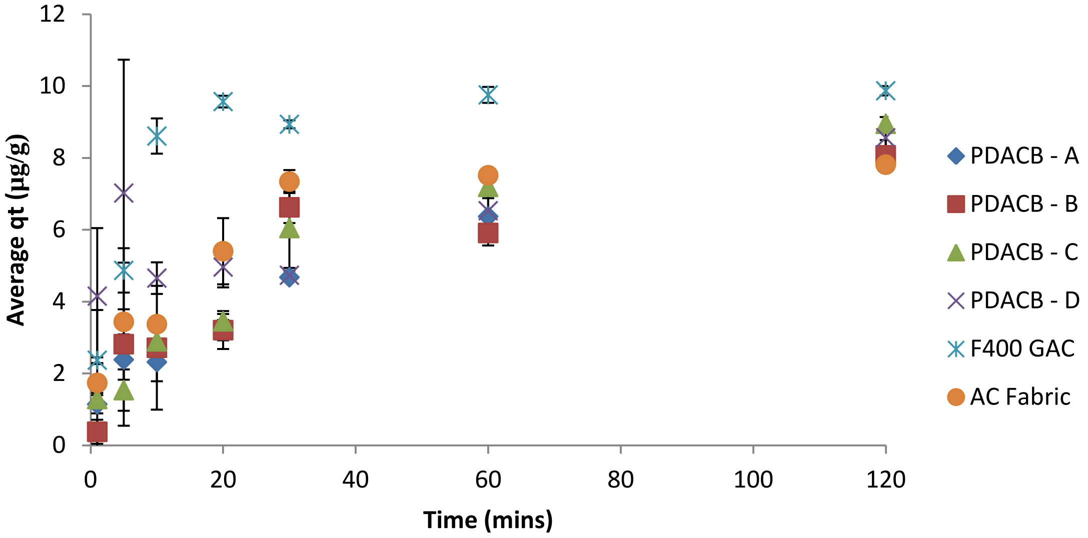

Figure 0.2– Average metazachlor removal from DI water over 120 minutes

Propyzamide removal occurred very quickly with average removals of 5.5 µg g^{-1} for PDACB–B to 6.9 µg g^{-1} for the AC fabric after just one min contact time (Figure 4.3). This equates to rates of 85 – 95% removal achieved for all media after one minute. However due to the fact that experiments were run in batches with two media in triplicate at each time point, total adsorption extent cannot be reliably compared for all media. Propyzamide removal fitted very well to the pseudo second order model with R^2 values of 0.998 – 0.999 for all media (Figure A-3, appendix A).

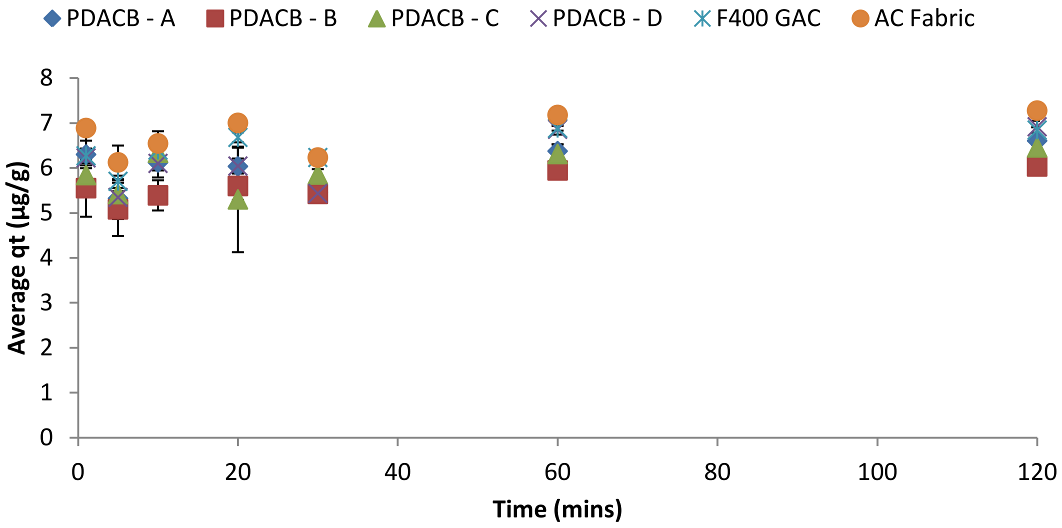

Figure 0.3– Average propyzamide removal from DI water over 120 minutes

For the intraparticle diffusion model, q_t was plotted against $t^{1/2}$ and linear regression was used to find the fit of the data. Linear regression was also used for the film diffusion model which was a plot of ln(1-qt/qe) against *t*. If the regression line dissects the origin, this shows that only a single factor (i.e. intraparticle or film diffusion) was the sole rate limiting step. If the line does not go through the origin, this indicates that more than one factor is responsible for limiting the rate of kinetic adsorption. Neither intraparticle diffusion nor film diffusion were sole limiting factors for any of the tested media for metaldehyde adsorption kinetics as shown by the regression analysis in appendix A (Figures A-4, A-5) which do not go through the origin. F400 GAC and AC fabric fit better to the intraparticle diffusion model compared to the film diffusion model suggesting that intraparticle diffusion is more of a limiting factor for these media. AC Fabric had the highest C value of 9.04 μg g^{-1}. The C value from Equation 4.4 is linked to boundary layer thickness and is indicative of the importance of boundary later effects (Tao and Fletcher, 2013). PDACB–A, PDACB–C and PDACB–D resulted in intercepts which were closest to the origin for the film diffusion model. These results were indicative that film diffusion was a greater limiting factor for metaldehyde adsorption onto the AC beads as compared to F400 GAC or the AC fabric.

For metazachlor, none of the media for either the intraparticle diffusion or film diffusion models went through the origin indicating that both intraparticle and film diffusion are factors affecting adsorption kinetics (Appendix A). PDACB–A to C fitted better to the film diffusion model with R^2 0.97, 0.76, 0.94 respectively. The highest value of the intercept and therefore indication of the largest boundary layer for metazachlor with the intraparticle diffusion model was 6.3 μg g^{-1} seen for F400 GAC. For propyzamide, neither the intraparticle diffusion model nor the film diffusion model went through the origin for any of the media (appendix A) showing that both film and intraparticle diffusion are factors in the kinetic rate removal for propyzamide. PDACB–B and PDACB–D fit fairly well to the film diffusion model (R^2 = 0.63, 0.68 respectively).

To determine if medium characteristics influenced the rate of adsorption, the adsorption rate constants (K_2) from the pseudo second order model were plotted against different properties of each media. A comparison of K_2 values was plotted to compare the rate constant for the six different media for each of the three pesticides (Figure 4.4). The K_2 was similar for each of the medium tested particularly for the pesticides metaldehyde and propyzamide. Metazachlor saw the greatest range of K_2 between 0.004 - 1.717 µg g^{-1} min^{-1}.

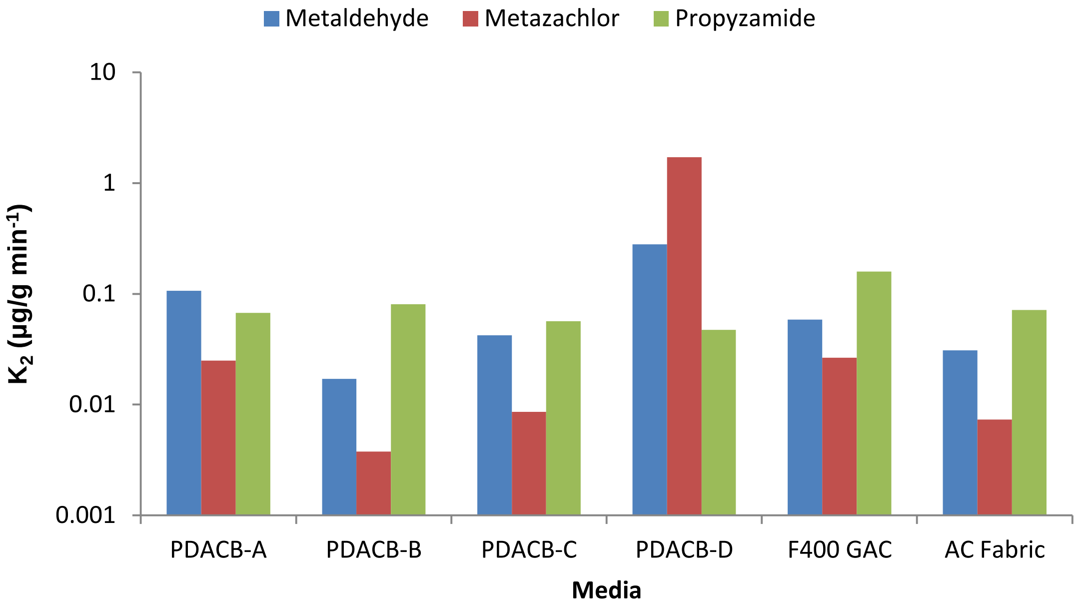

Figure 0.4 - A comparison of the K_2 values determined for each medium for the three pesticides: metaldehyde, metazachlor and propyzamide

Not all of the media were included in the analysis of K_2 and media property due to a lack of available data concerning pore sizes for PDACB–A and AC fabric and the fact that particle size was not applicable to the AC fabric. A negative trend was found between rate constants and specific surface area (SSA) (Figure 4.5). This suggests that media with a higher surface area were slower at adsorbing pesticides. This may be to do with the fact that much of this surface area is found on internal surfaces in the form of meso-, micro- and minimicropores (Table 4.2), and so adsorption takes longer due to slower intraparticle diffusion for media with a larger SSA.. This was supported by the results in Figure 4.6 which shows that the rate constant increases with increasing particle size suggesting that in terms of kinetics, a larger outer surface area supports faster adsorption. This outcome is in contrast to the results found by Busquets *et al*., (2014) who saw faster adsorption with smaller particle sizes. However very high concentrations of pesticide were used alongside contact periods of up to 3000 min. This can skew the K value obtained as the inclusion of data points close to equilibrium can act to increase the intercept and decrease the slope and therefore does not give an accurate representation of the kinetic adsorption rate.

The datum derived from the K_2 constants were in agreement with the results found from the film and intraparticle diffusion models in that a larger SSA together with a smaller particle size resulted in a slower kinetic rate. This was due to a higher amount of the surface area being available within the particle whereas the larger particle sizes will have a comparatively lower area of film through which the pesticide will need to travel in order to achieve adsorption as seen from the general trend of higher importance for intraparticle diffusion for the PDACB medium compared to F400 GAC and AC Fabric.

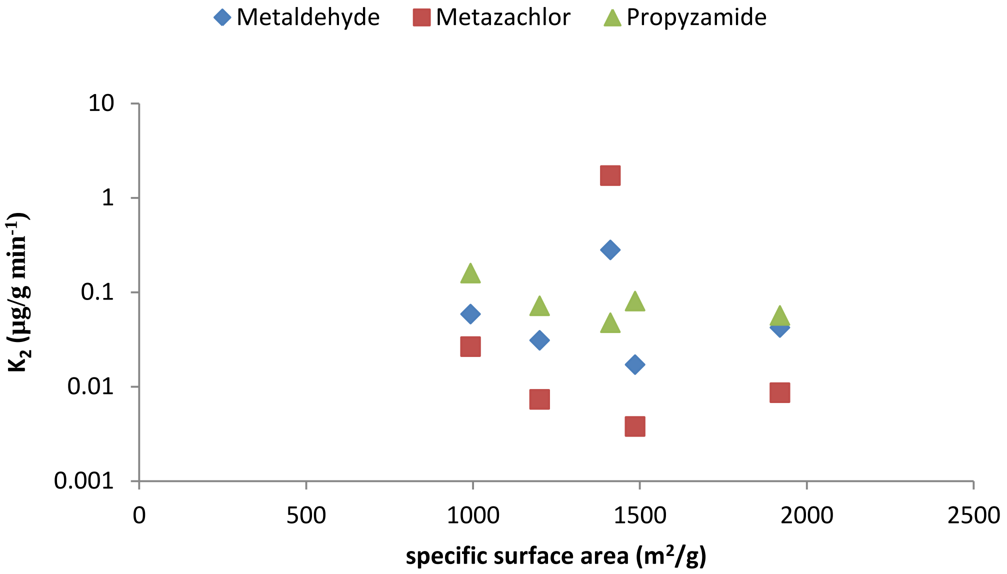

Figure 0.5– Rate constant derived from pseudo second order model vs. specific surface area for five media in DI water individually spiked with three different pesticides. Data shown on the y axis on a log scale to compensate for high K_2 value for PDACB-D in metazachlor spiked solution.

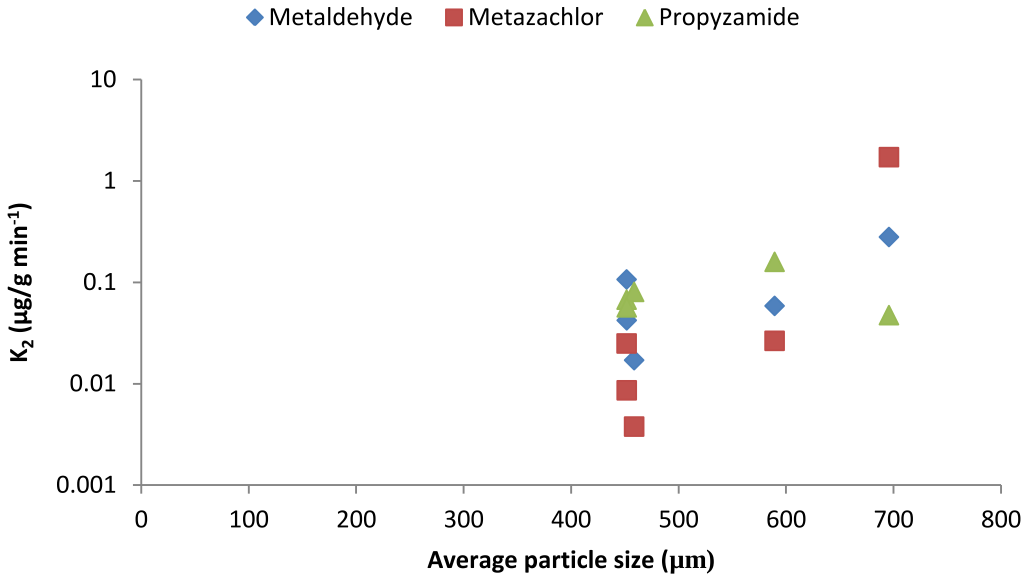

Figure 0.6- Rate constant derived from pseudo second order model vs. average particle size for five media in DI water individually spiked with three different pesticides. Data shown on the y axis on a log scale to compensate for high k value for medium D in metazachlor spiked solution.

Rate constants were also plotted against available pore size distribution data (Figure 4.7). There were no discernible relationships between the pore size distribution of minimicro- micro- or mesopores and the rate constant for metaldehyde and metazachlor. It may be that the availability of macro-pores were an important factor in terms of providing pathways to adsorption sites however this data was not available for the media. However, a positive trend was seen between the micro pore size distributions and the rate constant values for propyzamide which is in line with previous studies (Sorlini *et al*., 2015; Bonvin *et al*., 2016). There was no perceptible relationship between minimicropore size and rate constant or between rate constants and any of the physico-chemical properties of the pesticides tested. These results suggest that there are specific relationships between media property and pesticide property that could not wholly be explained by a single variable.

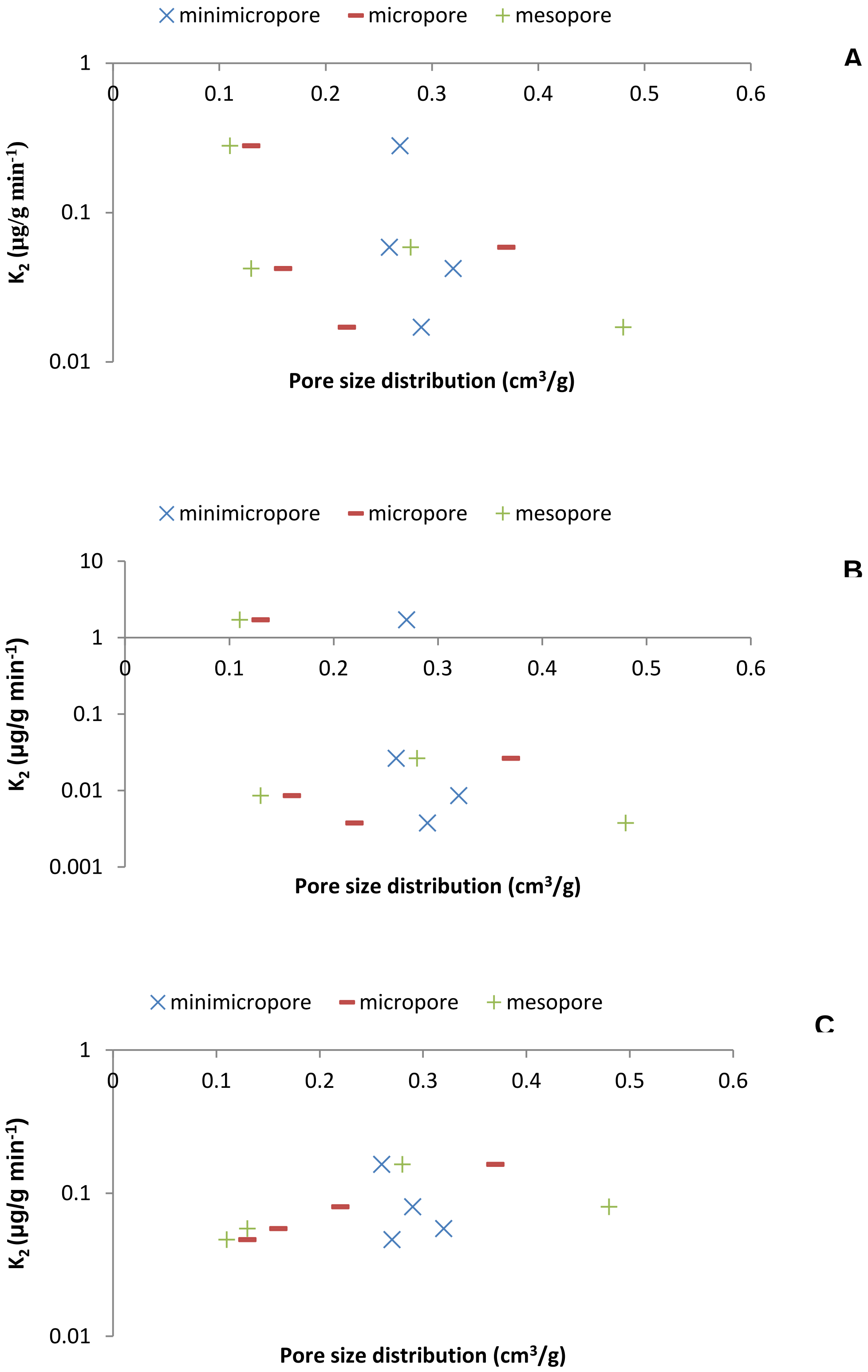

Figure 0.7– Pore size distribution vs. rate constant derived from pseudo second order model for DI water spiked with A) metaldehyde; B) metazachlor; C) propyzamide.

4.5.2 Batch equilibrium tests – Metaldehyde

Metaldehyde was further studied with respect to the amount of pesticide that could be adsorbed by the different media. This pesticide was selected as it presents the expected worst case for adsorption given the high number of drinking water compliance failures observed for metaldehyde in addition to its low log K_{oc} (2.4) value (Busquets *et al*., 2014). The removal of metaldehyde from both DI and raw waters were modelled using both Freundlich and Langmuir isotherms. However, the best fit to the data was the Freundlich model so only these isotherms are presented here (Figures 4.8, 4.9). See Appendix A for Langmuir data fit. Freundlich values were found by plotting the log q_e against log C_e. The Freundlich constant (K_f) is derived from the intercept of the linear regression line through the data. The strong fit of the data to the Freundlich model agrees with results seen for metaldehyde adsorption in other studies (Tao and Fletcher, 2013; Salvestrini *et al*., 2017).

These results suggests that multi-layered rather than single layer adsorption occurred for metaldehyde on to the various AC media (Crittenden *et al*., 2012). The K_f differences between DI and raw water (Table 4.3) show that raw water negatively affects the capacity for pesticide adsorption for all media; however the most significant differences were seen for PDACB–D where the capacity (K_f) reduced from 2960.74 to 14.89 (µg g^{-1})(µg L^{-1})$^{1/n}$ a reduction of 99.5%, and F400 GAC where the K_f decreased from 1189.05 to 81.32 (µg g^{-1})(µg L^{-1})$^{1/n}$ a reduction of 93.2%.

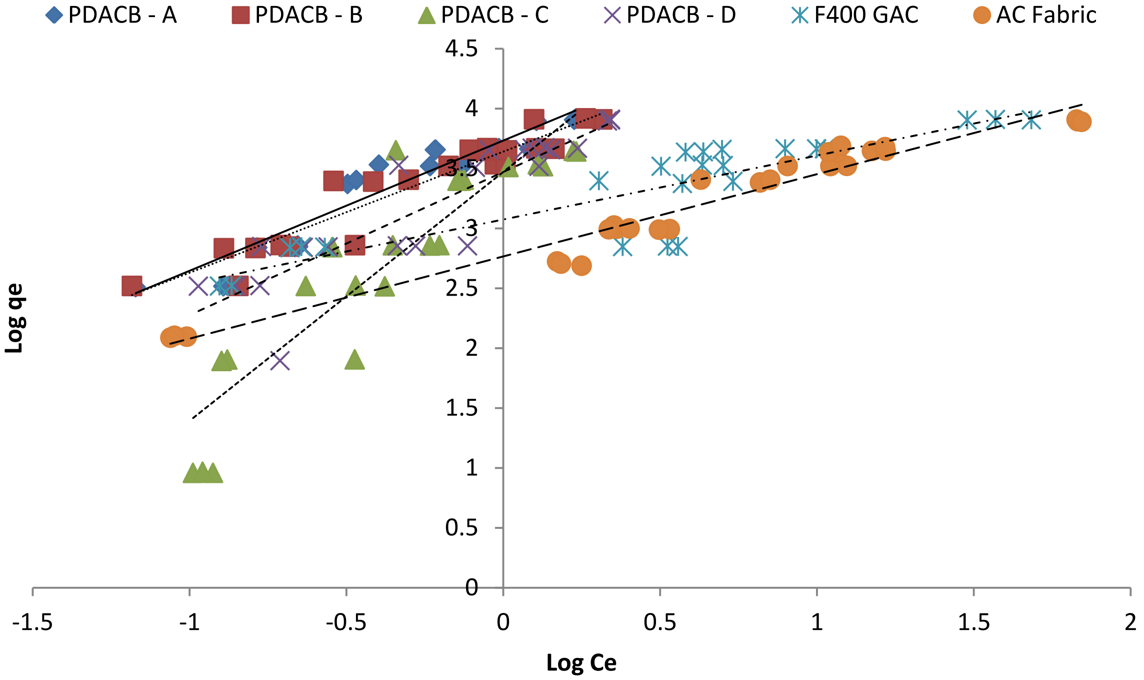

Figure 0.8– Freundlich isotherms for metaldehyde adsorption in DI water

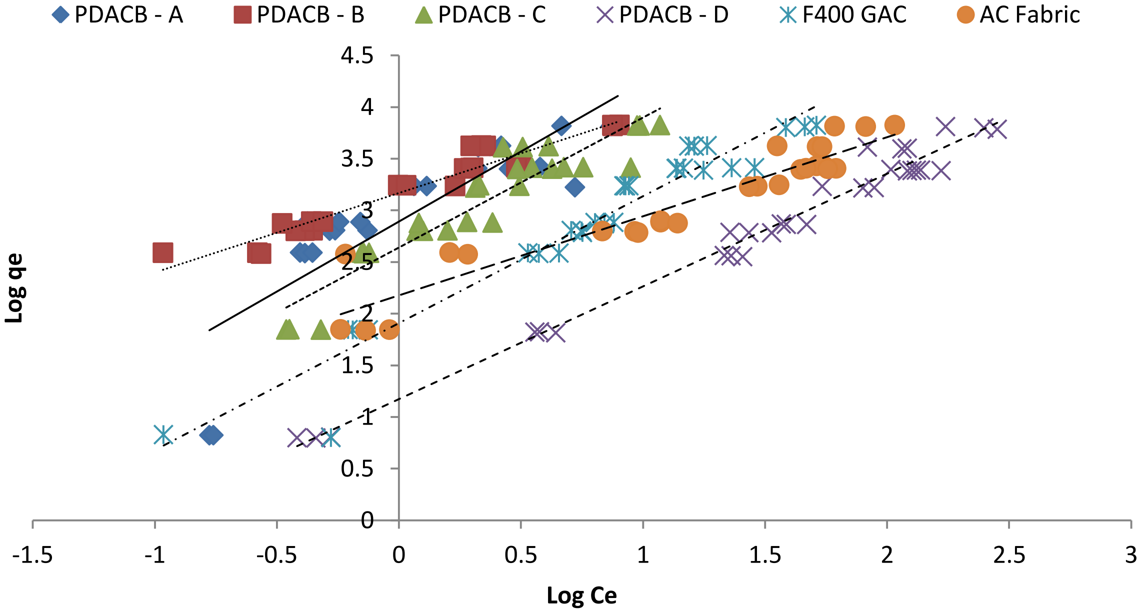

Figure 0.9– Freundlich isotherms for metaldehyde in raw water.

The media least affected by competing components in the raw water for metaldehyde adsorption were PDACB–B, where the K_f reduction was from 4383.29 to 1469.6 (μg g^{-1})(μg L^{-1})$^{1/n}$, a reduction of 66.5%; PDACB–C which saw a reduction in K_f from 2956.65 (μg g^{-1})(μg L^{-1})$^{1/n}$, to 436.01 (μg g^{-1})(μg L^{-1})$^{1/n}$ a reduction of 85.3%; and AC fabric where K_f reduction was from 583.98 (μg g^{-1})(μg L^{-1})$^{1/n}$ to 150.18 (μg g^{-1})(μg L^{-1})$^{1/n}$, a reduction of 74.3%.A comparison of the K_f constants show that the highest K_f rates were seen for the PDACB in DI water with values between 2956.65 – 5421.26 (μg g^{-1})(μg L^{-1})$^{1/n}$ and the lowest K_f was seen for PDACB–D and F400 GAC in raw water with values of 14.89 and 81.82(μg g^{-1})(μg L^{-1})$^{1/n}$ respectively (Figure 4.10).

The 1/n values greater than 1 are indicative of an S-type isotherm where slow uptake is seen at low concentrations followed subsequently by high uptake which then evens off as concentrations increase further (Ok *et al*., 2016). This was the case for PDACB–A to D in DI water and PDACB–A,C, D and F400 GAC in raw water. 1/n values less than 1 indicate an L-type isotherm whereby the adsorption decreases over time. This was seen for media F400 GAC and AC fabric in raw water and PDACB–B and AC fabric in raw water (Baskaran and Kennedy, 1999; Ng *et al*., 2017).

Table 0.3– Freundlich isotherm data for metaldehyde removal from DI and raw water

Medium	DI			Raw			
	1/n	*K_f* (μg g^{-1})(μg L^{-1})$^{1/n}$	R^2	1/n	*K_f* (μg g^{-1})(μg L^{-1})$^{1/n}$	R^2	Difference *K_f* (μg g^{-1})(μg L^{-1})$^{1/n}$
PDACB - A	1.19	5421.3	0.90	1.36	779.8	0.74	4641.4
PDACB - B	1.01	4383.3	0.90	0.77	1469.6	0.93	2913.7
PDACB - C	2.08	2956.7	0.81	1.26	436.0	0.88	2520.6
PDACB - D	1.19	2960.7	0.80	1.09	14.9	0.98	2945.9
F400 GAC	0.53	1189.1	0.77	1.23	81.3	0.94	1107.7
AC Fabric	0.69	584.0	0.95	0.77	150.2	0.89	433.8

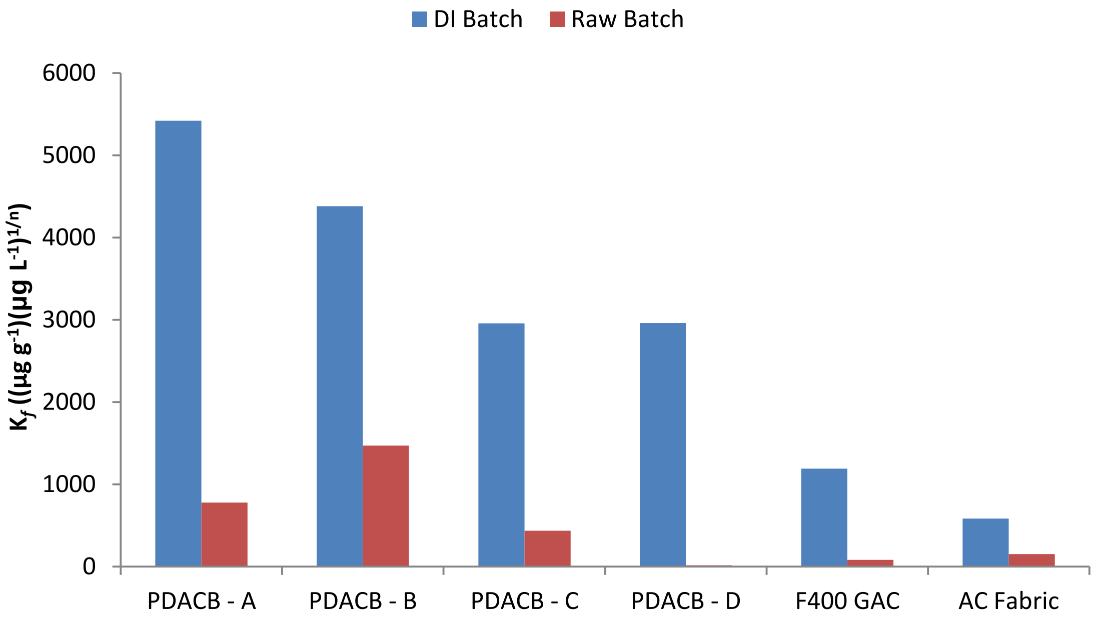

Figure 0.10 – *K_f* constant comparison for metaldehyde adsorption for Freundlich isotherms from batch test data in DI and raw waters for six AC based media

The Freundlich constants derived from the isotherms were plotted against properties of the AC media tested (Figure 4.11, 4.12). A higher adsorption capacity was found alongside an increase in SSA (Figure 4.11) which is in line with previous research (Arefieva *et al*., 2015; Salvestrini *et al*., 2017) as there are more available adsorption sites for adsorption to occur. The presence of raw water caused a decrease in the amount of adsorption that occurred likely due to competition for adsorption spaces from organic components found in the raw water.

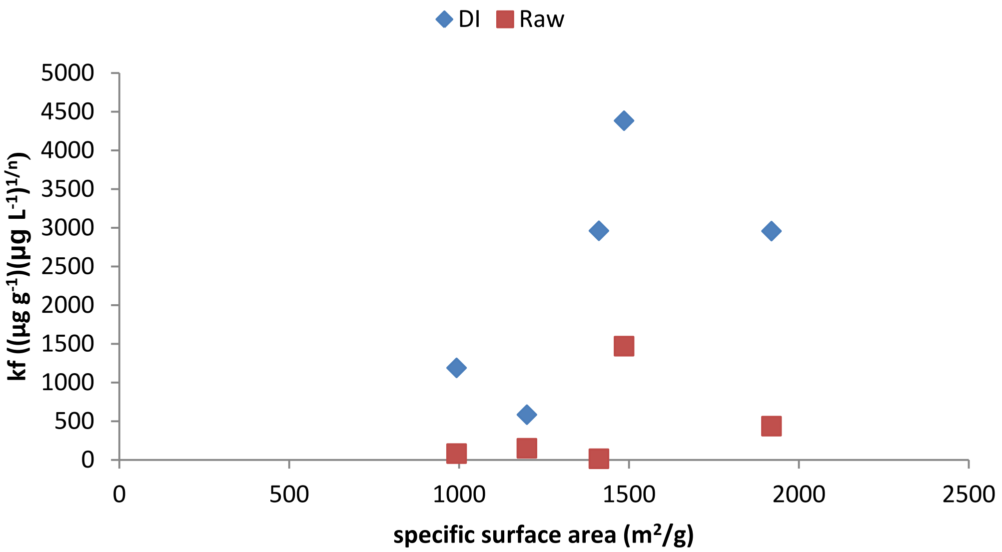

Figure 0.11– Freundlich constants derived from Freundlich isotherm data for metaldehyde adsorption against SSA of AC based media in DI and raw waters

No significant difference was seen between average particle size and adsorption capacity in DI water, however an increase in the average particle size had a negative effect on the amount of adsorption that occurred in raw water (Figure 4.12). This was likely to be due to the fact that the media which had the largest particle sizes also had the lowest SSAs. In addition, the largest particle sizes also had the lowest volume of minimicropores (Table 4.2). These factors together resulted in lower rate constants. Furthermore, the raw water had a significant negative effect on the rate of adsorption of metaldehyde indicating that PDACB-D was more impacted by the organic matter found in raw water.

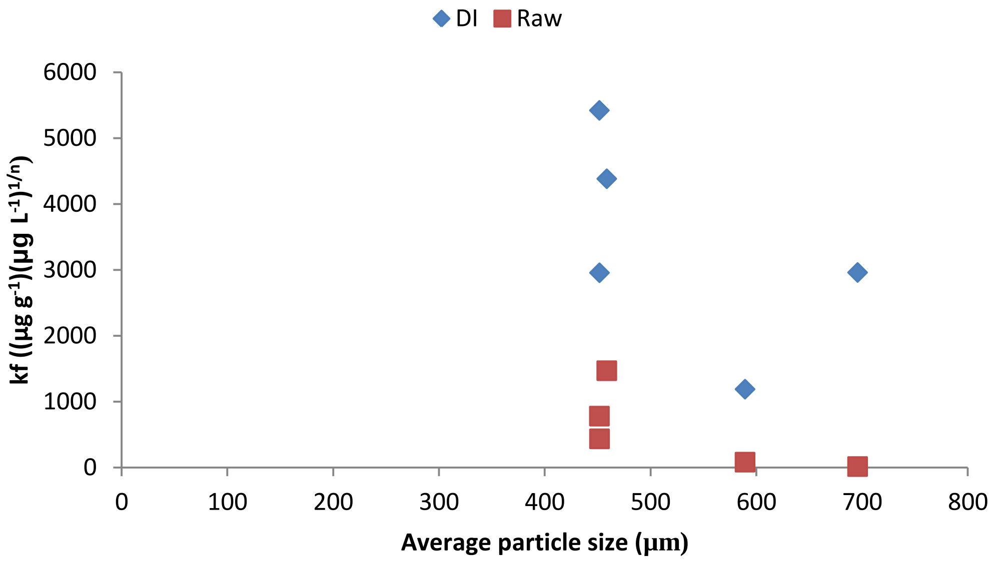

Figure 0.12– Freundlich constants derived from Freundlich isotherm data for metaldehyde adsorption against average particle size of AC based media in DI and raw water

No significant relationships were seen between the rate constant and the pore size distribution or the physico-chemical properties of metaldehyde.

AC fabric and F400 GAC showed the quickest adsorption, however PDACB–A to C showed the greatest capacity. Although both kinetic uptake and adsorption capacity are both important factors to consider, thought must also be given to how each individual medium would be applied into an agricultural environment. The following section considers the practicality of using the described medium in environmental settings.

4.5.3 Practicality of using adsorption media for application into farm drainage systems

The applicability and practicality of the media is another important factor that must be considered when looking at media application outside of a controlled WTW environment. It is likely that the bead and granular media would be best applied in a fixed bed as part of a constructed wetland. This is expected to be the best application method for the medium into the agricultural environment. This would enable an adsorption medium to remove pesticides from the water in the period shortly after run-off into drainage systems has occurred. Due to its flexible nature, there are multiple ways by which the AC fabric could be applied. For example it could be adapted into a removable filter that could be used at any suitable and accessible point in the farm drainage system such as drainage ditches dependent upon the filter design. Agricultural run-off can occur at high flow rates, for example flow rates up to 100 L s^{-1} were recorded by Bouchard *et al*., (1995) at a wetland-pond system collecting agricultural run-off. The addition of particulate adsorption media in a fixed bed are therefore vulnerable to significant headlosses at such high flow rates. Headlosses have been calculated for a 255 m^2 bed, the size of a typical farm pond, using the Kozeny Carmen equation (Equation 4.9) for a range of flow rates (Crittenden *et al*., 2012). Calculations were made for all of the particulate media (Table 4.4).

$$H_L = K_v \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{\mu L v}{\rho w g d^2} + K_I \frac{1-\varepsilon}{\varepsilon^3} \frac{L v^2}{g d}$$ **Equation 0.9**

H_L denotes headloss; K_v is the headloss coefficient due to viscous forces; K_I is the headloss coefficient due to inertial forces; ε is the porosity of AC, (assumed to be 0.641 according to the GAC porosity value used by Creek and Davidson (2000)); μ is the viscosity of water at a standard 10°C which was 0.0013 kg (m s) $^{-1}$ (Judd, 2013); L is the depth of medium assumed to be 0.5 m; v is the flow velocity (m s^{-1}); d is the diameter of the medium particle (m); g is acceleration due to gravity (9.8 m s^{-2}) and ρw is the density of water (999.73 kg m^{-3} at 10°C).

Headlosses of up to 1.5 m were considered to be manageable based on maximum potential headroom available in a constructed wetland for treatment of low to moderate strength effluents (i.e. diluted) (Macenzie and Mcllwraith, 2015). This headloss was breached at flows >10 L s^{-1}, increasing rapidly above 20 L s^{-1} (Figure 4.13). This is an issue as increased pesticide loads in run-off is commonly linked to storm events where flow rates above 30 L s^{-1} are typical (chapter 3) (Thomas *et al*., 2001; Borah *et al*., 2004, 2007; Stuart *et al*., 2012). Flow rates will vary between locations dependent upon the local conditions, such as the field slope, area being drained and soil conditions. Therefore large run-off events resulting in fast flow rates >10 L s^{-1} are less likely to receive treatment from adsorption by a bed containing the PDACB medium or the F400 GAC and would cause flooding or need an unfeasibly large area to hold storm water. While headloss calculations were not carried out for the Fabric AC, this medium could be configured into orientations that enabled a high degree of water conductivity and low headloss but also a large surface area contacting the water.

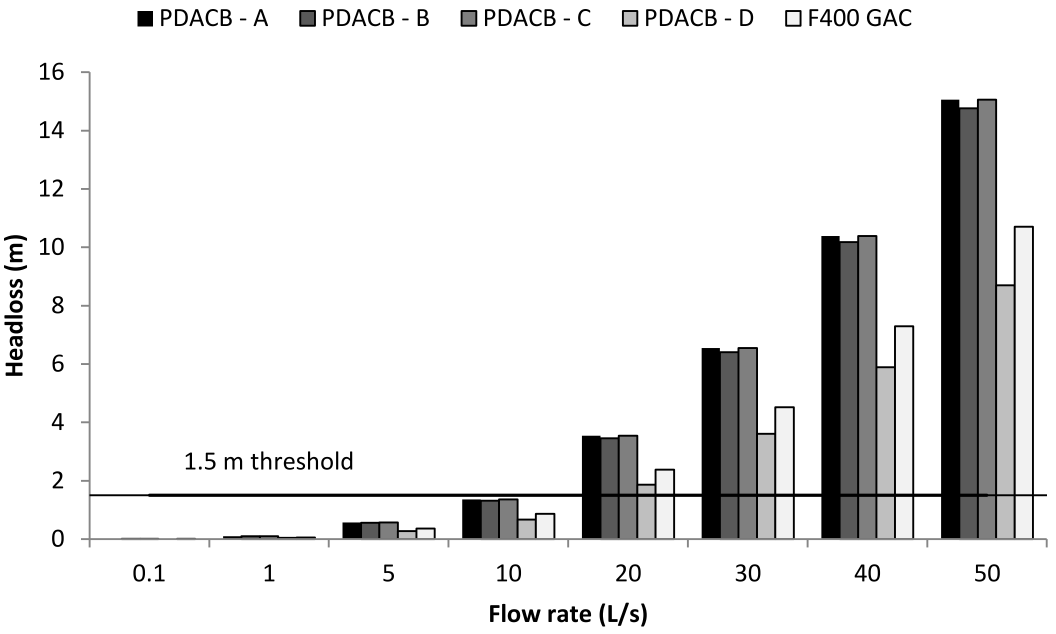

Figure 0.13– Calculated headlosses for each medium at different flow rates

Although the PDACB had the highest capacity for adsorbing pesticides, they were the slowest in the kinetics tests. This means that they would need a longer contact time to achieve effective adsorption and therefore a greater volume in which to hold the water would be required. Additionally the small size (<1 mm) of the PDACB and the GAC media would make it difficult to retain them in one place. Any containment structure would be an additional barrier to adsorption, as it would need to be strong enough to prevent breakage or piercing from debris caught up in the drainage system. In addition to this, the containment material must also be porous enough to allow easy and fast entrance for the water to avoid large headlosses and subsequent flooding. An increase of the bead size results in less capacity, although faster uptake due to the decrease of surface area to volume ratio. The capacity of the largeest bead size PDACB-D (696 μm) was also much more affected by raw water constituents and increasing the bead size would be the only environmentally safe way in which this medium could be used in the field. As a result PDACB were deemed not suitable for use in an in-field treatment system. The F400 GAC worked well in both the capacity and kinetics tests however again, it suffered the greatest decrease in performance when the raw water was treated and so would not be a favourable option under raw water conditions. The results of this study indicate that the AC fabric may be the best compromise with respect to capacity, uptake speed and applicability in the field environment. This was due to the comparatively lower impact of raw water on its adsorption performance alongside the potential flexibility in terms of different possible configurations of its application.

4.6 Conclusion

In conclusion, PDACB had the best adsorption capacity for metaldehyde although their small size would make it difficult to deploy them within an agricultural environment in a way by which they could be sufficiently contained. An increase in bead size appeared to result in a reduction in adsorption capacity, particularly in raw water. F400 GAC and AC fabric showed the fastest adsorption kinetics for the pesticides tested. However F400 GAC, like the PDACB, had a small particle size and thus would be subject to high headlosses at increased flow rates if used at velocities typically seen during storm events. AC fabric provided the best overall compromise of adsorbent capabilities in terms of the range of pesticides it can adsorb, its capacity, speed of uptake, performance in raw water and its potential practical applicability within an agricultural environment. The application of AC fabric may be able to overcome the headloss issue by offering an increased contact surface area under higher flow rates when pesticide risk is at its greatest as its use is not dependent on being used in a filter bed.

4.7 References

Arefieva, O.D., Zemnukhova, L.A., Morgun, N.P., Rybin, V.G., Tsvetnov, M.A., Kovshun, A.A. and Panasenko, A.E. (2015) ‘Removal of (2,4-dichlorophenoxy) acetic acid from aqueous solutions using low-cost sorbents’, *Air, Soil and Water Research*, 8, pp. 59–65.

Baskaran, S. and Kennedy, I.R. (1999) ‘Sorption and desorption kinetics of diuron, fluometuron, prometryn and pyrithiobac sodium in soils’, *Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes*, 34(6), pp. 943–963.

Bonvin, F., Jost, L., Randin, L., Bonvin, E. and Kohn, T. (2016) ‘Super-fine powdered activated carbon (SPAC) for efficient removal of micropollutants from wastewater treatment plant effluent’, *Water Research*, 90, pp. 90–99.

Borah, D.K., Arnold, J.G., Bera, M., Krug, E.C. and Liang, X.-Z. (2007) ‘Storm Event and Continuous Hydrologic Modeling for Comprehensive and Efficient Watershed Simulations’, *Journal of Hydrologic Engineering*, 12(6), pp. 605–616.

Borah, D.K., Bera, M. and Xia, R. (2004) ‘Storm Event Flow and Sediment Simulations in Agricultural Watersheds using DWSM’, *American Society of Agricultural Engineers*, 47(2003), pp. 1539–1560.

Bouchard, R., Higgins, M. and Rock, C. (1995) ‘Using constructed wetland-pond systems to treat agricultural runoff: A watershed perspective’, *Lake and Reservoir Management*, 11(1), pp. 29–36.

Boudesocque, S., Guillon, E., Aplincourt, M., Martel, F. and Noël, S. (2008) ‘Use of a Low-Cost Biosorbent to Remove Pesticides from Wastewater’, *Journal of Environment Quality*, 37(2), pp. 631–638.

Busquets, R., Kozynchenko, O.P., Whitby, R.L.D., Tennison, S.R. and Cundy, A.B. (2014) ‘Phenolic carbon tailored for the removal of polar organic contaminants from water: a solution to the metaldehyde problem?’, *Water Research*, 61, pp. 46–56.

Clarke, A. (2014) Campaign aims to save key oilseed rape herbicides, *Farmers Weekly*.

Creek, D. and Davidson, J. (2000) *Granular Activated Carbon*. California.

Crittenden, J.C., Rhodes Trussell, R., Hand, D.W., Howe, K.J. and Tchobanoglous, G. (2005) *Water Treatment: Principles and Design*. 2nd ed. New Jersey: John Wiley & Sons, Inc.

Crittenden, J.C., Rhodes Trussell, R., Hand, D.W., Howe, K.J. and Tchobanoglous, G. (2012) 'Adsorption', in *MWH's water treatment: principles and design*. 3rd ed. John Wiley & Sons, Inc, pp. 1117–1262.

Drinking Water Inspectorate (2016) *Annual Report., DWI Annual Report* Available at: http://www.dwi.gov.uk/about/annual-report/index.htm (Accessed: 13 June 2016).

Ferenczi, J., Ambrus, A., Wauchope, R.D. and Sumner, H.R. (2002) 'Persistence and runoff losses of 3 herbicides and chlorpyrifos from a corn field.asp.pdf'*, Journal of Environmental Science and Health*, B37(3), pp. 211–224.

Gakuba, E., Moodley, B., Ndungu, P. and Birungi, G. (2018) 'Partition distribution of selected organochlorine pesticides in water, sediment pore water and surface sediment from umngeni river, kwazulu-natal, south africa', *Water*, 44(2), pp. 232–249.

Borah, D.K., Arnold, J.G., Bera, M., Krug, E.C. and Liang, X.-Z. (2007) 'Storm Event and Continuous Hydrologic Modeling for Comprehensive and Efficient Watershed Simulations', *Journal of Hydrologic Engineering*, 12(6), pp. 605–616.

Borah, D.K., Bera, M. and Xia, R. (2004) 'Storm Event Flow and Sediment Simulations in Agricultural Watersheds using DWSM', *American Society of Agricultural Engineers*, 47(2003), pp. 1539–1560.

Golea, D. (2018) *Resilient small water treatment works*. PhD Cranfield University.

HGCA (2009) *Oilseed rape herbicides and water protection* HGCA, Warwickshire

Holvoet, K.M.A., Seuntjens, P. and Vanrolleghem, P.A. (2007) 'Monitoring and modelling pesticide fate in surface waters at the catchment scale', *Ecological Modelling*, 209(1), pp. 53–64.

Jonsson, J., O'Donoghue, N., Blaney, R. and Silver, J. (2016) *Evaluation of emergent adsorbent based process for removal of metaldehyde and other problem organic micropollutants - Phase 2 Saratech Final Report*. Swindon.

Judd, S. (2013) *Watermaths*. 2nd ed. Bedfordshire: Judd & Judd Ltd.

Jusoh, A., Hartini, W.J.H., Ali, N. and Endut, A. (2011) 'Study on the removal of pesticide in agricultural run off by granular activated carbon', *Bioresource Technology*, 102(9), pp. 5312–5318.

Kreuger, J. (1998) 'Pesticides in stream water within an agriculture catchment in southern Sweden, 1990-1996', *The Science of the Total Environment*, 216, pp. 227–251.

Lian, F., Xing, B. and Zhu, L. (2011) 'Comparative study on composition, structure, and adsorption behavior of activated carbons derived from different synthetic waste polymers', *Journal of Colloid and Interface Science*, 360(2), pp. 725–730.

Lowell, S., Shields, J.E., Thomas, M.A. and Thommes, M. (2004) *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*. New York: Springer Science+Buisness Media.

Lu, Q. and Sorial, G.A. (2004) 'The role of adsorbent pore size distribution in multicomponent adsorption on activated carbon', *Carbon*, 42(15), pp. 3133–3142.

Macenzie, S.M. and McIlwraith, C.L. (2015) *Constructed farm wetlands* Wildfowl and Wetlands Trust.

Mamta, Rao, R.J. and Wani, K.A. (2015) ‘Monitoring of organochlorine and organophosphorus pesticide residues in water during different seasons of Tighra reservoir Gwalior, Madhya Pradesh, India’, *Environmental Monitoring and Assessment*, 187(11) pp. 1–14

Mohr, S., Berghahn, R., Feibicke, M., Meinecke, S., Ottenströer, T., Schmiedling, I., Schmiediche, R. and Schmidt, R. (2007) ‘Effects of the herbicide metazachlor on macrophytes and ecosystem function in freshwater pond and stream mesocosms.’, *Aquatic Toxicology*, 82(2), pp. 73–84.

Nethaji, S., Sivasamy, A. and Mandal, A.B. (2013) ‘Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass’, *International Journal of Environmental Science and Technology*, 10(2), pp. 231–242.

Ng, K.C., Burhan, M., Shahzad, M.W. and Ismail, A. Bin (2017) ‘A Universal Isotherm Model to Capture Adsorption Uptake and Energy Distribution of Porous Heterogeneous Surface’, *Scientific Reports*, 7(1), pp. 1–11.

Njoku, V.O., Asif, M. and Hameed, B.H. (2015) ‘2,4-Dichlorophenoxyacetic acid adsorption onto coconut shell-activated carbon: isotherm and kinetic modeling’, *Desalination and Water Treatment*, 55(1), pp. 132–141.

Ok, Y. S., Uchimiya, S. M., Chang, S. X. and Bolan, N. (eds.) (2016) *Biochar: Production, Characterization and Applications.* CRC Press.

Pérez, D.J., Okada, E., De Gerónimo, E., Menone, M.L., Aparicio, V.C. and Costa, J.L. (2017) ‘Spatial and temporal trends and flow dynamics of glyphosate and other pesticides within an agricultural watershed in Argentina’, *Environmental Toxicology and Chemistry*, 36(12), pp. 3206–3216.

PPDB (2014) *University of Hertfordshire Pesticide Properties Database*. Available at: http://sitem.herts.ac.uk/aeru/ppdb/en/ (Accessed: 17 November 2014).

Qiu, H., Lv, L., Pan, B., Zhang, Q., Zhang, W. and Zhang, Q. (2009) ‘Critical review in adsorption kinetic models’, *Journal of Zhejiang University-SCIENCE A*, 10(5), pp. 716–724.

Saha, A., Shabeer, A.T.P., Gajbhiye, V.T., Gupta, S. and Kumar, R. (2013) ‘Removal of mixed pesticides from aqueous solutions using organoclays: evaluation of equilibrium and kinetic model.’, *Bulletin of Environmental Contamination and Toxicology*, 91(1), pp. 111–6.

Salvestrini, S., Vanore, P., Bogush, A., Mayadevi, S. and Campos, L.C. (2017) ‘Sorption of metaldehyde using granular activated carbon’, *Journal of Water Reuse and Desalination*, 7(3), pp. 280–287.

Sanchez Lopez, S. (2017) *Metaldehyde treatability by dissolved air floatation combined with powdered activated carbon adsorption*. MSc, Cranfield University.

Saucier, C., Adebayo, M.A., Lima, E.C., Cataluña, R., Thue, P.S., Prola, L.D.T., Puchana-Rosero, M.J., Machado, F.M., Pavan, F.A. and Dotto, G.L. (2015) ‘Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents’, *Journal of Hazardous Materials*, 289, pp. 18–27.

Shi, H., Cheng, X., Wu, Q., Mu, R. and Ma, Y. (2012) ‘Assessment and Removal of Emerging Water Contaminants’, *Environmental and Analytical Toxicology*, 2(7), pp. 1-14.

Silburn, D.M., Foley, J.L. and deVoil, R.C. (2013) ‘Managing runoff of herbicides under rainfall and furrow irrigation with wheel traffic and banded spraying’, *Agriculture, Ecosystems and Environment*, 180, pp. 40–53.

Smith, R., Middlebrook, R., Turner, R., Huggins, R., Vardy, S. and Warne, M. (2012) ‘Large-scale pesticide monitoring across Great Barrier Reef catchments--Paddock to Reef Integrated Monitoring, Modelling and Reporting Program.’, *Marine pollution bulletin*, 65(4–9), pp. 117–27.

Sorlini, S., Collivignarelli, M.C. and Canato, M. (2015) ‘Effectiveness in chlorite removal by two activated carbons under different working conditions: A laboratory study’, *Journal of Water Supply: Research and Technology - AQUA*, 64(4), pp. 450–461.

Stuart, M., Lapworth, D., Crane, E. and Hart, A. (2012) ‘Review of risk from potential emerging contaminants in UK groundwater.’, *The Science of the Total Environment*, 416, pp. 1–21.

Tao, B. and Fletcher, A.A.J. (2013) ‘Metaldehyde removal from aqueous solution by adsorption and ion exchange mechanisms onto activated carbon and polymeric sorbents’, *Journal of Hazardous Materials*, 244–5(1), pp. 240–250.

Tediosi, A., Whelan, M.J., Rushton, K.R., Thompson, T.R.E., Gandolfi, C. and Pullan, S.P. (2012) ‘Measurement and conceptual modelling of herbicide transport to field drains in a heavy clay soil with implications for catchment-scale water quality management.’, *The Science of the Total Environment*, 438, pp. 103–12.

Thomas, K. V., Hurst, M.R., Matthiessen, P., Sheahan, D. and Williams, R.J. (2001) ‘Toxicity characterisation of organic contaminants in stormwaters from an agricultural headwater stream in South East England’, *Water Research*, 35(10), pp. 2411–2416.

Twining, S., Clarke, J., Harris, D., Wynn, S. and Peers, D. (2009) *Future of UK winter oilseed rape production*. United Kingdom.

Voluntary Initiative (2015) *The Voluntary Initiative: Promoting responsible pesticide use*. Available at: http://www.voluntaryinitiative.org.uk/en/home (Accessed: 20 September 2015).

Vymazal, J. and Březinová, T. (2015) ‘The use of constructed wetlands for removal of pesticides from agricultural runoff and drainage: A review’, *Environment International*, 75, pp. 11–20.

5 Application of activated carbon fabric for the removal of metaldehyde from dynamic aqueous systems

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5.1 Abstract

The use of granular activated carbon (GAC) as an adsorbent is common for the treatment of polluted waters. However, GAC is not suitable for use outside of a water treatment plant for treatment of high flows in environmental settings due to the small size of the granular particles. The small particle size would make particle movement difficult to control and beds of medium would be subject to high headlosses under high flow rates. The research presented here looks at the potential of AC fabric to be used within an agricultural environment for the purpose of pesticide removal during storm events. AC fabric was tested for pesticide removal under dynamic flow rates at both laboratory and pilot scale. Metaldehyde was removed under all conditions culminating in a 46% removal rate over 700 L at pilot scale testing.

5.2 Introduction

The use of pesticides in agriculture is often necessary in order to keep up with the demands of a growing population. This however creates issues for water utility companies in terms of complying to a strict limit of 0.1 µg L^{-1} for pesticides in drinking water, set by the Drinking Water Inspectorate (Drinking Water Inspectorate, 2017). Certain pesticides such as metaldehyde are particularly difficult to remove once they get into solution so can move in relatively high concentrations and can present as shock loads once they reach the treatment works (Giribaldi, 2013; Tao and Fletcher, 2013; Salvestrini, *et al*., 2017). A study of the Thames catchment at the end of 2016 found metaldehyde peaks of up to 0.9 µg L^{-1} in surface waters with previous studies reporting peaks as high as 9.8 µg/L (Kay and Grayson, 2014; NFU, 2017). A report from the Pesticides Forum (2014) stated that metaldehyde is a cause of risk for 20% of drinking water protected areas and contributed towards the failure of good status of groundwater at two UK sites.

The removal of pesticides from water at an agricultural stage is difficult for a number of reasons. Firstly run-off events are associated with high rainfall and in turn increased flows (>10 L s^{-1}) (Maillard *et al*., 2011; Xu, *et al*., 2015). The application of adsorption media such as granular activated carbon (GAC), the standard adsorption medium used by water treatment companies for pesticides removal, at this stage would result in a very high headloss. This in turn would necessitate an extremely high area requirement in order to get the contact time needed to sufficiently remove the pesticides (chapter 4). Due to the often dispersed nature of land ownership, alongside the fact that the UK is a fairly small country with space at a premium, this approach is unlikely to make much headway. There would also be a high cost and energy requirement associated with the application and replacement of the medium once it was exhausted. The exhaustion of the medium would be exacerbated by the presence of other compounds in the water such as humic acid leading to a more regular need for replacement.

The idea of using an AC fabric medium is that it could be applied easily and temporarily in the case of a high rainfall event in the time period following pesticide application. Due to the fact that the AC is in a fabric form, it could be oriented to counteract the high headloss issue that would be caused by the application of granular media and so retain a high surface contact area under greater flow rates. An increased land area may still be required, however because of the greater contact surface area achievable by the AC fabric, this requirement should be lower than that needed for an equivalent GAC bed. It must be noted that the concept of using fabric AC is for it to act as a buffer and reduce peak concentrations so that the pesticides can be better dealt with when they reach the treatment works.

There have been a number of studies looking at catchment management and the modelling of metaldehyde to get better predictability of when it may be an issue in rivers and affect extraction for potable water (Lu, *et al*., 2017; Asfaw, *et al*., 2018). A few studies have explored the use of activated or modified cloths for the purpose of pesticide removal from aqueous mixture at laboratory scale studies (Ayranci and Hoda, 2004, 2005; Abdelhameed *et al*., 2018). Other studies have looked at techniques and means of metaldehyde removal at the water treatment stage such as adsorption by AC and using purpose built adsorption resins (Busquets, *et al*., 2014; Salvestrini *et al*., 2017), advanced oxidation processes using UV/H_2O_2 and UV/TiO_2 (Autin, 2012; Jefferson *et al*., 2016) and biological means of degradation (Thomas *et al*., 2017). This research therefore helps to bridge the gap between these two areas of research in terms of providing a low cost, low energy means of preliminary treatment in the field. This would enable treatment to be maintained at increased flow rates to help reduce pesticide movement in water courses and reduce the impact and loading of pesticides on to water treatment facilities. To the authors knowledge, the use of fabric to remove metaldehyde has not been reported before nor has the use of AC fabric as an in catchment solution.

5.3 Materials and methods

AC fabric was obtained from Calgon Carbon (Tyne & Wear, UK). The fabric was 1 m wide and 1 mm thick and was made from woven fibres of AC (Figure 5.1). The fabric used in this study cost £25.80 per meter. Pesticide standards for metaldehyde were acquired from Sigma-aldrich (Darmstadt, Germany) and made into 1 g L^{-1} stock solutions with DI water (conductivity = 0.05 mS cm^{-1}) and then diluted down to the required test concentration using DI water. Raw water was collected from field run-off from the Cranfield university campus adjacent to the pilot hall building and used for the laboratory scale testing. The run-off flowed into Chicheley Brook which runs alongside campus roads, student accommodation and bordering arable farmland which contained oilseed rape at the time of collection. Characterisation of the raw water revealed a concentration of: TOC 7.1 ± 0.5 mg L^{-1}, NPOC 4.6 ± 0.5 mg L^{-1}, TN 2.7 ± 0.5

mg L^{-1}, UV254 0.14 ± 0.003 AU, pH 7.7. Raw water was also analysed for metaldehyde, metazachlor and propyzamide however no traces of these pesticides were found.

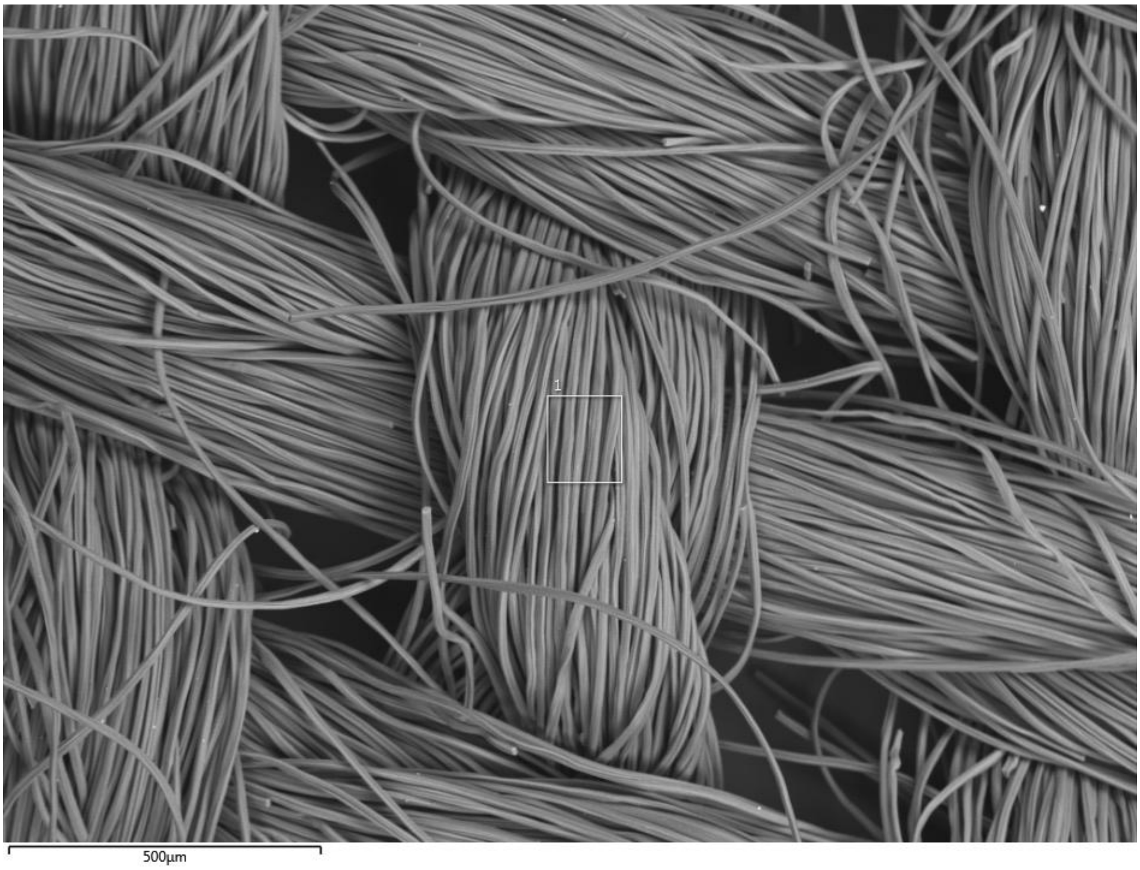

Figure 0.1- Electron microscope image of AC fabric

5.3.1 Laboratory testing

Initial cross flow tests were carried out using a Sterlitech membrane distillation cell (Washington, USA) (Figure 5.2) with flow rates between 0.5 to 2 L min^{-1} using a Watson Marlow 520S peristaltic pump (Falmouth, UK). These tests were carried out in circulating 1 L batches with a starting concentration of 10 µg L^{-1}. The active membrane area was 140 cm^2 (Sterlitech, 2016). A shim (spacer) was used in the setup to give a cross sectional area of 141 mm^2 such that the cross flow velocity was varied between 0.06 and 0.24 m s^{-1}. The permeate outlet was blocked off so that all outlet flow from the cell was from retentate flow across the fabric. Aliquot samples of 1 mL were taken from the batch at timed intervals. Further tests were carried out in recirculated batches with the batch concentration renewed to the 10 µg L^{-1} starting concentration after 100 minutes run time.

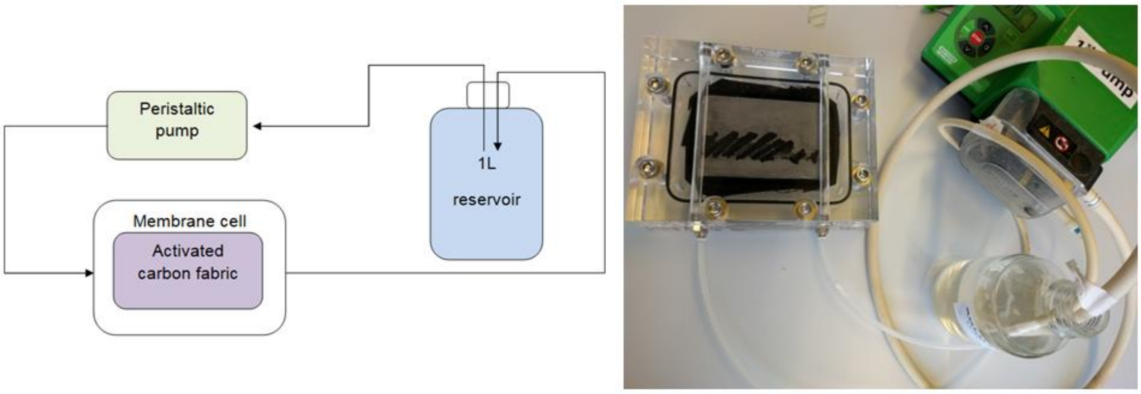

Figure 0.2- Fabric membrane cell setup schematic and photograph

5.3.2 Pilot testing

Pilot scale trials were conducted in a 30 L flume with dimensions of 2.5 m length, 0.1 m wide and 0.12 m water depth controlled by a weir (Figure 5.3). Strips of 0.1 m x 1 m AC fabric were cut and collected into 2 m^2 and 8 m^2 bundles and fixed into the flume to filter the flow of water (Figure 5.4). Plastic beads (5 mm) were used as spacers between fabric sheets in order to maintain an even distribution of fabric across the width of the flume. Bundles were held in place using carabiner clips attached to chains that ran the length of the flume. The carabiner clips attached to short lengths of stainless steel cable which were blocked off at the ends in order to keep the bundles of fabric as distinct packages (Figure 5.4). The flume was operated at flow rates of 2 L min^{-1} and 10 L min^{-1} equivalent to a velocity of 0.003 and 0.014 m s^{-1} at a water level of 120 mm. As such this ensured that the whole fabric area was fully submerged in the water. Raw water was spiked with pesticide to ensure a 10 µg L^{-1} concentration was reached. The solutions were made up as 1000 L batches which were used as a single pass through the flume for each run. After each run, solution from the outlet IBC was pumped back into the inlet IBC and the concentration in the inlet was topped back up to 10 µg L^{-1}. The characteristics of the feed water were measured at the beginning of the trial and revealed concentrations of: TOC 4.6 ± 0.5 mg L^{-1}, NPOC 6.0 ± 0.5 mg L^{-1}, TN 4.5 ± 0.5 mg L^{-1}, pH 9.3, UV254 0.083 ± 0.003 AU, Turbidity 5.27 NTU. Aliquots of 1 mL were taken and filtered in preparation for analysis at timed intervals.

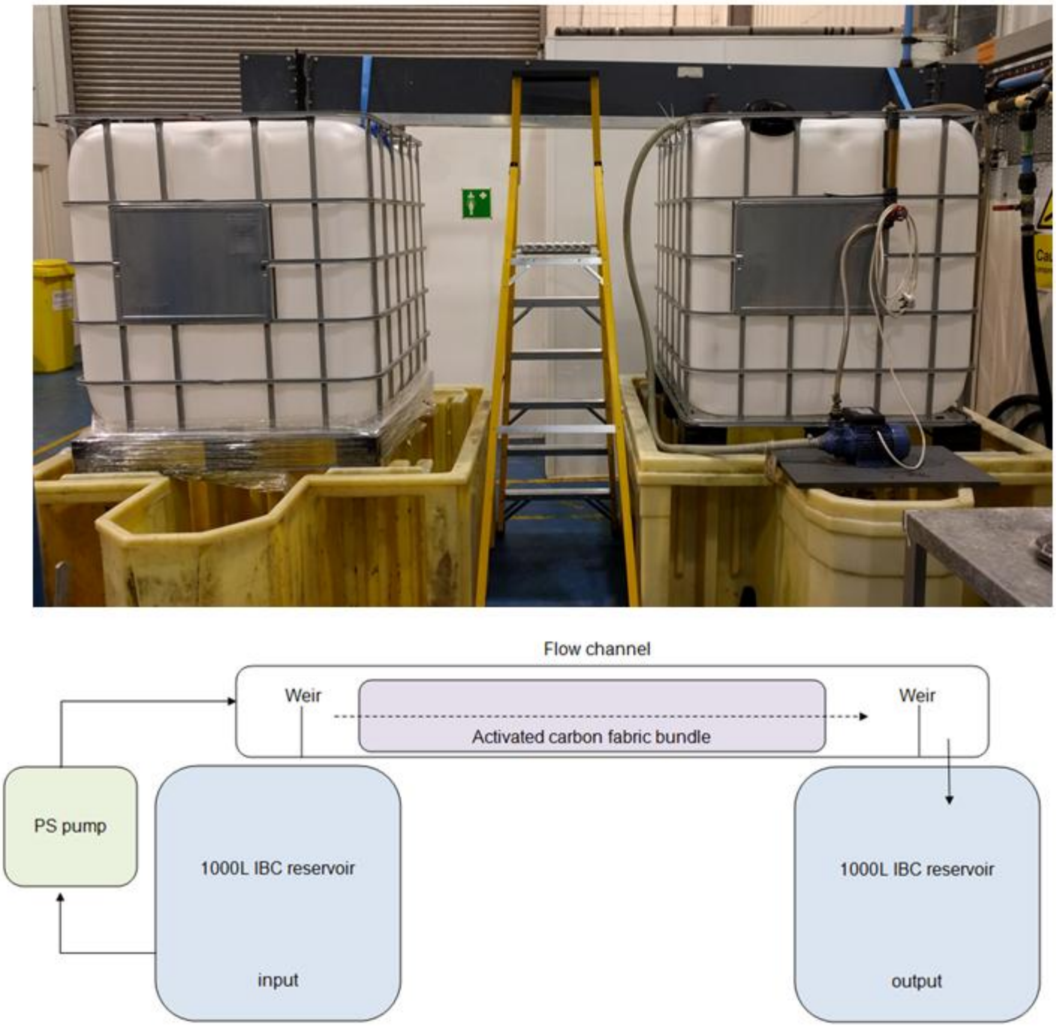

Figure 0.3- Set up of pilot channel and schematic

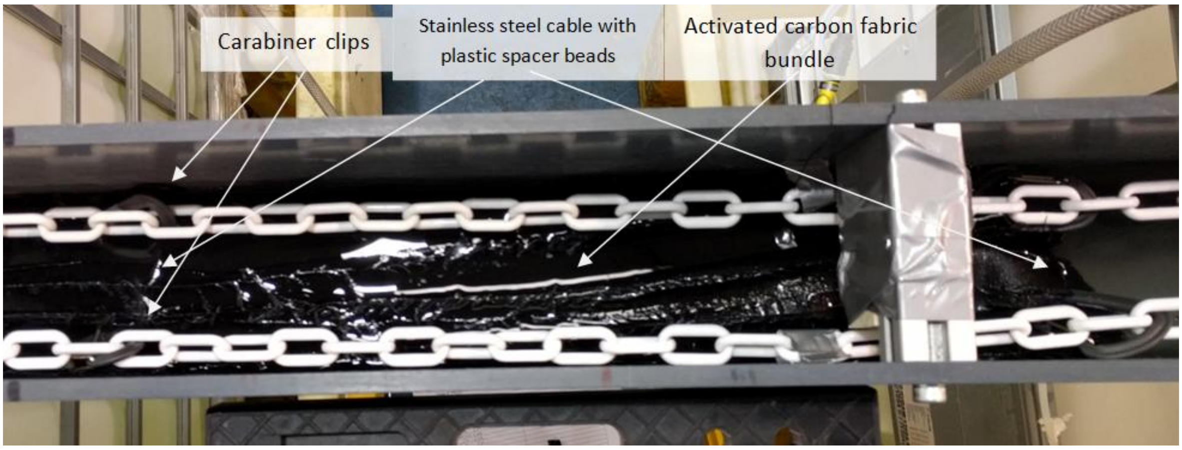

Figure 0.4- Annotated picture of how bundles were attached into the channel using stainless steel cables that punctured the fabric that were attached to chains using carabiner clips to hold the fabric upright in the flow of water. Photograph shows the edge of a 2 m^2 bundle.

5.4 Analysis

Humic acid concentration was measured in terms of UV254 on a Jenway spectrophotometer (Staffordshire, UK). Pesticide analysis was undertaken using a direct injection method on Waters LC-MS/MS, Aquity UPLC-MS/MS and Sciex LC-MS/MS. 1 mL samples were filtered using 0.25 μm filters into glass vials immediately after being taken. Metaldehyde calibration standards for LC-MS/MS methods were carried out within a range of 0.1-10 μg L^{-1}. Quality controls of 5 μg L^{-1} were used throughout the analysis alongside blank standards to ensure accuracy.

5.5 Results and discussion

5.5.1 Laboratory scale tests

The metaldehyde concentration continually decreased across all trials reaching final values of 0.1 μg L^{-1} for the 1 L min^{-1} and 2 L min^{-1} runs and between 0.17 and 0.26 μg L^{-1} for the 0.5 L min^{-1} runs (Figure 5.5). The time required to reach the final levels varied with flowrate such that it was achieved after 3.5, 14 and 56 minutes for the 2, 1 and 0.5 L min^{-1} runs respectively. Accordingly, the 0.014 m^2 of adsorbent fabric treated a total of 7, 14 and 28 L of water before removal of all the available metaldehyde from the batch solution. The equivalent mass removal rates are 0.08, 0.26 and 1.01 μg g^{-1} min^{-1} (15.4, 51.9 and 202.5 μg m^{-2} min^{-1}) indicating that the systems is mass loading limited, as the rate of removal increases as the flowrate was increased. Results from the batch adsorption experiments compared the AC fabric with a commercial GAC (F400) with respective uptake rates of 0.41 and 0.34 μg g^{-1} min^{-1} (chapter 4). Equilibrium and kinetic modelling revealed the AC fabric to follow an L type Freundlich isotherm with the uptake best described through an intraparticle diffusion model (Chapter 4). Equilibrium capacity constants for the AC fabric were 583 μg g^{-1} in DI water reducing to 150 μg g^{-1} in raw water. The equivalent data for F400 was 1189 μg g^{-1} and 81.3 μg g^{-1} respectively indicating that the AC fabric enables fast uptake but had reduced capacity compared to traditional ACs. The total uptake during the current trial using the AC fabric was 3.8 μg g^{-1}, representing 0.32% of the previously measured equilibrium capacity.

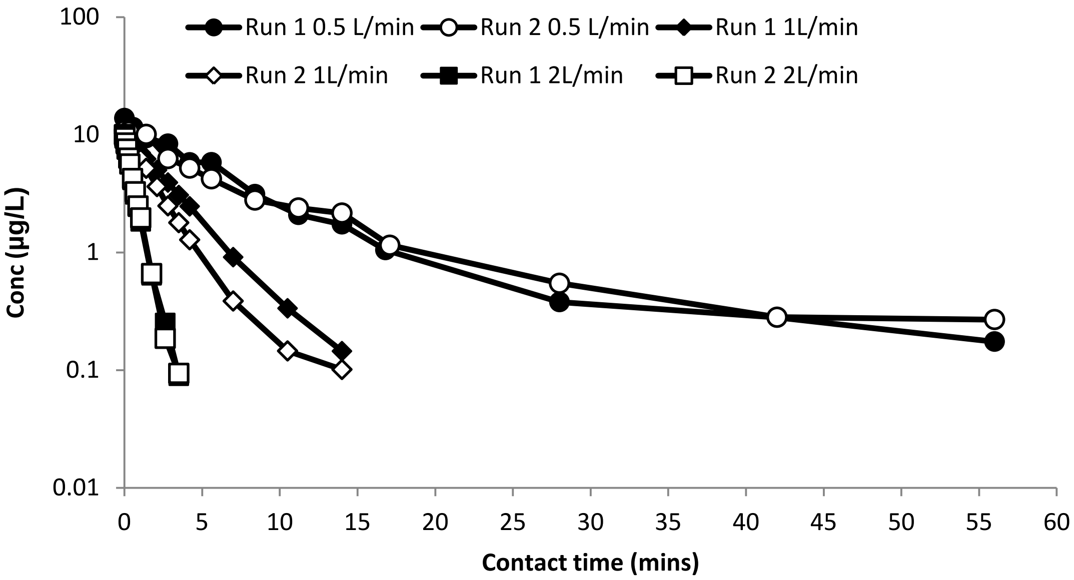

Figure 0.5–Removal of metaldehyde in the membrane flow cell at different flow rates.

The above runs indicated that the metaldehyde uptake rate onto the AC fabric was mass limited and underutilised, implying it could treat substantially more volume. To test this, a single piece of fabric was repeatedly used to treat multiple batches of water containing 10 µg L^{-1} metaldehyde solution. Each cycle consisted of 200 circulations through the membrane and was run at 2 L min^{-1} to give a contact time of 3.5 minutes. Metaldehyde removal continued throughout the fifteen batches tested during the DI water trial, with only a small decrease in uptake such that the overall residual in the batch was 1.4 mg L^{-1} higher at the end of the fifteenth cycle as compared to the first cycle (Figure 5.5). This equates to a residual metaldehyde concentration at the end of each cycle which increased from 0.08 µg L^{-1} after the first cycle to 1.48 µg L^{-1} after the fifteenth cycle demonstrating that the fabric was still effectively removing metaldehyde. Across the whole trial the 0.014 m^2 sheet of fabric removed 138.6 µg of metaldehyde representing a capacity of 9900 µg m^{-2}. The residual concentration was best fitted to a linear regression with the expression:

Residual metaldehyde concentration (µg/L) = 0.0265(contact time (minutes)) + 0.0127

The expression has a regression coefficient (R^2) of 0.989.

The equivalent trials in raw water reduced the uptake of metaldehyde during each cycle, which also decreased in the adsorbed capacity more significantly than observed in the case of DI water (Figure 5.6). To illustrate, the residual metaldehyde concentration in the batch after each set of 200 circulations was 2.2, 4.0, 4.83, 5.86. 6.15 and 6.86 µg L^{-1} for cycles 1 to 6. This equated to a total removal of metaldehyde of 30.1 µg as compared to 57.9 µg during the equivalent six cycles treated in DI water. This equates to a 52% reduction in capacity congruent with competition for adsorption sites from other molecules within the water (Rolph *et al., 2018)*. This, compared with the 74.3% reduction seen during equilibrium batch studies, reflects the impact that kinetics has over the overall affinity of adsorption. The residual metaldehyde concentration after each cycle followed a logarithmic expression with an R^2 of 0.994.

Residual metaldehyde concentration (µg L^{-1}*) = 2.516ln(contact time(min)) - 0.9121*

Applying this expression indicated that during the fifteenth batch cycle, the fabric would remove approximately 1 µg L^{-1} of metaldehyde. This would represent a total metaldehyde removal of 46.21 μg of metaldehyde, equivalent to a capacity of 3300.7 μg m^{-2}. This was only a reduction in capacity to 33.3% as compared to the value obtained in DI water. This was a closer approximation to the reduction seen during the batch trials and a clearer representation of the operational capacity of the AC fabric when used in raw water. Whilst the capacity in raw waters is related to the nature of the other constituents present, previous trials exploring the impact of competitive uptake have indicated that metaldehyde removal tends to be independent of the concentration of the competing species (Rolph *et al,* 2018). As such that the operational capacity reported here can be used as a first approximation for larger scale trials. One reported trial using an AC fabric for pesticide removal, reported a tenfold reduction in the concentration of 2,4-D, metribuzin, bromacil and atrazine after 125 minutes using approximately 0.75 cm^2 of AC cloth (Ayranci and Hoda, 2004). This equates to a capacity of 128.4 g m^{-2} with the concentrations reducing from 10.4 to 1 mg L^{-1} for 2,4-D, 12.2 to 1.2 mg L^{-1} for bromacil, 10.1 to 1 mg L^{-1} for metribuzin and 10.1 to 1 for atrazine (Ayranci and Hoda, 2004). The equivalent equilibrium capacity onto AC for these pesticides varies from 63.8 mg g^{-1} for atrazine to 756.4 mg g^{-1} for metribuzin indicating they have an equivalent range of removal capacity as compared to metaldehyde (Aksu and Kabasakal, 2005; Al Mardini and Legube, 2010; Shirmardi *et al*., 2016; Santana *et al*., 2017)

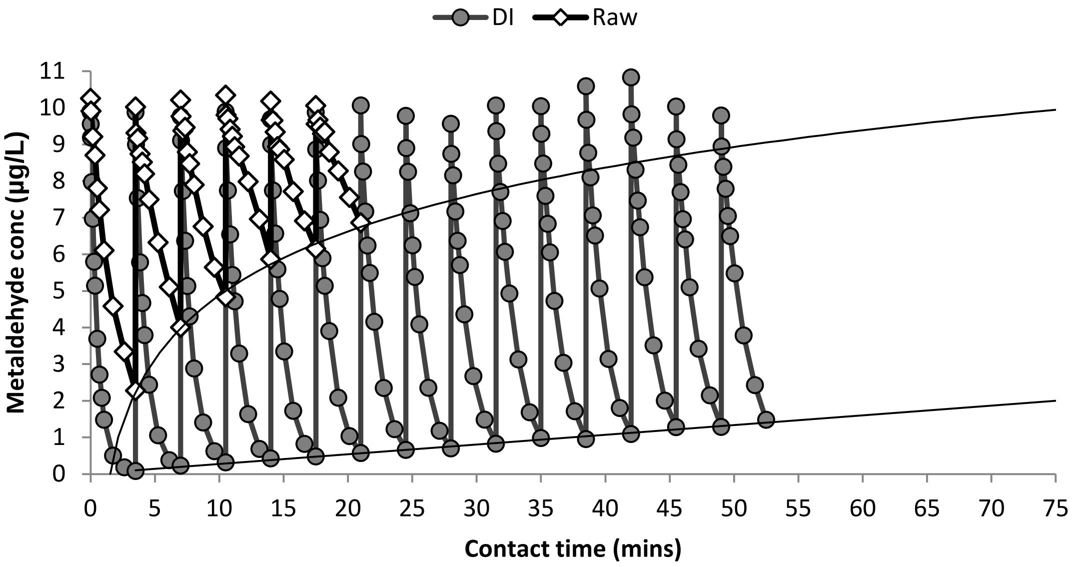

Figure 0.6– Metaldehyde removal from DI and raw water per cycle with a projection of diminishing removal of metaldehyde per subsequent cycles.

5.5.2 Pilot scale tests

Larger scale pilot tests were carried out with 2 m^2 AC fabric at 2 and 10 L min^{-1} flow rates, equivalent to cross flow velocities of 0.003 and 0.014 m s^{-1} and contact time with the medium of approximately 60 and 12 seconds. Contact time would have been longer for the first 30 L of water until the level reached a sufficiently high enough depth to overtop the weir. Subsequent dilution from this initial longer contact period explains the increased dip in concentration level beyond the first 30 L of water treated (Figure 5.7). Metaldehyde was removed throughout treatment of 540 L of water with the concentration initially dropping to a minimum before increasing up to a stabilised value slightly below that of the feed (Figure 5.7). For example, in the case of the first of the 2 L min^{-1} trials, the metaldehyde concentration decreased from an initial level of 11.29 µg L^{-1} to a minimum value of 6.44 µg L^{-1} after a cumulative flow of 10 L before inclining up to a stabilised level of 10.6 - 10.9 μg L^{-1} after 80 L were treated. Increasing the flowrate had no appreciable impact on the removal of metaldehyde with the minimum occurring at the same volume of 10 L reaching concentrations of 6.7 and 7.4 μg L^{-1} during the repeat trials. The stabilised levels were also similar representing an uptake of between 0.7 and 1.8 µg L^{-1} for all flow rates (Figure 5.7). This demonstrates a resilience of uptake to changing flowrates which is likely to be important in field applications. Further, the initial reduction reflects the volume required to fill the channel representing a surrogate of the initial flow of a heavy rainfall event. This again shows the resilience of the fabric to the rate of flow, indicating that kinetic loading is not impacting removal. In total, across the trial, this represents total uptake of 884 μg of metaldehyde, equivalent to a capacity of 442 μg m^{-2} (2.21 μg g^{-1}).

Increasing the area of the fabric in the channel to 8 m^2 had a significant impact on the residual profile. In this case the metaldehyde concentration reached a minimum value of 2.8 μg L^{-1} after treating 30 L before inclining to a stabilised value of between 5.1 and 6.1 μg L^{-1}. Across the trial, this represented an average residual of 4.5 µg L^{-1}, a 46% removal from the starting concentration. The corresponding capacity was 454 μg m^{-2} (2.27 μg g^{-1}) indicating that the increase in contact area has a slightly increased effect on the capacity. Accordingly, the improved performance reflects an increase in the total contact time between the water and the fabric to a time of 48 seconds. The total amount of metaldehyde removed using 8 m^2 of fabric was 3632 µg.

Previous lab trials with the fabric had shown an uptake of 535 μg m^{-2} (2.7 μg g^{-1}) in the same time indicating the efficiency of the cloth in the current set up.

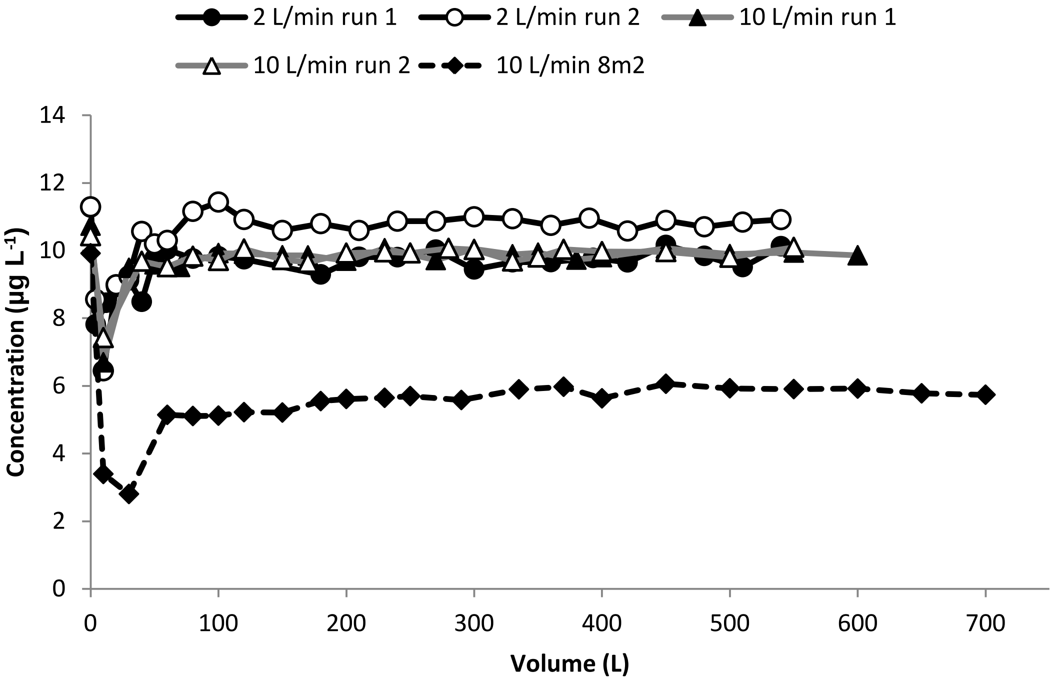

Figure 0.7– Metaldehyde removal at flow rates of 2 and 10 L min^{-1} with 2 m^2 AC fabric and 10 L min^{-1} with 8 m^2 of AC fabric

5.6 Conclusion

Overall, the trials with the AC fabric have demonstrated the efficacy of using AC carbon fabric as an in-catchment tool to reduce peak loads of metaldehyde. The potential to use the fabric as a temporary load reducing tool within catchments, provides a novel opportunity to respond to identified peak flush periods that catchment models predict. The solution appears to be resilient to variable flowrates and offers a meaningful level of removal which should assist in reducing problems at drinking water production sites. Further tests need to be carried out using a mix of pesticides and to find out the effect of raw water constituents on removal performance at pilot scale before moving on to field testing.

5.7 References

Abdelhameed, R.M., El-Zawahry, M. and Emam, H.E. (2018) ‘Efficient removal of organophosphorus pesticides from wastewater using polyethylenimine-modified fabrics’, *Polymer*, 155, pp. 225–234.

Aksu, Z. and Kabasakal, E. (2005) ‘Adsorption characteristics of 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution on powdered activated carbon’, *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, 40(4), pp. 545–570.

Asfaw, A., Maher, K. and Shucksmith, J.D. (2018) ‘Modelling of metaldehyde concentrations in surface waters: A travel time based approach’, *Journal of Hydrology*, 562, pp. 397–410.

Autin, O. (2012) *Micropollutant Removal By Advanced Oxidation Processes*. PhD Cranfield University.

Ayranci, E. and Hoda, N. (2004) ‘Studies on removal of metribuzin, bromacil, 2,4-D and atrazine from water by adsorption on high area carbon cloth’, *Journal of Hazardous Materials*, 112(1–2), pp. 163–168.

Ayranci, E. and Hoda, N. (2005) ‘Adsorption kinetics and isotherms of pesticides onto activated carbon-cloth’, *Chemosphere*, 60(11), pp. 1600–1607.

Busquets, R., Kozynchenko, O.P., Whitby, R.L.D., Tennison, S.R. and Cundy, A.B. (2014) ‘Phenolic carbon tailored for the removal of polar organic contaminants from water: a solution to the metaldehyde problem?’, *Water Research*, 61, pp. 46–56.

Drinking Water Inspectorate (2017) Drinking Water 2016: Q3. London.

Giribaldi, C. (2013) *Adsorption of metaldehyde in water using resins*. MSc Cranfield University.

Jefferson, B., Jarvis, P., Bhagianathan, G.K., Smith, H., Autin, O., Goslan, E.H., MacAdam, J. and Carra, I. (2016) ‘Effect of elevated UV dose and alkalinity on metaldehyde removal and THM formation with UV/TiO2and UV/H2O2’, *Chemical Engineering Journal*, 288, pp. 359–367.

Kay, P. and Grayson, R. (2014) ‘Using water industry data to assess the metaldehyde pollution problem’, *Water and Environment Journal*, 28, pp. 410–417.

Lu, Q., Whitehead, P.G., Bussi, G., Futter, M.N. and Nizzetto, L. (2017) ‘Modelling metaldehyde in catchments: a River Thames case-study’, *Environmental Science: Processes & Impacts*, 19(4), pp. 586–595.

Maillard, E., Payraudeau, S., Faivre, E., Grégoire, C., Gangloff, S. and Imfeld, G. (2011) ‘Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment.’, *The Science of the Total Environment*, 409(11), pp. 2317–24.

Al Mardini, F. and Legube, B. (2010) ‘Effect of the adsorbate (Bromacil) equilibrium concentration in water on its adsorption on powdered activated carbon. Part 3: Competition with natural organic matter', *Journal of Hazardous Materials*, 182(1–3), pp. 10–17.

NFU (2017) *Metaldehyde in the Thames catchment*., NFU online Available at: https://www.nfuonline.com/assets/92768 (Accessed: 25 November 2018).

Pesticides Forum (2014) *Pesticides in the UK*. York.

Rolph, C.A., Jefferson, B., Hassard, F. and Villa, R. (2018) 'Metaldehyde removal from drinking water by adsorption onto filtration media: mechanisms and optimisation', *Environmental Science: Water Research & Technology*, 4, pp. 1543–1552.

Salvestrini, S., Vanore, P., Bogush, A., Mayadevi, S. and Campos, L.C. (2017) 'Sorption of metaldehyde using granular activated carbon', *Journal of Water Reuse and Desalination*, 7(3), pp. 280–287.

Santana, G.M., Lelis, R.C.C., Jaguaribe, E.F., Morais, R. de M., Paes, J.B. and Trugilho, P.F. (2017) 'Desenvolvimento de carvão ativado a partir de bambu (bambusa vulgaris) para remoção de pesticidas de soluções aquosas', *Cerne*, 23(1), pp. 123–132.

Shirmardi, M., Alavi, N., Lima, E.C., Takdastan, A., Mahvi, A.H. and Babaei, A.A. (2016) 'Removal of atrazine as an organic micro-pollutant from aqueous solutions: a comparative study', *Process Safety and Environmental Protection*, 103, pp. 23–35.

Sterlitech (2016) *Membrane Distillation Cell* Sterlitech Corporation, Washington

Tao, B. and Fletcher, A.A.J. (2013) 'Metaldehyde removal from aqueous solution by adsorption and ion exchange mechanisms onto activated carbon and polymeric sorbents', *Journal of Hazardous Materials*, 244–5(1), pp. 240–250.

Thomas, J.C., Helgason, T., Sinclair, C.J. and Moir, J.W.B. (2017) 'Isolation and characterization of metaldehyde-degrading bacteria from domestic soils', *Microbial Biotechnology*, 10(6), pp. 1824–1829.

Xu, J., Lo, S.L. and Xu, L. (2015) ‘Removal of pollutants during storm and non-storm events by two wetlands’, *Desalination and Water Treatment*, 57(22), pp. 1–12.

6 Overall discussion: Implications of the work

The first aim of this research was to gain a greater understanding of the conditions that contribute towards elevated pesticide concentrations in agricultural run-off water. As many previous studies have found, weather patterns play an important role in the degree of runoff observed (Silburn *et al*., 2013; Sebastian *et al*., 2014; Franco and Matamoros, 2016). The analysis carried out in chapter two using existing compliance data alongside historical rainfall data supports these findings and furthermore gives an insight into the conditions that have led to high levels of metaldehyde seen in surface waters in the past. Specifically, this is that a dry summer followed by a wet autumn, with a deficit in average rainfall up to 40 mm between the months of [August + September] and October gives the highest risk of seeing compliance failures due to metaldehyde detection (Figure 2.7). This information can be used by water companies to give them an indication as to the extent to which metaldehyde (and other pesticides) may be a problem in meeting compliance standards based on the prevailing weather patterns.

Furthermore, at a smaller scale, rainfall dependent monitoring is useful for identifying peak run-off concentrations at catchment scale (chapter 2). This methodology could be used by water companies to assess catchments and identify areas of increased pesticide run-off concentrations in high risk regions. This information could then be used in conjunction with pesticide fate models to help reduce pesticide presence in surface waters at key locations. Such models predict pesticide mobility by analyzing important factors such as slope, soil type, rainfall and pesticide application according to land use and predicts the movement of pesticides from the field into wider sources in order to give advanced warning of high concentrations in surface waters (Holvoet *et al*., 2007; Asfaw *et al*., 2018). While the models are useful for predicting high run-off at a wider scale, rain dependent sampling could then be used on a much more localized scale to identify at what point during a storm event the pesticide concentration in the run-off significantly increases. This information could then be used to identify when a temporary application of media would be most effective. For example, the media could be applied during high risk temporal periods identified by the analysis and when models predict elevated levels of pesticide. In addition, monitoring rainfall would be easier to install and maintain compared to flow proportional sampling as it would not require any in-stream installation such as installing a weir, which would also make them safer from a health and safety standpoint.

The physico-chemical properties of different pesticides were analysed in terms of the number of compliance failures each pesticide had caused. It was found that the ones that had the highest number of compliance failures fell into the polar mobile category. This was not unexpected as these attributes make a compound less likely to be in the adsorbed phase. The identification of pesticide characteristics in this way can be used as a simple graphical way to help water companies easily identify which pesticides are most likely to appear in run-off at higher concentrations and identify which chemicals may appear as emerging contaminants and so cause water compliance issues.

The second aim of the thesis was to understand the impact of design and operating conditions of potential solutions for the management of elevated pesticide concentrations in agricultural run-off. At present, constructed or stormwater wetlands, buffer strips and vegetated ditches are the most commonly used means of preventing or treating run-off from agricultural lands. It has been noted in a review of previous studies that pesticide removal using these techniques is highly variable (Vymazal and Březinová, 2015). It is often the case that in order to perform effective pesticide removal, comparatively high hydraulic residence times in the region of hours to days are needed (Sherrard, 2004; Maillard *et al*., 2011; Vallée *et al*., 2015). This is in comparison to the fabric medium described in this research which needed contact times of only seconds to minutes to be effective. Additionally, these systems rely on biodegradation to completely remove pesticides (Vymazal and Březinová, 2015). Biodegradation becomes less effective in deeper waters (Avery, 2012; Tournebize *et al.*, 2013). This is supported by results in chapter 3 with the continued detection of metaldehyde three years since application had ceased. The main application period for pesticides, and specifically metaldehyde, in the UK is over the autumn-winter period (Asfaw *et al*., 2018). During this time of year temperatures will be lower and biological activity lessened. In addition, the combination of high rainfall and lower temperatures mean that lower rates of evaporation will be observed during these months leading to higher water levels in soils and ponds/ditches leading to anaerobic conditions and therefore, again, biodegradation will be decreased. It would therefore be preferable to utilise temporary medium structures into the system which are able to provide additional adsorption sites and can then be completely removed along with the adsorbed pesticides from the agricultural environment after which the fabric can be regenerated and reused.

Examples of temporary devices in the catchment include filtration socks that are designed for use within an agricultural environment. These use filtration materials such as compost, straw or woodbark contained within a mesh sock (Auckland Council, 2018). Filtration socks are generally used to catch and retain sediment rather than to filter out pollutants such as pesticides, although some filter socks have been tested with special additives to improve the removal of pollutants such as metals and hydrocarbons (Faucette *et al*., 2009). Shipitalo et al. (2010) found reductions in concentration of glyphosate (5%) and alachlor (18%) when the filter socks were used, however these reductions are still much lower than was seen for the 8 m^2 fabric filter described in this thesis (chapter 5). Furthermore it was noted that these reductions were not sufficient to reduce pesticide concentrations to acceptable levels. The study also noted that the filter socks used in the study significantly increased the release of nutrients such as nitrate, sulphate and P into the water (Shipitalo *et al*., 2010). Additionally the build up of sediment behind filter socks would be likely to cause headloss issues through decreasing flow-through rates (Keener *et al*., 2007).

AC fabric was identified as a potential medium that could achieve uptake at faster speeds compared to other media tested and was least affected by the presence of raw water. Added to this, the flow rates seen in the field studies when high run-off was present (chapter 3) combined with the large headloss seen for the small sized media (chapter 4) prevents the application of the particulate media assessed in this work. Although the fabric had a lower overall capacity, issues with application and environmental safety of using particulate media in terms of keeping it within its intended application area, in addition to its slower kinetic capabilities, make it a less favourable option. Furthermore, the overall capacity of the AC fabric should not cause a major issue if the fabric is only used for short periods when the chance of pesticide run-off is high. Additionally, reaching the adsorption capacity of the medium over such a short period is not likely to occur. The medium can then be regenerated and reused during subsequent storm events.

The fabric medium was able to remove pesticides under a variety of flow rates, had faster kinetic uptake and had least reduction in efficiency compared to particulate media. Although it had less capacity, it has more options in terms of design potential.

A filter using AC fabric could be designed for a temporary application within agricultural ditches or ponds. By applying the fabric in this way, it could just be used when needed such as during rain events (e.g. >10 mm in 24 h) after pesticide application when increased pesticide concentrations in waters from agricultural land are known to be detected (chapter 4). An example of a decision making process as to the most appropriate timing to apply the filter into the agricultural environment is shown in the flow chart in Figure 6.1. This would ensure that the fabric would be working at its best when most needed and reduce the space needed to hold excess water, as would be the case with the headloss if particulate media was used.

The decision making process was developed (Figure 6.1) in order to help determine when the most beneficial time to apply the medium would be. This decision making process would help farmers/water companies to identify whether the application of a filter module would be necessary according to the pesticide to be used in the catchment. The flowsheet then moves on to assess whether the pesticide is likely to run-off in high concentrations according to the timescale since last application. The next step determines whether site conditions are known so that the correct number of filter modules can be established. The following step assesses whether there is an imminent chance of high run-off rates occurring. The final step in the process provides instructions as to how many filter modules to apply according to site conditions. A number of assumptions were made for the development of the flow diagram and these were as follows:

- A typical ditch assumed to be 1m wide by a 1 m depth by an undetermined length.
- A 'module' containing AC fabric sheets would be 1 m^3 and fit tightly into the ditch.
- The AC fabric would account for 80% of module volume (0.8 m^3 which would be 800 sheets of fabric, this was scaled up from the 8 m^2 flume which contained 80 fabric sheets in 100 mm).
- Contact time would be a minimum of 50 s (this was rounded up from 48 s as was calculated for the 8 m^2 carbon cloth flume experiment).
- The percentage decrease in concentration was assumed to be same as in 8 m^2 pilot run.

The values marked with an asterisk (Figure 6.1) denote that the number is likely to change according to the pesticide that has been targeted for removal. The values currently proposed are:

- 4 months from the last pesticide application. This was determined from chapter 3 for the time it took for propyzamide to consistently fall below 1 µg L^{-1} in subsequent storm events.
- 10 mm of rainfall in 24 h, which was also determined from chapter 3 according to when high pesticide concentrations in run-off were seen.
- 46% pesticide removal was determined from chapter 5. It was assumed that the same percentage removal of pesticide would be achieved with the scaled up system as was seen for metaldehyde removal from the 8 m^2 pilot experiments.

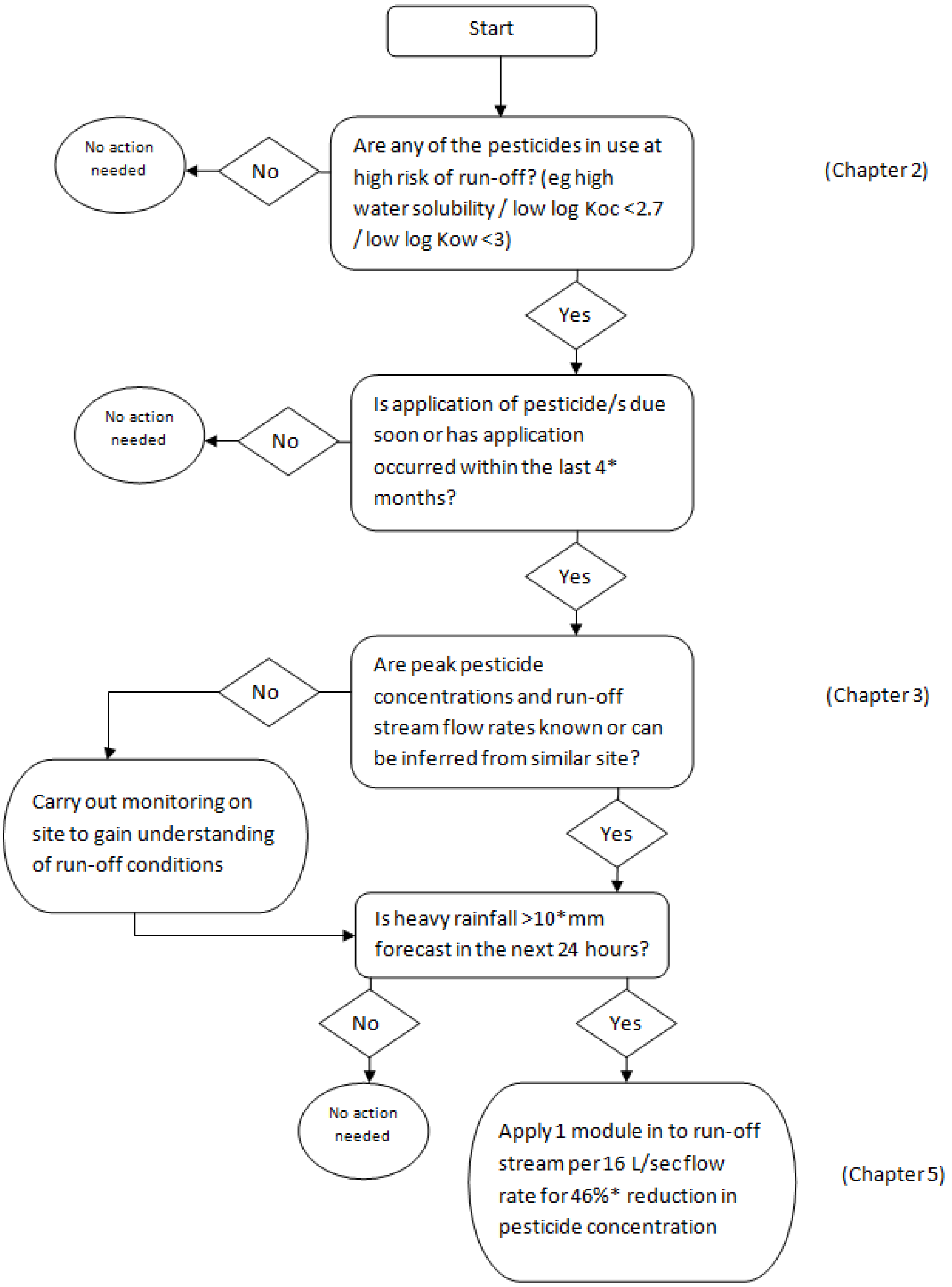

Figure 0.1 - Decision making process as to when the adsorption filter should be applied. Numbers marked with * denote factors that may change due to pesticide or properties such as K_{oc} or application rate or due to environmental factors such as slope or soil type.

6.1 References

Asfaw, A., Maher, K. and Shucksmith, J.D. (2018) ‘Modelling of metaldehyde concentrations in surface waters: A travel time based approach’, *Journal of Hydrology*, 562, pp. 397–410.

Auckland Council (2018) *Silt socks., Auckland design manuals* Available at: http://content.aucklanddesignmanual.co.nz/regulations/technical-guidance/erosionsedimentcontrol/details/guidance/sedimentcontrolpractices/sections/structuralapproaches/siltsocks/Pages/default.aspx (Accessed: 26 November 2018).

Avery, L.M. (2012) *Rural Sustainable Drainage Systems (RSuDS).*

Faucette, L.B., Cardoso-Gendreau, F.A., Codling, E., Sadeghi, A.M., Pachepsky, Y.A. and Shelton, D.R. (2009) ‘Storm Water Pollutant Removal Performance of Compost Filter Socks’, *Journal of Environment Quality*, 38(3), pp. 1233-1239.

Franco, J. and Matamoros, V. (2016) ‘Mitigation of polar pesticides across a vegetative filter strip. A mesocosm study’, *Environmental Science and Pollution Research*, 23(24), pp. 25402–25411.

Holvoet, K.M.A., Seuntjens, P. and Vanrolleghem, P.A. (2007) ‘Monitoring and modeling pesticide fate in surface waters at the catchment scale’, *Ecological Modelling,* 209(1), pp. 53–64.

Keener, H.M., Faucette, L.B. and Klingman, M.H. (2007) ‘Flow-Through Rates and Evaluation of Solids Separation of Compost Filter Socks versus Silt Fence in Sediment Control Applications’, *Journal of Environment Quality*, 36(3), pp. 742-752.

Maillard, E., Payraudeau, S., Faivre, E., Grégoire, C., Gangloff, S. and Imfeld, G. (2011) ‘Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment.', *The Science of the Total Environment*, 409(11), pp. 2317–24.

Sebastian, C., Becouze-Lareure, C., Kouyi, G.L. and Barraud, S. (2014) 'Event-based quantification of emerging pollutant removal for an open stormwater retention basin - Loads, efficiency and importance of uncertainties', *Water Research*, 72, pp. 239–250.

Sherrard, R. (2004) 'Feasibility of constructed wetlands for removing chlorothalonil and chlorpyrifos from aqueous mixtures', *Environmental Pollution*, 127(3), pp. 385–394.

Shipitalo, M.J., Bonta, J. V., Dayton, E.A. and Owens, L.B. (2010) 'Impact of Grassed Waterways and Compost Filter Socks on the Quality of Surface Runoff from Corn Fields', *Journal of Environment Quality*, 39(3), p. 1009-1018.

Silburn, D.M., Foley, J.L. and deVoil, R.C. (2013) 'Managing runoff of herbicides under rainfall and furrow irrigation with wheel traffic and banded spraying', *Agriculture, Ecosystems and Environment*, 180, pp. 40–53.

Tournebize, J., Passeport, E., Chaumont, C., Fesneau, C., Guenne, A. and Vincent, B. (2013) 'Pesticide de-contamination of surface waters as a wetland ecosystem service in agricultural landscapes', *Ecological Engineering*, 56, pp. 51–59.

Vallée, R., Dousset, S. and Billet, D. (2015) 'Influence of substrate water saturation on pesticide dissipation in constructed wetlands', *Environmental Science and Pollution Research,* 23(1), pp. 109–119.

Vymazal, J. and Březinová, T. (2015) 'The use of constructed wetlands for removal of pesticides from agricultural runoff and drainage: A review', *Environment International*, 75, pp. 11–20.

7 Conclusions

- Metaldehyde presence in potable water sources is greatly increased to levels which cause high numbers of compliance failures during years where the rainfall seen in October is within 40 mm or exceeds that which has occurred in the previous two months.
- Pesticide physico-chemical factors affect the likelihood of a pesticide to appear in high concentrations in run-off, with those that are within the polar and mobile grouping being the ones that are most likely to cause compliance failures.
- Pesticide concentration in agricultural waters increased with rainfall and with the subsequent flow rate, particularly if rainfall was greater than 10 mm in 24 h.
- Particulate media for pesticide concentration attenuation would be ineffective due to slower kinetic performance and high headlosses caused by high flow rates, which is when increased pesticide concentrations are present.
- AC fabric medium could overcome the headloss issue and maintain higher contact surface area under high flow rates as it does not need to be applied in a bed format.
- Little loss in performance seen in fabric with higher flow rates and the fabric had least loss of performance in raw water tests making it the most suitable medium for application within pesticide contaminated run-off.

8 Further work

The findings presented in chapter 2 with regards to rainfall patterns and metaldehyde compliance failures would benefit from further research. A more detailed analysis with in-depth spacial information about where the high metaldehyde peaks were detected along with localised rainfall patterns could help to determine whether the trends detected are still apparent. If this is the case, this information could help to give water companies an advanced warning as to the extent to which metaldehyde and other pesticides are likely to cause compliance failures.

The rain dependent data presented in chapter 3 shows that this form of sampling can gain efficient and in-depth information as to how pesticide concentrations change throughout a storm event. This study however was only able to be carried out over a single farm catchment. Further work could test this technology at different locations that have differing environmental parameters such as steeper field slopes, presence/absence of field drains and varied soil types. This would provide valuable information as to the impacts of these factors on the rainfall threshold at which increased levels of run-off are seen. In addition, it would be interesting to directly compare sampling carried out by rain dependent and flow proportional methods. This would provide a direct comparison of sampling efficiency and granularity of data points throughout a storm event. This would help to give future researchers better insight into their sampling options allowing them to pick the option that best suits their sampling requirements.

Like the rain dependent sampling, the AC fabric solution presented in chapter 5 was a proof of concept and so there are a number of gaps in the data that need to be filled before a final product can be created. Laboratory scale membrane studies of other pesticides would be useful to see how different pesticide characteristics impact upon removal under dynamic conditions. Pilot scale channel tests using batches of mixed pesticides in raw water with high sediment load would provide valuable information into how the fabric would behave under real in-field conditions. It would also be useful to understand what conditions are likely to occur in terms of sediment build up. This could inform upon whether other measures would need to be taken in the field to reduce sediment levels in the water prior to filtration by the fabric.

Pilot scale testing repeatedly treating batches of water would give additional insight into the level of deterioration of pesticide removal with continued loads. This would also help to determine whether the fabric behaves any differently when applied as a bundle, as compared to a single sheet. This in turn would help to determine the amount of time for which the fabric will provide effective pesticide concentration attenuation in the field and help to establish the timescale for the most appropriate means of application.

Studies in to the effect of regeneration on the adsorption ability of the fabric would also be beneficial. This would help inform whether regeneration has any impact on the capacity and kinetic adsorption of the pesticides to the fabric. It would also help to determine the most efficient regeneration frequency needed to ensure maximum adsorption while keeping regeneration costs at a minimum.

A study into the most common shapes and sizes of agricultural waterways would be advantageous in terms of developing a design for the filter that would be most effective and easily applicable. This would also need to consider any barriers to application or removal of the filters from the waterways in addition to the best means of holding them in place. Furthermore, an understanding of whether the application of the medium could be automated and triggered by rainfall would be possible. This would be preferable due to the possibility that there may be no one around to trigger application manually. Alternatively it may be necessary to consider whether it would be better to have the application manually triggered because of there being other factors such as predicted rainfall or time since application that may not be fully considered using an automated system.

Finally, once a best design has been produced and the most effective timings of use considered, field trials of the filtration device need to be undertaken. These would need to sample before and after the filter in order to determine whether it has any effect. This would also help to determine whether multiple blocks of filters would be needed on a single site or whether a single filter prior to run-off joining more extensive water courses would provide a sufficient reduction in pesticide concentration. Furthermore, it would help to highlight any unforeseen issues that may arise from application under real conditions so that they can be addressed prior to use of the fabric filters at a wider scale.

Appendix A

Batch paper graphs

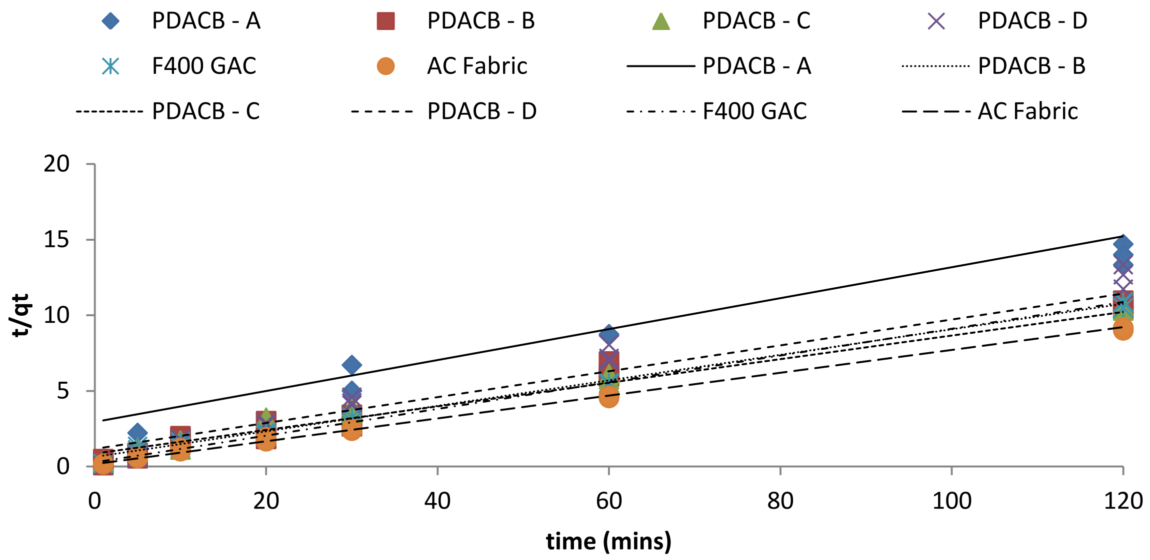

Figure A- 1- Pseudo second order model for six AC based media in DI water spiked with metaldehyde

Table A- 1 - Extrapolated data from pseudo second order model for six AC based media in DI water spiked with metaldehyde

Media	Slope (1/qe)	intercept (k)	R2
PDACB-A	0.102	2.952	0.903
PDACB-B	0.084	0.632	0.998
PDACB-C	0.078	0.865	0.998
PDACB-D	0.085	1.161	0.995
F400 GAC	0.088	0.268	0.998
AC Fabric	0.075	0.168	0.998

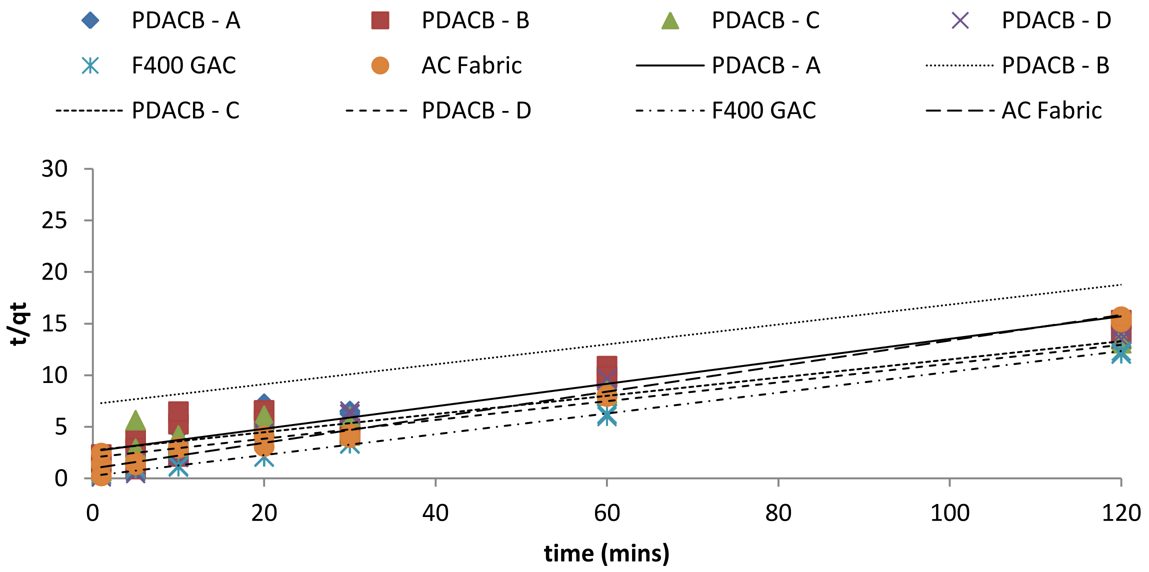

Figure A- 2- Pseudo second order model for six AC based media in DI water spiked with metazachlor

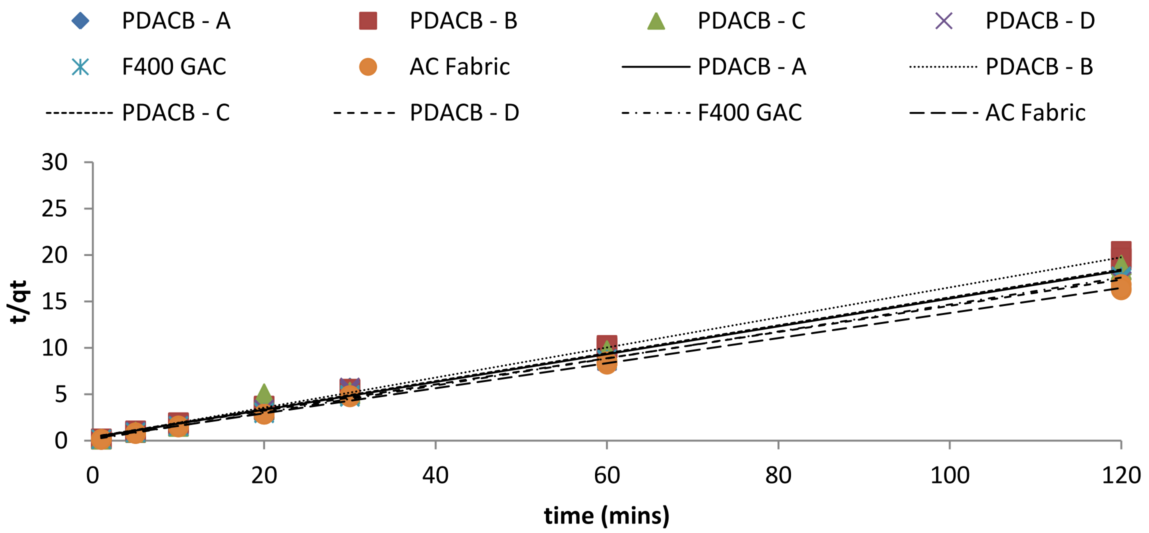

Figure A- 3- Pseudo second order model for six AC based media in DI water spiked with propyzamide

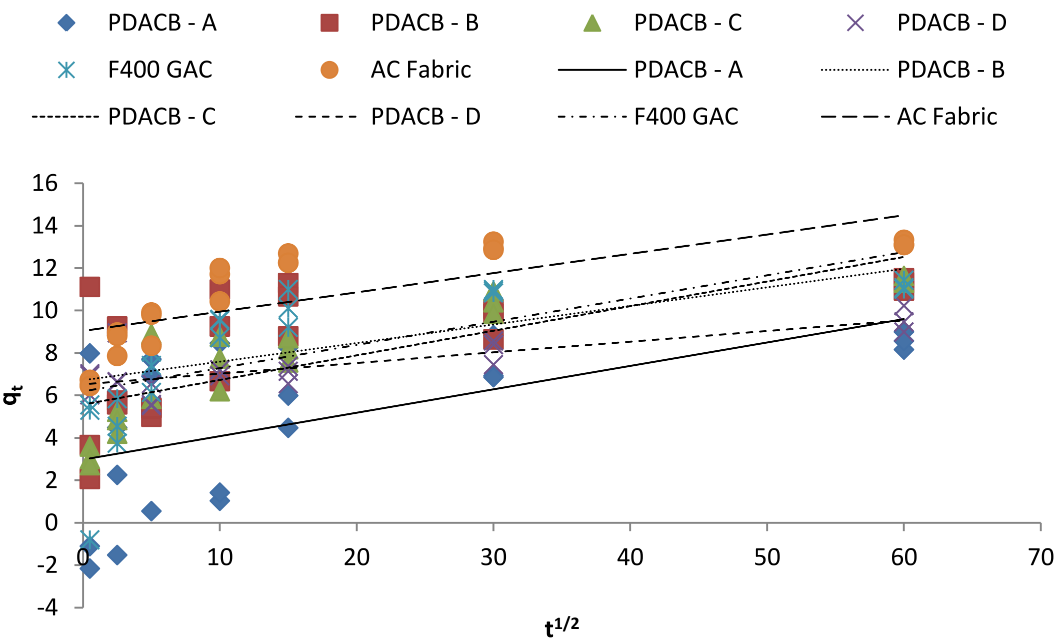

Figure A- 4– Intraparticle diffusion model for metaldehyde adsorption in DI water by six different media

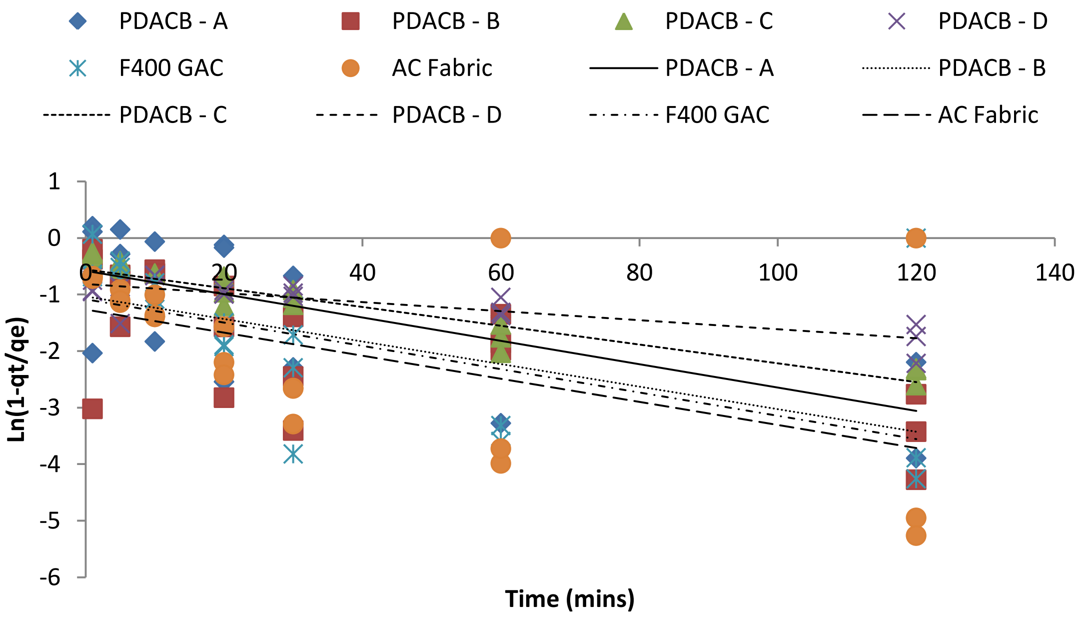

Figure A- 5– Film diffusion model for metaldehyde adsorption in DI water by six different media

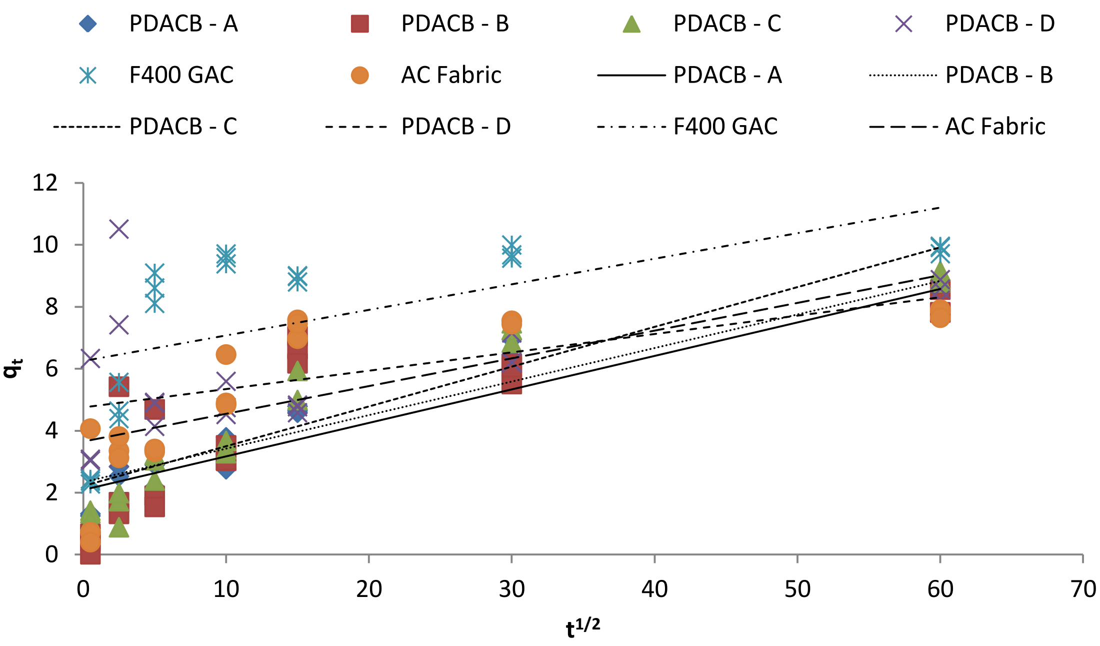

Figure A- 6– Intraparticle diffusion model for metazachlor removal for six different media from DI water

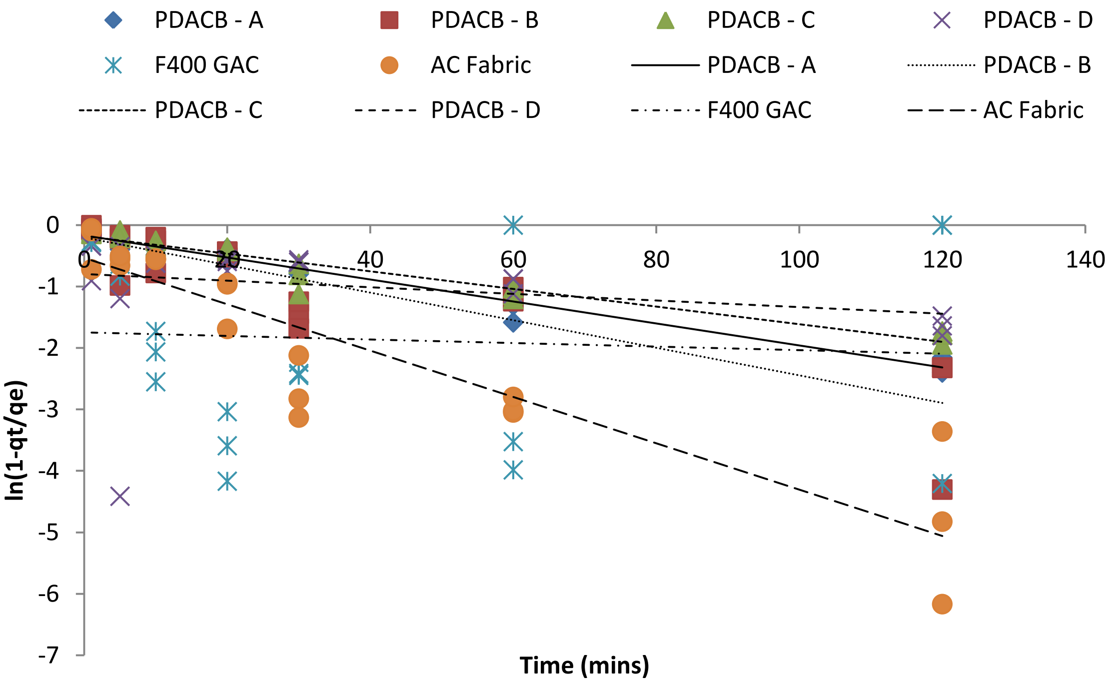

Figure A- 7– Film diffusion model for metazachlor removal by six different media from DI water

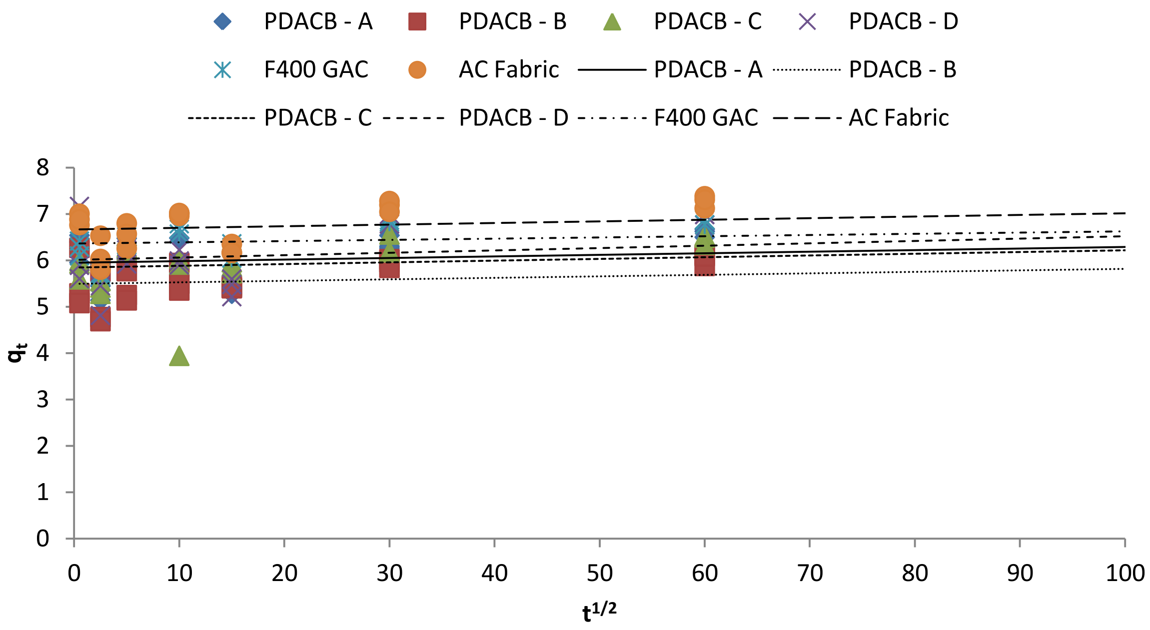

Figure A- 8– Intraparticle diffusion model for propyzamide removal from DI water

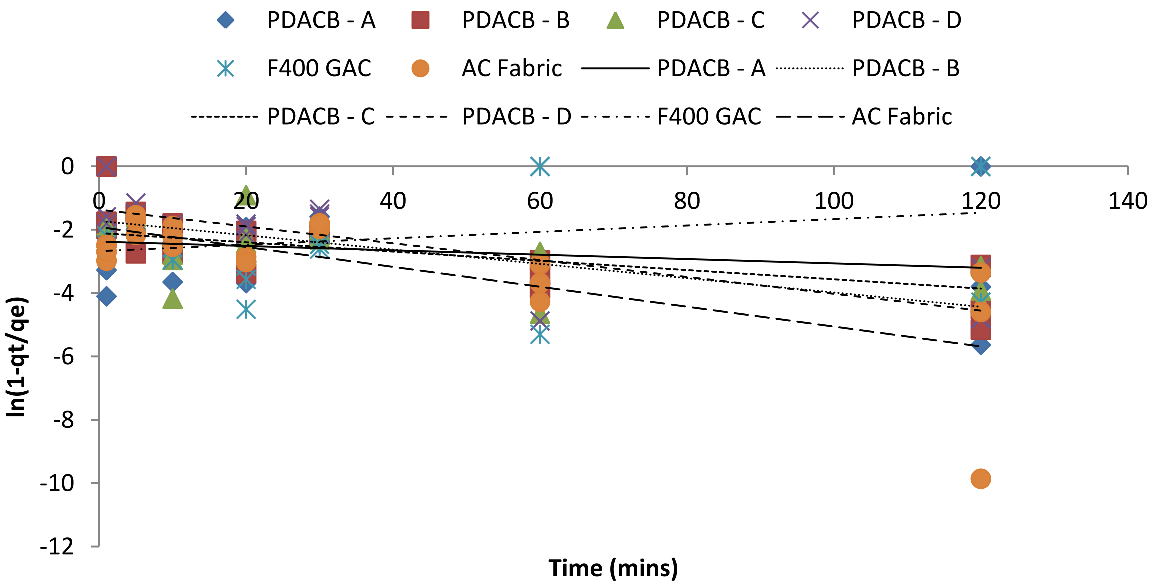

Figure A- 9– Film diffusion model for propyzamide removal from DI water

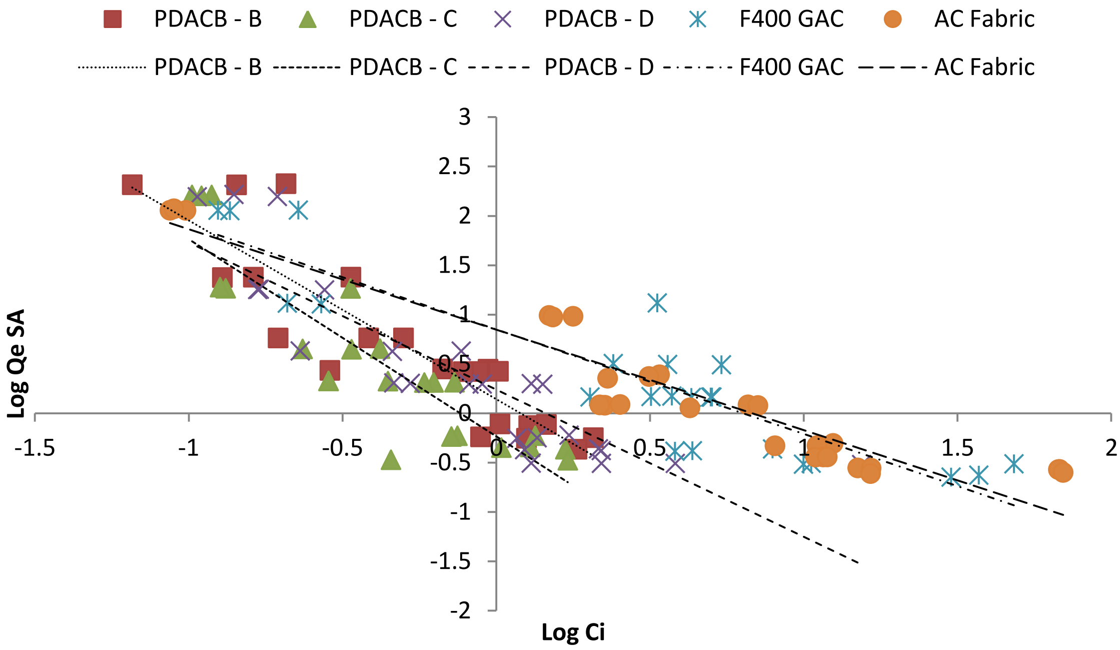

Figure A- 10– Freundlich isotherm using surface area for metaldehyde in DI water

Table A- 2– extracted data from Freundlich isotherm using surface area for metaldehyde in DI water

DI	1/n	log K		
Freundlich (surface area)				
	Slope	Intercept	R2	K_f(μg m^{-2})(μg L^{-1})$^{1/n}$
PDACB – B	-1.81	0.14	0.80	1.39
PDACB – C	-2.00	-0.23	0.80	0.58
PDACB – D	-1.49	0.24	0.76	1.75
F400 GAC	-1.06	0.85	0.82	7.06
AC Fabric	-1.02	0.85	0.90	7.05

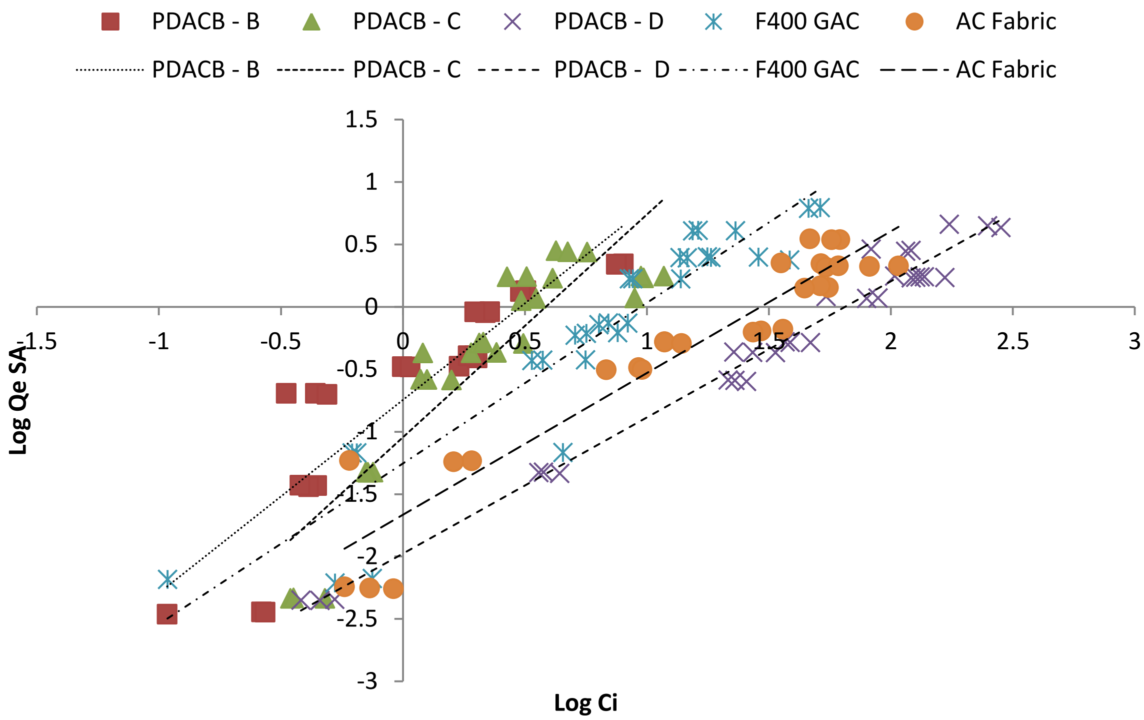

Figure A- 11- Freundlich isotherm using surface area for metaldehyde in raw water

Table A- 3– extrapolated data from Freundlich isotherm using surface area for metaldehyde in raw water

Raw	1/n	log K		
Freundlich (surface area)				
	Slope	Intercept	R2	K_f(μg m^{-2})(μg L^{-1})$^{1/n}$
PDACB – B	1.55	-0.74	0.82	0.18
PDACB – C	1.79	-1.04	0.82	0.09
PDACB – D	1.09	-1.98	0.98	0.01
F400 GAC	1.29	-1.26	0.88	0.06
AC Fabric	1.14	-1.67	0.91	0.02

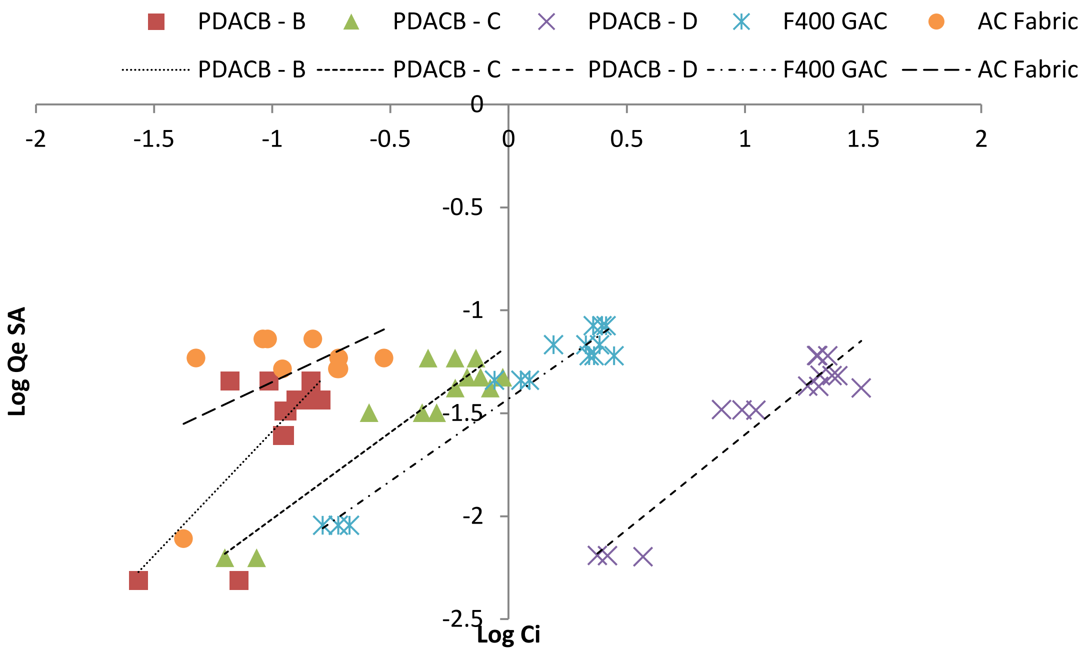

Figure A- 12- Freundlich isotherm using surface area for metazachlor in raw water

Table A- 4– extrapolated data from Freundlich isotherm using surface area for metazachlor in raw water

	1/n	log K		
Freundlich				
	Slope	Intercept	R2	K_f (µg m^{-2})(µg L^{-1})$^{1/n}$
PDACB – B	1.21	-0.38	0.53	0.41
PDACB – C	0.84	-1.17	0.88	0.07
PDACB – D	0.92	-2.53	0.89	0.00
F400 GAC	0.80	-1.43	0.95	0.04
AC Fabric	0.54	-0.81	0.27	0.16

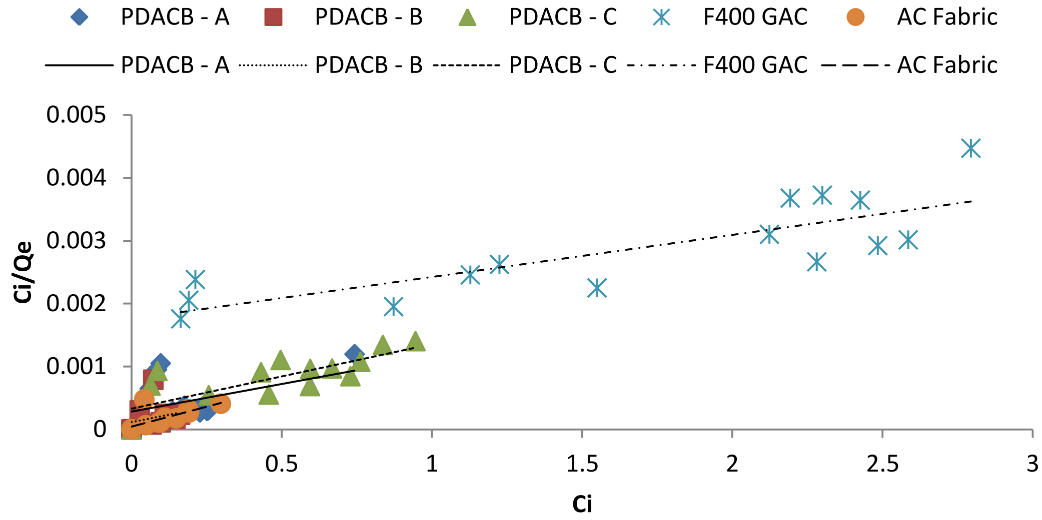

Figure A- 13– Langmuir isotherm for metazachlor in raw water. *PDACB – D was excluded from the graph due to it skewing the axis

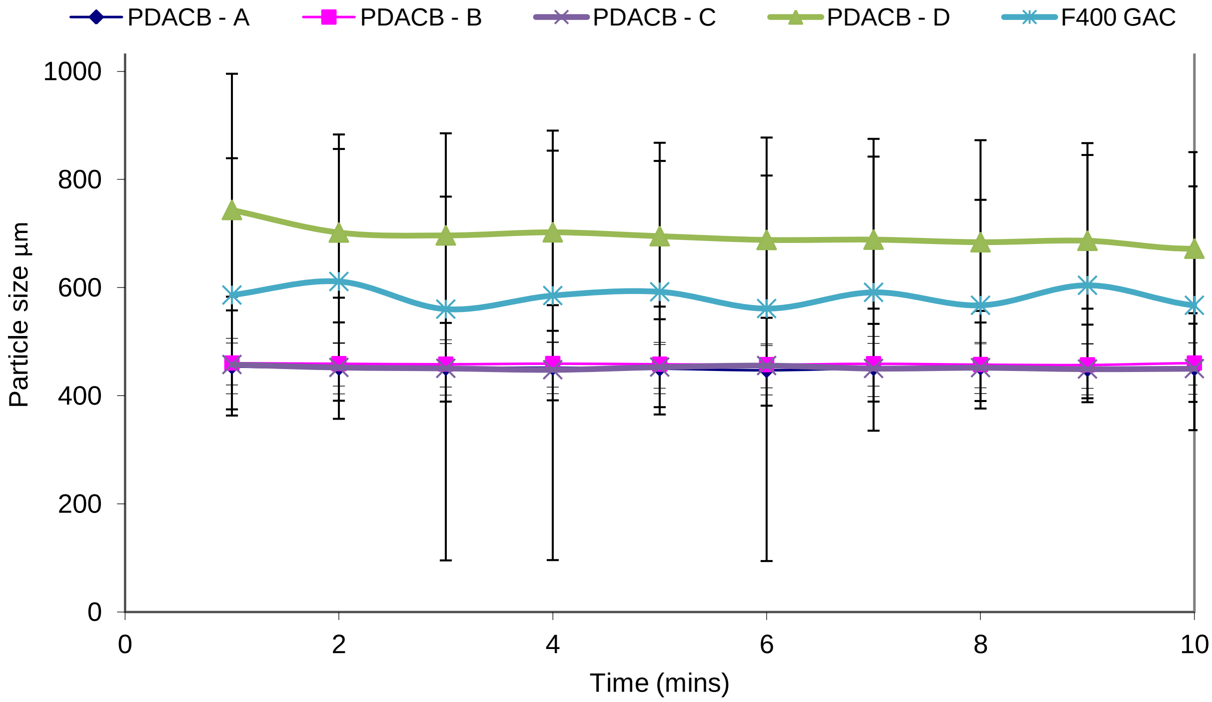

Figure A- 14– Particle size distribution mastersizer results for the five particulate AC media

Metazachlor isotherms

Isotherms were able to be produced for all media for metazachlor in raw water (Table A-4). In this case most of the medium fit well to the Freundlich isotherm with the exception of the AC fabric which fits better to the Langmuir isotherm. This suggests that for metazachlor adsorption to the PDACB–A-D and F400 GAC, multilayer adsorption is taking place however for AC fabric the adsorption is single layered. As was the case for metaldehyde, PDACB–D performed particularly poorly with a K_f value of 40.72 (μg/g)(μg/L)$^{1/n}$ for metazachlor adsorption in raw water (Table A-4). PDACB–A and B adsorption for metazachlor displayed S-type adsorption as shown by a 1/n>1, PDACB – C, D, F400 GAC and AC Fabric showed L-type adsorption as their 1/n values were below 1.

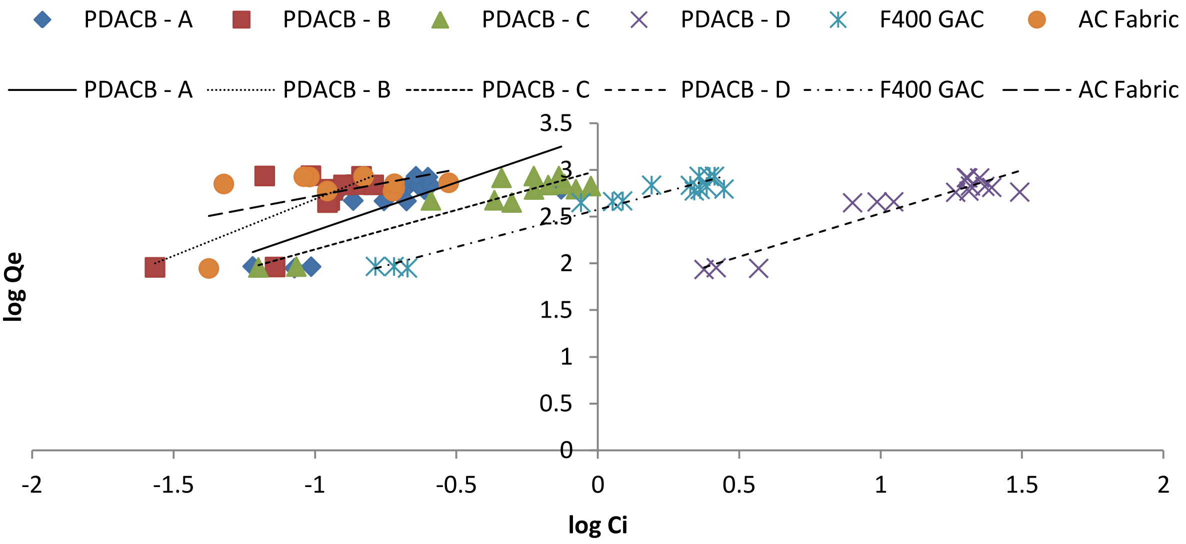

Figure A- 15– Freundlich isotherm for metazachlor in raw water

Table A- 5– Freundlich and Langmuir isotherm data for metazachlor removal from raw water

	Freundlich			Langmuir		
	1/n	K_f (µg/g)(µg/L)$^{1/n}$	R2	R2	1/Qm	1/baQm
A	1.03	2421.03	0.57	0.19	0.0009	0.0003
B	1.21	7892.24	0.53	0.08	0.0009	0.0001
C	0.84	984.24	0.88	0.63	0.001	0.0003
D	0.92	40.72	0.89	0.20	0.0004	0.0237
E	0.80	375.92	0.96	0.67	0.0007	0.0018
F	0.57	1949.85	0.28	0.54	0.0013	0.00004

For all media tested with a single pesticide dose of either metaldehyde, metazachlor or propyzamide, high levels of removal were seen from doses in both DI and raw water. PDACB-D, a polymer derived AC bead of a slightly larger size and which has a specific surface area of 1412 m^2 g^{-1}, a lower area compared to the available data for the other beads tested which were 1486 m^2 g^{-1} for PDACB–B and 1920 m^2/g for PDACB–C, resulted in the greatest impact from its use in raw waters where removal dropped from a K_f of 2961 to 15 (µg g^{-1})(µg L^{-1})$^{1/n}$ (Table 4.3) for metaldehyde. This was also the case for metazachlor where the K_f was particularly low with a value of 41 (µg g^{-1})(µg L^{-1})$^{1/n}$.

Batch tests – mixed pesticides

Average percentage removal for each pesticide was calculated for all media tested across a range of concentrations between 0.8 - 1034 µg/L (Figure A-16). Removal of metaldehyde under mixed pesticide conditions in DI water was in the range of 99 – 100% removal for all media. PDACB-A, B and C – the smaller sized AC beads maintained 98 – 100% removal of all mixed pesticides in raw water. Metaldehyde removal for F400 GAC and AC fabric dropped slightly in the mixed pesticide raw water solutions with removals between 96 – 100%. PDACB-D, the larger sized AC bead saw a larger drop in performance in the mixed pesticide in raw water with removals dropping to 92 – 99% for all pesticides. Metazachlor removal ranged between 99.97% for F400 GAC to 100% for PDACB-B in DI water and 97.25% for PDACB-D to 99.98% for PDACB-B in raw water. Very high removal rates were seen for propyzamide across all media with the lowest performance being 99.83% for PDACB–D in raw water.

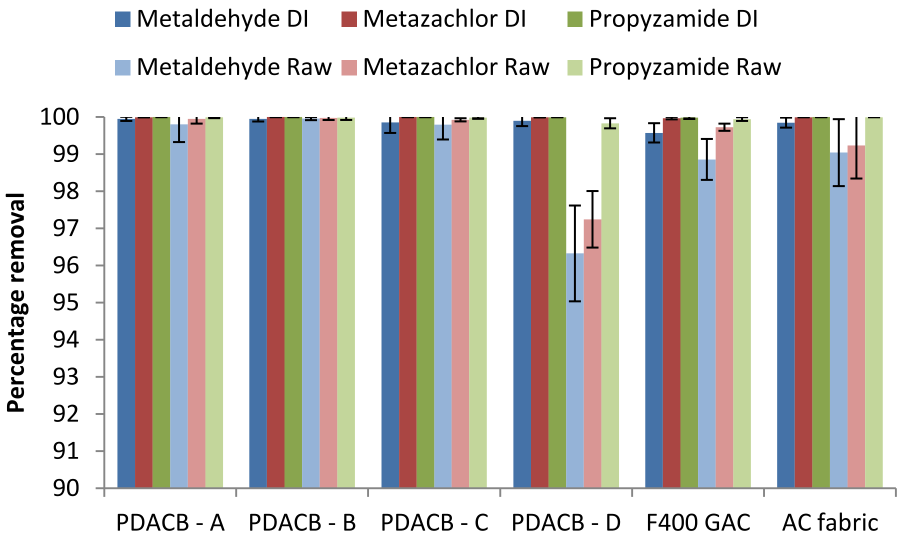

Figure A- 16– Average percentage removal for each medium in DI and Raw water for the three pesticides tested. Due to high removal levels, y-axis shows 90-100%

Appendix B

An analytical method was developed for the determination of pesticide concentration from raw water collected from agricultural environments. The analytical method was developed for six pesticides however only three of these; metaldehyde, metazachlor and propyzamide, were used in this study and so are described here.

After collection from the field, raw water samples were filtered using 0.2 μm filters before being analysed by direct injection LC-MS/MS analysis. The analytical equipment used included Waters Alliance 2695 liquid-chromatography and a Quattro premier XE tandem quadrupole. A C18 column was used to sepererate the pesticides which was held at a temperature of 60°C.

An injection volume of 50 μL of sample was used at a flow rate of 0.3 mL min^{-1}. The mobile phase was UP water with 0.1% acetic acid in A and methanol with 0.1% acetic acid in B. The elution moved from 10% to 98% B over 12 minutes. Multiple reaction monitoring mode was used with positive electrospray ionisation. Two transitions were detected for propyzamide and metazachlor and one transition for metaldehyde (Table B- 1).

Pesticide	First transition				Second transition				
	Precursor ion (m/z)	Product ion (m/z)	Cone	Collision	Precursor ion (m/z)	Product ion (m/z)	Cone	Collision	Retention time (min)
Metaldehyde	198.9	66.9	25	12	n/a	n/a	n/a	n/a	5.69
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

Table B- 1 Transitions and instrument settings for the analytical detection of 3 pesticides metaldehyde, metazachlor and propyzamide.

The limit of detection was 0.09 µg L^{-1} for metaldehyde and metazachlor and 0.05 µg L^{-1} for propyzamide. The limit of quantification was 0.3 µg L^{-1} for metaldehyde and metazachlor and 0.2 µg L^{-1} for propyzamide.

Calibration standards were run at the start and end of each run to create a calibration from which concentrations of unknown samples were determined. Calibration standards consisted of pesticide concentrations of 0.1, 0.2, 0.5, 1, 2, 5, 8 and 10 µg L^{-1}. Quality controls of 5 µg L^{-1} were used alongside blank samples of UP water to ensure the accuracy of the results. For a detailed description of the method used see Ramos et al. (2017).

B.1 References

Ramos, A.M., Whelan, M.J., Cosgrove, S., Villa, R., Jefferson, B., Campo, P., Jarvis, P. and Guymer, I. (2017) 'A multi-component method to determine pesticides in surface water by liquid-chromatography tandem quadrupole mass spectrometry', *Water and Environment Journal*, 31(3), pp. 380–387.