MULTI-DISCIPLINARY APPROACH TO ASSESSING METALDEHYDE TRANSPORT AND FATE IN THE ENVIRONMENT AT A CATCHMENT SCALE

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THESIS

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To my child Boris -

Thank you for making me a better human and fulfilling my life

Abstract

Metaldehyde is the molluscicide with a long legacy of use in the UK and globally. Due to its physico-chemical characteristics and common use, this pesticide is commonly detected in the aquatic environment. At times its concentration in surface water exceeds the EU Drinking Water Directive (DWD) limit of 0.1 $\mu g\ L^{-1}$ for a single pesticide. Since metaldehyde cannot be removed from water using conventional water treatment methods, best management practices and catchment-based initiatives are especially important to control metaldehyde transfer to aquatic systems. Yet, studies on agricultural land management practices and outcomes for metaldehyde diffuse pollution abatement remain limited. To address this research need, this project investigated the drivers, pathways and sources of agrochemical diffuse pollution of metaldehyde in the Ardleigh catchment, Essex where farmers are incentivised to use alternative slug control methods in place of metaldehyde.

A ^{14}C respirometry method was applied to provide insights into the ubiquity of soil microbes to degrade metaldehyde in dissimilar soils. The influence of soil attributes (texture, pH, soil organic matter content) on metaldehyde biodegradation capacity was examined. Using a range of quantitative techniques, the annual trends and seasonal variations in metaldehyde concentrations and fluxes over a decadal period (2008-2018) were assessed. Long-term water chemistry, hydrological and agronomical datasets were analysed to investigate what factors control pesticide levels observed in surface water in two lowland, semi-agricultural catchments in the UK.

A 14-month fieldwork period was completed and included sampling of surface water, field drain runoff and precipitation at a sub-catchment scale. Physico-chemical attributes of these media were assessed *in situ* and in the laboratory. Measured data were combined with climatic/terrestrial variables to develop a conceptual model of metaldehyde transport in the study area. A metaldehyde mass budget and the scale of individual sources of metaldehyde influx in the catchment reservoir were quantified, including atmospheric deposition of metaldehyde.

Collectively, this research provided new insight into the understanding of metaldehyde transport and fate in the freshwater environment at a catchment scale. The findings suggest that metaldehyde has a ubiquitously high biodegradation potential in soils (^{14}C-

metaldehyde mineralisation values across all soils ranged from 17.7–60.0% range). The high mobility of the pesticide and its transfer via surface and sub-surface runoff are the key factors affecting metaldehyde occurrence in water resources. Metaldehyde fluxes were primarily controlled by streamflow and precipitation (R^2=0.9). The rise in metaldehyde concentration and flux displayed a seasonal pattern, mainly occurring during the autumn-winter application period (August-December), typically within the range of 0.03–0.1 μg L^{-1}. Concentration exceedances above the EU DWD regulatory limit in stream water were short-lived, and a continuous decrease in metaldehyde concentrations in surface water is expected to be observed in the UK following the withdrawal of metaldehyde for outdoor use from March 2022. Future monitoring of metaldehyde in soil, sediment, water and rainwater, following the outdoor use ban in the UK, and the benchmarking of these data with that contained herein will provide insights of metaldehyde legacy.

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Dissemination

Peer reviewed journal publications

Balashova, N., Hiscock, K. M., Reid, B. J. and Reynolds, R. (2021). Trends in metaldehyde concentrations and fluxes in a lowland, semi-agricultural catchment in the UK (2008-2018). *Science of Total Environment*, 795, 1-13.

Balashova, N., Wilderspin, S., Cai, C., Reid, B. J. (2020). Ubiquity of microbial capacity to degrade metaldehyde in dissimilar agricultural, garden and allotment soils. *Science of Total Environment*, 704, 1-9.

Conference contributions

Poster presentation *"Temporal and spatial patterns of metaldehyde in semi-agricultural catchments in Essex, UK: The influence of application regimes and hydrological conditions"*
AGU Fall Meeting, 9 December 2020, online.

Poster presentation *"How effective are catchment-based approaches in reducing metaldehyde loss to water supply at a catchment scale"*
Land Use and Water Quality Conference, 4 June 2019, Aarhus, Denmark.

Poster presentation *"Microbial catabolic competence to degrade metaldehyde in garden and allotment soils"*
Metaldehyde Conference, 13 September 2018, York, UK.

Chapter 1 Introduction

World population growth, increasing urbanisation, change in diets and climate change lead to rising demand for food production. Agriculture plays a vital role in meeting this demand (Popp et al., 2013). It was estimated that approximately 35% of potential crop yield worldwide is lost due to pests in the fields (pre-harvest losses) (Oerke, 2005). Pesticide use allows farmers to increase crop productivity, leading to economic and labour benefits (Aktar et al., 2009).

Crop damage caused by slugs and snails is a significant concern in many countries, particularly in the UK due to its mild and humid climate. In the UK, slug control methods using molluscicides are limited to two products: metaldehyde and ferric phosphate. Over 80% of the arable crop area in the UK is widely treated by metaldehyde – a molluscicide that is normally applied to crops in autumn and winter, if required (Environment Agency (EA), 2009). Crops that are treated with metaldehyde commonly include winter wheat, oilseed rape and vegetables (Lu et al., 2017). At a particular risk of slug damage are oilseed rape and cereal crops that are successfully produced on heavy clay soils of the East Anglian region – one of the most productive agricultural areas in the UK (Mohamad Ibrahim et al., 2017).

No satisfactory approach to determine metaldehyde in treated water existed until 2008. Once a new technology had been developed, it was evident that metaldehyde is widely present in surface water and groundwater (Stuart et al., 2011). Whilst metaldehyde concentrations measured in surface water is unlikely to impact humans (Kay and Grayson, 2014), metaldehyde concentrations in water should not exceed the drinking water regulatory limit. Conventional water treatment processes, such as powdered activated carbon, are not effective in removing metaldehyde to comply with the drinking water regulatory limits of 0.1 $\mu g\ L^{-1}$ and 0.5 $\mu g\ L^{-1}$ for individual and total pesticides set by the Drinking Water Directive (Directive 98/83/EC, DWD further in text) (EA, 2009; European Commission (EC), 1998).

Moreover, the Water Framework Directive (Directive 2000/60/EC, WFD further in text) promotes a shift from end of pipe treatment measures to integrated catchment management, leading to achievement of better chemical, biological and morphological status of aquatic ecosystems through a Sustainable Process Design (EC, 2000). Article 11 of Water Framework Directive introduced measures to tackle diffuse pollution. To meet this objective, supplementary directives, including the Urban Waste Treatment Directive and the Directive on Sustainable Use of Pesticides were issued to reduce diffuse and point-source water pollution from agriculture, industry and households. Additionally, the WFD state that measures against groundwater pollution should be introduced. Consequently, such measures were listed in the Groundwater Directive (2006/118/EC), which is another ‘daughter’ directive of the WFD.

1.1 Rationale and motivations

Although metaldehyde has been used for over seven decades and a vast amount of metaldehyde concentration data measured in watercourses are available, limited research of metaldehyde transport, persistence and fate of the pesticide in the environment are available (Castle et al., 2017; Lu et al., 2017). To bridge the knowledge gap, an improved understanding of metaldehyde behaviour to identify the pesticide’s fate in soil and the key drivers of metaldehyde loss to surface waters is required.

Furthermore, due to the risk that metaldehyde poses to wildlife, including birds and mammals, the outdoor use of metaldehyde in the UK will cease from March 2022. This decision was made following advice from the Health and Safely Executive (ECP) and the UK Expert Committee on Pesticides (ECP) (DEFRA, 2020). With this ban soon to come into effect, this research project contributes knowledge required to establish robust baselines that can be used to qualify the efficacy of the ban.

1.2 Research aim and objectives

The aim of this project is to advance understanding of metaldehyde transport and fate in the environment at a catchment scale. This aim leads to the following objectives:

1. To evaluate metaldehyde biodegradation potential in dissimilar soils and to assess the influence of soil attributes on biodegradation potential.
2. To provide a prognosis regarding long-term levels and persistency of metaldehyde in aquatic environment by:
    a. Examining long-term and seasonal trends in metaldehyde concentrations and fluxes in surface waters (the River Colne) over a decade.

    b. Evaluating the impact of hydrological conditions (precipitation and stream discharge (flow)) and metaldehyde application regime (application timing and annual application rates) metaldehyde levels in the stream network.
3. To explore processes that control transport of metaldehyde by:
    a. Understanding metaldehyde pathways within the study area.
    b. Exploring the relationship between metaldehyde concentrations, water quality parameters and climatic/terrestrial system variables.
    c. Evaluating sources of metaldehyde and the scale of these sources.
4. To quantify and evaluate mass budget and dynamics of metaldehyde in Ardleigh Reservoir.

1.3 Thesis structure

In line with the research motivations and objectives outlined above, the thesis consists of six chapters.

Chapter 1 “Introduction” reviews metaldehyde transport and fate in aquatic and terrestrial environments. The purpose of this chapter is to provide background information regarding the metaldehyde pollution problem, including factors and processes that affect pesticide transport, fate and persistency in the environment. This chapter also includes the research rationale, aims and objectives.

Chapter 2 “Study area description” outlines the key information pertaining to the research study area: the River Colne and Ardleigh Reservoir catchments in Essex, southeast England.

Chapter 3 “Ubiquity of microbial capacity to degrade metaldehyde in dissimilar agricultural, allotment and garden soils” presents the findings of a ^{14}C-mineralisation experiment designed to assess the capacity of soil microbial communities to degrade metaldehyde. Metaldehyde biodegradation rates in dissimilar soils collected from contrasting settings were established and discussed.

Chapter 4 “Long-term and seasonal trends in metaldehyde concentrations and fluxes in lowland semi-agricultural catchments in Essex, UK” focuses on temporal and spatial patterns and trends in long-term metaldehyde concentrations and fluxes for the period 2008-2018 period. Along with annual trends, seasonal variations in metaldehyde concentrations are discussed in the context of the pesticide application regime and hydrological conditions.

Chapter 5 “Metaldehyde transport and processes driving its transfer at a small catchment scale” further explores variations of metaldehyde levels within the Ardleigh Reservoir catchment at a finer, sub-catchment scale during the period January 2019-February 2020. This chapter discusses metaldehyde transport within the catchment and provides further insight into concentrations detected not only in surface water but also in field drain runoff and precipitation. Finally, this chapter presents a mass balance of metaldehyde in the Ardleigh Reservoir and discusses changes in metaldehyde dynamics.

Chapter 6 “Conclusions” summarises the key findings of the research and contributions to knowledge, discusses policy implications and research limitations, as well as suggests recommendations for future work.

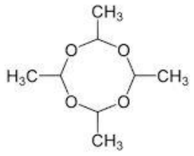
1.4 Review of metaldehyde transport and fate in aquatic and terrestrial environments

1.4.1 Physical and chemical properties of metaldehyde

Metaldehyde (2,4,6,8-tetramethyl-1,3,5,7-tetraoxacyclo-octane) is an oligomer of acetaldehyde (CH_3CHO) (Table 1.1). This molluscicide is commonly available in pellets that release the active component for approximately 10 days in moderately moist settings (Puschner, 2006). In the environment, metaldehyde first degrades to acetaldehyde and acetic acid, which then breaks down into carbon dioxide and water (Bieri, 2003). Being a solid alcohol, metaldehyde is also used as a solid fuel in the US and some other countries (Puschner, 2006).

With average water solubility of 190 $\mu g\ L^{-1}$ (PAN, 2016), metaldehyde is highly soluble in water. Due to the physical and chemical characteristics of metaldehyde (Table 1.1 (PAN, 2016; PPDB, 2017)), it has a high mobility in the environment and is susceptible to surface runoff during precipitation events. Hence, the water contamination potential of metaldehyde is high.

Table 1. 1 Physico-chemical properties of metaldehyde.

Property	Value
Molecular formula	$C_8H_{16}O_4$ *
Structural formula	
Molecular mass	176 g mol^{-1}*
Vapour pressure at 25°C	0.66 mmHg*
Henry's law constant at 25°C	3.50 Pa m^3 mol^{-1} *
Melting point (°C)	$246^{\sim}$
Boiling point (°C)	191*
GUS leaching potential index	1.50*
Average water solubility	190 mg $L^{-1\$}$
Adsorption coefficient (K_{oc})	$35.0^{\$}$
Aerobic soil half-life (average)	67.0 $d^{\$}$

$^{\sim}$National Institutes of Health
$^{\$}$ Pesticides Network Action (PAN) Pesticides Database
* PPDB: Pesticide Properties Database

1.4.2 Source-mobilisation-pathway-delivery paradigm and processes within the continuum for metaldehyde

Source-mobilisation-pathway-delivery is the continuum that describes processes involved in pollutant fate in a hydrological context (Table 1.2). Haygarth et al. (2005) applied this paradigm to describe phosphorus transport from source to a water body. The continuum was later implemented to model other pollutant fate originated from grasslands on heavy soils (Granger et al., 2010). The paradigm with its key components for metaldehyde is illustrated below (Figure 1.1).

Table 1. 2 Terminology related to metaldehyde transport in the environment (based on Haygarth et al., 2005).

Term	Definition
Transport	Metaldehyde movement through the land-water environment
Source	Metaldehyde input. Could be agricultural and non-agricultural (urban: e.g. gardens and allotments)
Mobilisation	Movement of molecules through soil. Mobilisation includes chemical and biological processes (solubilisation) and detachment (sorption to soil particles).
Pathway	Transit of a chemical through surface runoff, drain flow and groundwater. Non-hydrological pathways include pesticide drift, spillage etc.
Delivery	Connection from mobilisation to the point of the channelised flow

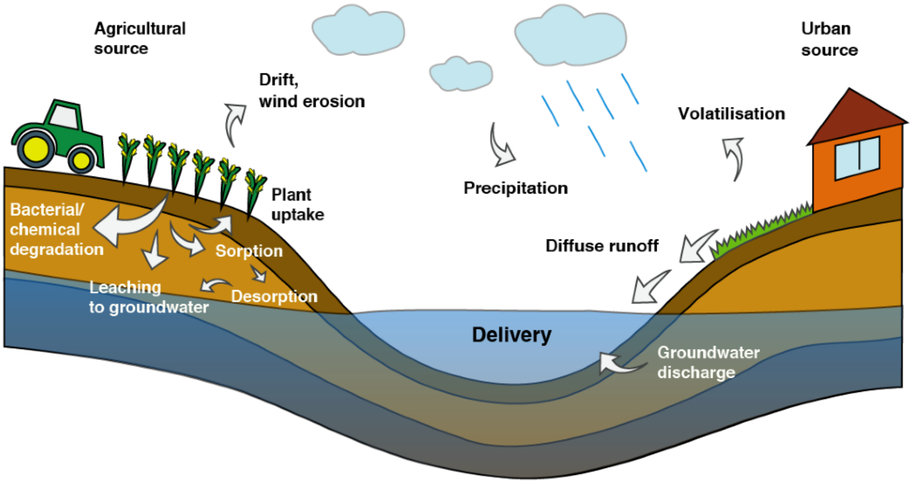


Figure 1. 1 Processes of metaldehyde transport in the environment. An arrow size represents a scale of individual processes.

1.4.3 Metaldehyde sources

According to Granger et al. (2010), sources could be classified as internal, external and cycled. Internal sources of pollutant are characterised by natural occurrence of pollutant (e.g. from atmospheric deposition). Pollutants originated from outside of natural systems belong to external sources. When external pollutants enter natural systems, processes such as application of inorganic fertilizers and pesticides within an agricultural system are associated with the cycled sources. Cycled sources are generated as a function of processes and materials that are cycled through the farm system (Granger et al., 2010).

Metaldehyde has external and cycled sources, according to this classification system. Although insignificant data are available on the extent of metaldehyde application in household gardens and allotments by members of the public, this external souse of metaldehyde could be substantial (Environment Agency, 2009). Point sources of metaldehyde pollution include spills during metaldehyde application and unintentional application directly into watercourses (Kay and Grayson, 2014; Castle et al., 2017). Additional external sources include landfills and consented discharge (Bullock, 2014).

1.4.4 Non-hydrological pathways of metaldehyde

Pathway/delivery processes are mainly hydrological and represent a route from the mobilisation point to the point of delivery to channelised flow (Haygarth et al., 2005). Pathways that are not linked to hydrology include volatilization. Having a vapour pressure of 6.6 Pa (negligible at room temperatures) and a Henry's law constant of 3.5 Pa m^3 mol^{-1} at 25 °C (PPDB, 2017), metaldehyde has a potential to volatilise (ECHA, 2012; Kamrin, 1997).

Degradation of metaldehyde in the troposphere is rapid as its photochemical oxidative half-life (DT_{50}) has been calculated to be 1.7 hours (Voget, 1994). However, it should be noted that the type of product is the factor that will determine the likelihood of this pathway in the environment. Furthermore, products in the form of dust and liquid sprays are prone to drift loss, and pesticides in wettable powder forms are likely to be washed off as runoff (National Research Council, 1993). In addition to liquid form and pellets, metaldehyde is applied to the ground around crops in the form of spays, dusts and grain bait (Kamrin, 1997).

Metaldehyde can also be transported from fields by small organisms such as worms. A study by Gavin et al. (2012) demonstrated that 17% of metaldehyde pellets were removed by earthworms from the field overnight; it took up to 6.4 days for 100% of the pellets to disappear.

1.4.5 Metaldehyde fate and behaviour in various environmental media

1.4.5.1 Metaldehyde fate in soil

Once metaldehyde molecules separate from their sources, mobilisation processes take place in the soil. Mobilisation occurs in the soil profile and includes solubilisation and detachment (Haygarth et al., 2005). Solubilisation is related to chemical, biological and biochemical processes that transform the chemical. These include such mechanisms, as sorption (binding of pesticides to soil particles), chemical degradation (mineralisation) and biological degradation (breakdown of a pesticide by microorganisms). Solubilisation is influenced by the chemical characteristics of a pesticide and the properties of soil and environmental factors, such as weather, topography, hydrological settings and ground cover (Kerle et al., 2007).

The half-life of a pesticide (i.e. its persistence in the environment) will vary depending on soil moisture, texture, type and temperature, microbial population and other dependent variables (National Research Council, 1993). Consequently, metaldehyde mobility is complex and site specific. Detachment of soil particles and chemicals associated with these represent physical mobilisation of a pesticide from soil to water (Haygarth et al., 2005).

Metaldehyde attenuation in soil is relatively low due to its low K_{oc}. Clay and organic matter in soils weakly sorb metaldehyde causing its low persistence in soil environment (Bieri, 2003, Castle et al., 2017). The adsorption properties of soil will impact the concentration of a contaminant in soil material. Spatial variation of clay and organic matter content results in vertical and lateral disparity in contaminant concentration in soils (Van der Perk, 2007). While pesticides with high sorption capacity and low solubility tend to be related to high energy delivery; pesticides like metaldehyde (low sorption and high/moderate solubility) are associated with both high and low energy delivery processes (Bloodworth et al., 2015).

Zhang et al. (2011) studied metaldehyde persistence at three different locations with initial residues of metaldehyde between 1.48 and 6.07 mg kg^{-1}. The half-lives of metaldehyde were 0.75, 0.89 and 1.02 days. Similar results were derived by Dong et al. (2017): DT_{50} values of metaldehyde in soil were 2.3– 2.4 days. According to Bieri (2003), metaldehyde completely degrades within several days in top soils under aerobic conditions. Furthermore, DT_{50} varied between 5.3 to 9.9 days in average agricultural soils in Germany (Bieri, 2003).

Thanawong et al. measured metaldehyde concentrations in sediment during dry and wet seasons in rice paddy fields, and reported concentration up to 10 mg kg^{-1} (concentraitons were lower in the wet season, presumably also due to dilution) (Thanawong et al., 2014). Another report of metaldehyde in rice paddy fields accounted metaldehyde concentrations in paddy soil and water of 0.008 mg kg^{-1} and 0.03 mg L^{-1}, respectively (Calumpang et al., 1995).

Bacterial degradation of metaldehyde in soil

Carbon within metaldehyde chemical structure is a readily utilisable source for microorganisms to depolimerise it into acetaldehyde (Simms et al. 2006). Laboratory study of metaldehyde in soil under aerobic conditions in the dark indicated that metaldehyde did not initially degrade (EFSA, 2010). However, its low persistence was recorded after a lag phase up to 19 days. ^{14}C-Metaldehyde studies have demonstrated high levels of metaldehyde degradation in soils; with mineralisation to $^{14}CO_2$ accounting for 50–78% of the ^{14}C-metaldehyde applied. In contrast, metaldehyde was stable in anaerobic soil conditions (EFSA, 2010). This observation suggests that microbial activity enhances degradation of metaldehyde in soil. Thomas et al. (2013) studied several metaldehyde-degrading bacteria that were isolated from domestic soils. Whilst *Acinetobacter E1* bacteria degraded metaldehyde to a concentration less than 1 nM, its closely related strain *Acinetobacter* was unable to degrade the pesticide (Thomas et al., 2013).

Metaldehyde concentrations in plants

Acetaldehyde residues were detected in plants following metaldehyde application in agricultural fields. Although it showed low persistence with a half-live of 2.4–4.3 days in pak choi (Dong et al., 2017), another study highlights that its concentrations were ten times higher in cabbage (17.4 mg kg^{-1} –68.6 mg kg^{-1}) when compared with residue values in soil (Zhang et al., 2011). At the same time, a much lower concentration of metaldehyde (0.075 mg kg^{-1}) was measured in a rice plants (Calumpang et al., 1995).

Simms et al. (2006) studied factors impacting metaldehyde uptake by wheat and oilseed rape seedlings; concluding that the presence of microorganisms in soil had a significant influence on reduced metaldehyde concentration in plants when compared with those grown in sterile soil (Simms et al., 2006).

1.4.5.2 Metaldehyde concentrations in water

Metaldehyde concentrations in rivers and lakes

Once metaldehyde enters the aquatic environment it becomes semi-persistent as its degradation rate in water is lower than in soil (Bieri, 2003). Typically, metaldehyde enters surface water networks via diffuse runoff, which due to its high mobility occurs during wet periods when it enters surface waters (Castle et al., 2017). Runoff or preferential flow belongs to high energy delivery processes (Bloodworth et al., 2015). Furthermore, runoff can be classified as saturation and infiltration excess runoff. Infiltration excess runoff occurs when precipitation exceeds infiltration and surface storage capacity. Saturation excess runoff is generated once the water table reaches the soil surface level (Reichenberger et al., 2007).

The monitoring data reflect metaldehyde loss to waterbodies within up to four days after its application on land. Kay and Grayson (2014) monitored metaldehyde concentrations in river channels and treatment works in the Ouse catchment in Yorkshire in 2018–2011. Metaldehyde concentrations in samples from treatment works generally varied between 0.2–0.4 $\mu g\ L^{-1}$ (up to a maximum of 2.7 $\mu g\ L^{-1}$). Metaldehyde regulatory limit was observed to be exceeded at 11 out of 21 river channels. Metaldehyde concentrations at these monitoring locations ranged between 0.02 and 1.08 $\mu g\ L^{-1}$ (Kay and Grayson, 2014). Metaldehyde concentrations measured in Upper Thames in October–November 2012 were recorded up to 8.0 $\mu g\ L^{-1}$; maximum concentrations of metaldehyde in water treatment works in this area was also noted to be high (up to 6 $\mu g\ L^{-1}$) (Henehan, 2013).

Metaldehyde prevalence is not limited to the UK. High metaldehyde concentrations up to 6.98 $\mu g\ L^{-1}$ from agricultural runoff were observed in fish farming ponds in northern France in the Moselle River Basin (Lazartigues et al., 2012). However, while metaldehyde applications in continental Europe are normally more intense than in the UK, drinking water supplies are located in groundwater in the majority of these countries

(Castle et al., 2017). This reduces the risk of metaldehyde contamination in drinking water. In contrast, in England and Wales two thirds of potable water supplies of comes from surface water, including rivers and reservoirs (Water UK, 2021). Hence, the risk associated with diffused pollution runoff is higher.

Metaldehyde in groundwater

Relatively high aqueous solubility combined with low adsorption and the sorption properties of pesticides lead to an increased leaching potential in groundwater (Carafa et al., 2007; FAO, 2000). Such properties for metaldehyde make this pesticide available for leaching to groundwater. Leaching to groundwater along with lateral throughflow are pathway-delivery processes associated with low flow (Bloodworth et al., 2015). However, the leaching transport mechanism can often be rapid, since pollutants are able to enter groundwater quickly by bypassing the unsaturated soil zone (Arias-Estévez et al., 2007). Metaldehyde leaches through the shallow subsurface and subsequently enters field drainage systems. Stuart et al. (2012) reviewed emerging organic compounds, including metaldehyde in groundwater, and indicated that the presence of metaldehyde in groundwater, and its metabolite acetaldehyde, is likely to cause a high risk to drinking water. Acetaldehyde also occurs in plants naturally and could be a fermentation by-product.

Metaldehyde has been detected in groundwater in the saturated zone around closed landfills (Bullock, 2014). Metaldehyde concentrations up to 0.9 $\mu g\ L^{-1}$ in Chalk aquifers with a saturated thickness of 30-60 m depth have been reported. These sampling locations were up to 1500 m away from the landfill. The highest metaldehyde concentration (3.0 $\mu g\ L^{-1}$) was detected at a borehole below a landfill site, where a saturated thickness of the Chalk aquifer was 30 m (Bullock, 2014).

1.4.5.3 Metaldehyde in aquatic sediment systems

Metaldehyde transport and fate in aquatic sediment systems should also be considered, since sediments in aquatic environments act as natural sorbents, but can both uptake and re-release pesticides. McKnight et al. (2015) studied the legacy of pesticides in streams and found that both contemporary and banned pesticides were widely present in the sediment-bound phase. Biodegradation and sorption-adsorption mechanisms are the main factors that impact pesticide fate in aquatic sediments (Holvoet et al, 2007). Holvoet et al. (2007) studied sandy and loamy water sediment systems to determine metaldehyde degradation rates and found that metaldehyde dissipated from water with DT_{50} of 11.35 days in a sandy system and 10.25 days in a loamy system. The DT_{50} values of metaldehyde in sediment samples were slightly lower: 10.78 and 9.78 days (sandy and loamy systems, respectively). The DT_{50} values of metaldehyde dissipation from total sandy and loamy systems (sediment and water) were 11.35 and 10.78 days, respectively (Möllerfeld et al., 1993).

In another study it was reported that metaldehyde had a DT_{50} value of 12 days, with further complete degradation in water sediments under moderate temperature conditions. Acetaldehyde was shown to rapidly form (Bieri, 2003). Similar observations were made of metaldehyde concentrations measured in the sediment from fish ponds, with a total concentration decreased from 80 mg kg^{-1} to 1 mg kg^{-1} on the 15th day (Coloso et al., 1998). The observed rapid decrease in concentration may be due to biodegradation and dilution in water.

Metaldehyde concentrations in four natural sediment-water systems were studied in dark, aerobic conditions in laboratory incubations (EFSA, 2010). Metaldehyde had low persistence in more oxidising systems which had the major metabolite acetaldehyde. Metaldehyde persistence in sediment water systems was reported to depend on pH. No major metabolites and high persistence of metaldehyde were observed in less oxidising systems (EFSA, 2010).

Cui et al. (2020) studied concentrations of metaldehyde and other pesticides in water, soil and sediment in the River Ugie catchment in Scotland. Concentrations up to 0.7 μg kg^{-1} (dry weigh) were detected in sediments. Lower fugacity fraction (ff) values (ff<0.5) indicate that the pesticide is likely to remain in the sediment rather than in the water phase. Sediment acting as a sink for metaldehyde was only observed during the metaldehyde application period in autumn–winter months (Cui et al., 2020). It was concluded that the role of sediments to act as a sink or a secondary source of metaldehyde is less relevant, since it is more likely that metaldehyde remains in solution due to its relatively low K_{ow} value (Log K_{ow}=0.12), high water solubility and low adsorption to organic matter in sediment (Cui et al., 2020).

1.4.6 Factors affecting pesticide behaviour and distribution in the environment

Biological degradation and chemical transformation processes that determine the variation in spatial distribution of metaldehyde are governed by such factors as time of application, crop uptake rates and rates of transport. In general, individual factors that have an impact on pesticide pathways and degradation rates belong to one of four categories: soil characteristics, climate, pesticide properties and application rates/methods (Borgesen et al., 2015) (Figure 1.2).

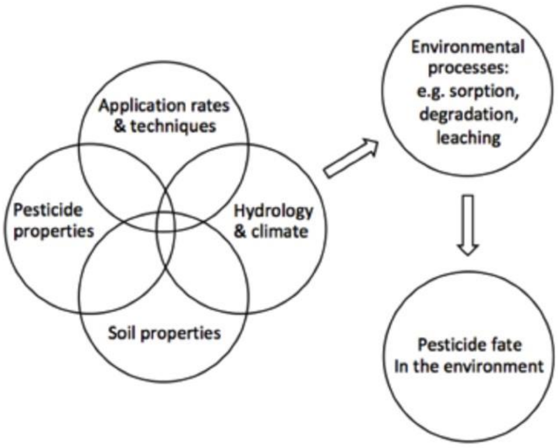


Figure 1. 2 Interactions of factors affecting pesticide fate in the environment (Borgesen et al., 2015).

1.4.6.1 Farming practices

Variations in management practices and differences in land use between agricultural plots impact concentrations of pesticides in topsoil. Metaldehyde concentration data were measured in a catchment with no arable agriculture (93% of grassland) and a catchment with 51% of grassland (Kay and Grayson, 2014). Peak concentrations of metaldehyde in sites with little arable agriculture were much lower. Kay and Grayson (2014) argued that catchment characteristics such as soil type and land use are minor factors impacting metaldehyde loss, while practices carried out on individual farms are more important to consider as a factor that drives differences in metaldehyde loss to water. These include such attributes as application technique and timing, application rates and type of product (Kay and Grayson, 2014). Furthermore, farming interventions as well as application timing have direct impact on pesticide loss to surface waters. Nature-based solutions on farmland, such as such as swales and buffer zones, help to reduce the runoff, which helps to reduce the amount of pesticide loss from the terrestrial to the aquatic system. Similarly, sustainable pesticide management practices have positive impact on reducing pesticide concentration in surface waters. Such practices outlined in the Metaldehyde Stewardship Group guidelines (MSG, 2020) include the following recommendations: i) the use of the minimum amount of active compound per hectare; ii) that soil conditions, topography and fields proximity to watercourses are factors to be considered in assessing the risk of metaldehyde loss to streams, and iii) that metaldehyde application is discouraged during heavy rain events and if field drains are flowing (MSG, 2020).

1.4.6.2 Climatic factors and impact of climate change on pesticide transport and fate

Seasonal variations also influence the concentration and distribution of metaldehyde. Metaldehyde has the capacity to be more mobile and persistent during autumn and winter when the pesticide is applied (Kay and Grayson, 2014). This increased mobility could be caused by more intense applications of metaldehyde due to more frequent and prolonged precipitation events associated with these periods. Increased precipitation intensity results in higher erosion rates when soil particles, enriched with pesticide, are transported to watercourses from agricultural fields. Decreasing temperature along with higher pesticide persistence and increasing precipitation result in higher pesticides loss modelled for drainage and leaching scenarios (Nolan et al., 2008). Modelling by Nolan et al. (2008) showed that short-term climatic changes had a larger impact on clayey soils. Soils with high clay content also provided rapid pesticide transport to tile drains through micro pores (Nolan et al., 2008).

Higher temperatures and water content in soil will increase pesticide degradation rates (Bloomfield et al., 2006). Bloomfield et al. (2006) showed how climate change may affect factors involved in the source-pathway-receptor paradigm. More intensive application rates would be expected with increased number of weeds and pests that have a high potential to successfully evolve with climate change. Higher temperatures will also increase pesticide volatilisation, which will reduce pesticide concentrations in the shallow unsaturated zone but will have low impact on deeper saturated and unsaturated zones (Bloomfield et al., 2006). However, increased volatilization would lead to larger amounts of chemicals subject to long-range atmospheric transport (Balbus et al., 2013).

Furthermore, increased temperatures will cause more intensive atmospheric degradation of organic molecules due to greater photochemical activity (Bloomfield et al., 2006). Changes in hydrology and soil characteristics caused by climate change may also have an impact on pesticide transport and dilution potential in watercourses (Balbus et al., 2013).

1.4.6.3 Soil properties

Soil properties, particularly texture, also affect delivery processes of pesticides. Soils with coarse texture, such as sandy soils, tend to have higher permeability; chemicals in such soils are readily infiltrated into the soil and are more likely to be leached into groundwater (National Research Council, 1993). Additionally, sandy soils generally have lower amounts of microorganisms in comparison with loamy and clayey soils. In contrast, organic matter-rich soils are expected to have higher biodegradation potential due to the abundance of bacteria.

1.4.7 Improved understanding of metaldehyde sources and pathways

1.4.7.1 Sampling and monitoring

Sampling regime and type of sampling are additional components impacting the accuracy of metaldehyde loss measurements and its transport in aquatic systems. Grab sampling commonly takes place weeks apart, and metaldehyde concentration rates in between sampling dates are unknown. To improve accuracy in the detection of metaldehyde loss patterns, more temporally and spatially intense sampling is preferable (Kay and Grayson, 2014). Sufficient amount of data at different scales is necessary to adequately reflect natural variability of the catchment and assess the most suitable parameters for hydrological modelling (Borgesen et al., 2015). In their review, Vereecken et al. (2011) demonstrated that pesticide K_{oc} values varied considerably when assessed at different scales. K_{oc} values are normally derived during lab experiments; but experimental conditions are considerably different from catchment scale conditions.

Should monitoring activities only take place during the highest periods of metaldehyde applications, the average data would be skewed by higher concentrations detected at this time. For this reason, sampling throughout the year is recommended (Napier, 2016). Pesticide concentration peaks are also associated with precipitation events, and low frequency monitoring can underestimate maximum concentrations. The study by Rabiet et al. (2010) demonstrated that infrequent monitoring significantly underestimated pesticide fluxes and concentrations, when grab sampling was compared with other sampling strategies.

Furthermore, when spot and passive sampling strategies were compared, it has been demonstrated that a passive sampling technique is more suitable for pesticide flux estimation and quantification of contaminants when concentrations are low (Zhang et al., 2016). Detailed high frequency monitoring during storm events also improves understanding pesticide sources and their pathways (Lefrancq et al., 2017).

1.4.7.2 Modelling

Amounts of a pesticide applied are an indicator of expected losses in the environment. Hence, the accuracy of predictions can be enhanced by regular and site-specific data updates on pesticide usage and crop type (Altenburger et al., 1993). Lu et al. (2017) applied predictive modelling to understand metaldehyde dynamics in the River Thames basin. They used the INCA-contaminants model (Nizzetto et al., 2016) that included land cover, crop type and climate data, together with water quality, flow and pesticide input data. As limited data on metaldehyde application rates, methods and time of application were available, application rates were estimated in line with the metaldehyde Stewardship Group guidelines (MSG, 2020). In their study, Lu et al. (2017) established that application rate is a fundamental factor in understanding metaldehyde behaviour in watercourses.

Application rates can vary significantly from year to year, depending on meteorological conditions. Therefore, to accurately reflect current metaldehyde contamination risk, such predictive modelling should include up-to-date parameters, particularly data on metaldehyde application patterns.

Furthermore, hydrological conditions play an important role in pesticide transport processes. Asfaw et al. (2018) developed a surface runoff transport model to describe short-term metaldehyde dynamics in the River Leam catchment (central England, UK) using high resolution metaldehyde concentration data and precipitation data for four separate precipitation events (9–35 h duration).

With respect to the area considered in this thesis, a SWAT model with input data collected in 2008–2012 was used in the metaldehyde transport study by Nineham et al. (2015) for East Anglian region in the UK. Nineham et al. (2015) indicated, based on metaldehyde transport modelling, that in order to successfully reduce metaldehyde concentration below 0.1 $\mu g\ L^{-1}$ in the Ardleigh Reservoir, the maximum application rate in the Colne catchment, that partly supplies the reservoir, should be reduced to 60 $g\ ha^{-1}$. In addition, no metaldehyde application was recommended in the areas with impeded drainage.

Chapter 2 Study area description

The following chapter outlines the key information about the study area that is considered in this research, and includes the following categories: geographical position, elevation, topography, climate, land use and crops, hydrology, soils, and geology.

2.1 Geographical position

The River Colne catchment is located in Essex, UK, and starts in the area of Steeple Bumpstead. From there, the River Colne flows in a south-eastern direction through Halsted (the central part of the catchment), towards Colchester. The much smaller Ardleigh catchment boundary, comprising the Ardleigh Reservoir, the Northern and the Western Salary Brooks, is adjacent to the Colne catchment to the north of Colchester (Figure 2.1). The total areas of the Colne and the Ardleigh catchments are 242 km^2 and 14 km^2, respectively.

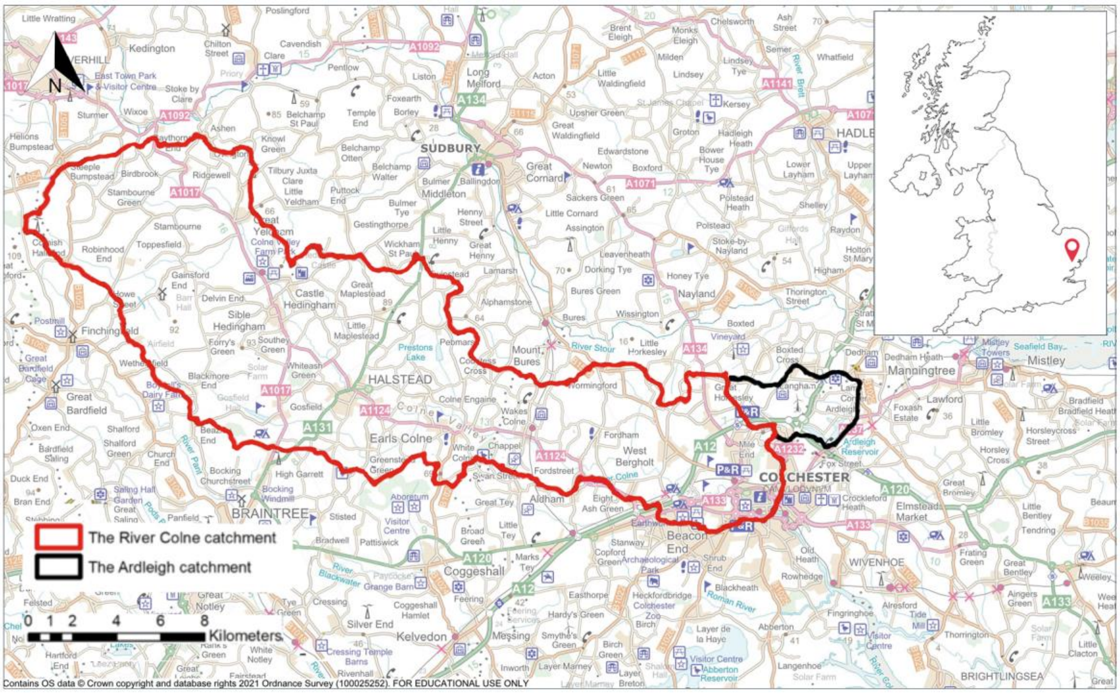


Figure 2. 1 A map showing the River Colne and Ardleigh catchments (OS Raster base map, 1:200,000 scale) (OS, 2021).

2.2 Topography

2.2.1 Colne catchment

Topographically, the River Colne and Ardleigh catchments are located on a plain. Elevation levels vary from 115 m above Ordnance Datum (AOD) from the top part of the catchment in the northwest to 7 m AOD in the Colchester area in the southeast of the catchment. Elevation gradually decreases downstream of the catchment (Figure 2.2).

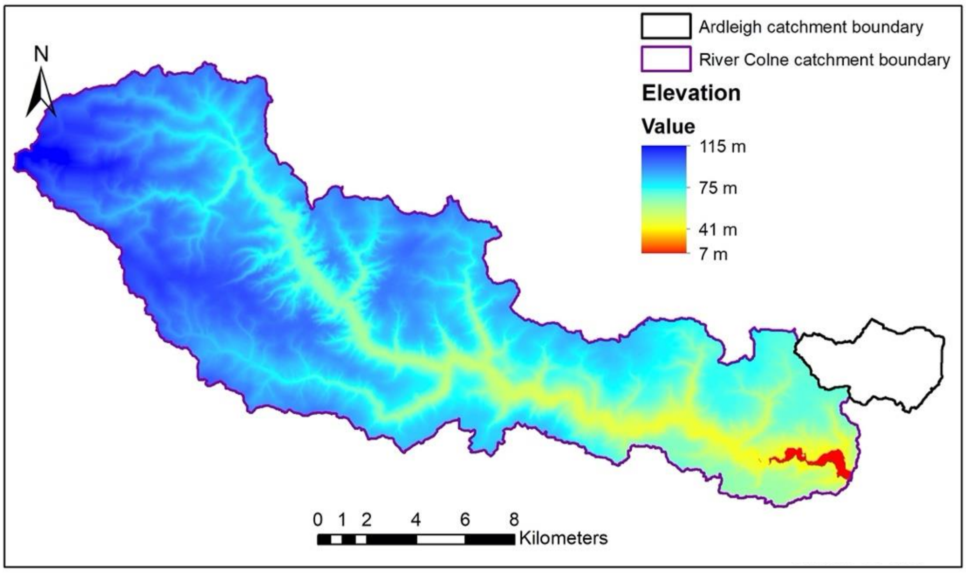


Figure 2. 2. Topographic map of the River Colne catchment based on the Ordnance Survey (OS) Terrain 50 data product - Digital Elevation Model data (50 m grid, 1:50,000 scale) (OS 2019).

2.2.2 Ardleigh catchment

Elevation within the Ardleigh catchment varies from 49 m AOD at the north western boundary of the catchment to 21 m AOD adjacent to the southern end of the Ardleigh Reservoir. Slope gradually falls from the north-west to the south-east of the catchment (Figure 2.3).

Based on the topography and land use of the catchment, the Western Salary Brook receives runoff from both agricultural areas (east and north-east of the catchment), and an urban area in the south east of the catchment, including road runoff from the A12 dual carriage way. The Northern Salary Brook, a smaller stream, accommodates runoff from agricultural land and, to a lesser extent, a number of households along Hart's Lane (a minor road located to the north-west of the catchment).

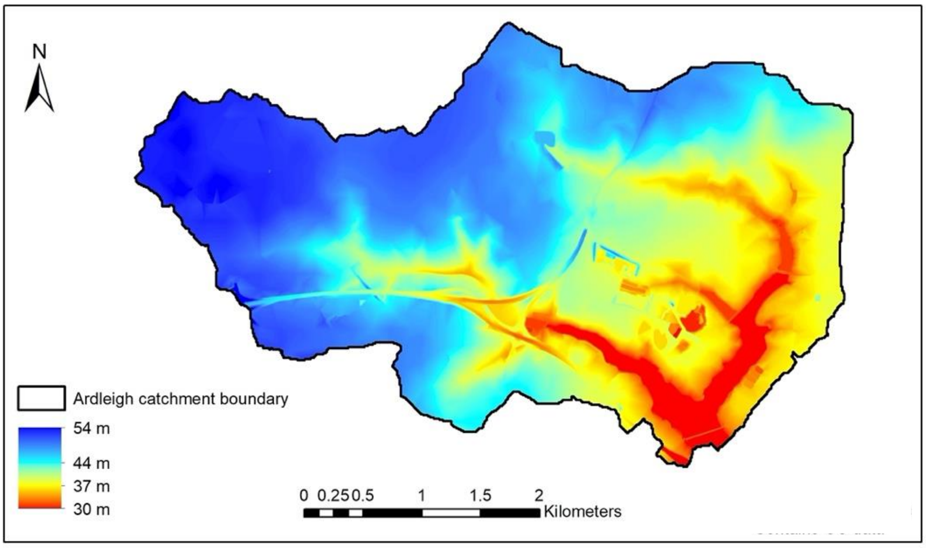


Figure 2. 3. Topographic map of the Ardleigh catchment based on the OS Terrain 50 data product - Digital Elevation Model data (50 m grid, 1:50,000 scale) (OS, 2019).

2.3 Climate

The Colne and Ardleigh catchments are located in East Anglia – an area of temperate maritime climate. The mean annual temperature across the region varies between 9.5 °C to 10.5 °C and is subject to seasonal variation. Mean daily minimum temperatures in January and February, the coldest months, are close to 1 °C. Mean daily minimum and maximum temperatures vary between –8 °C in winter months to 20–23 °C during the summer (Table 2.1; Met Office, 2019).

The number of days a year with frost is approximately 55 within both catchments, an inland area that is, at minimum, 17 km from the coast. At the coast, the days of frost are less than 30 per calendar year (Table 1; Met Office, 2019). The least amount of sunshine in the area occurs during December, while July is the sunniest month. On average, Essex, in which the catchments are located, is experiences over 1600 hours of sunshine throughout the year (Met Office, 2019).

The winter months (December – February) include approximately 30 days of precipitation and less than 20 days of snowfall. The summer months (June – August) include less than 20 days of precipitation events. February is the driest month (average precipitation 40.7 mm), with most precipitation occurring in October (64.8 mm) (Table 2.1; Met Office, 2019).

Since the East of England is considered a sheltered region due to its easterly position, there is less than two days of gales (a day when the mean wind speed is 34 knots ($17.5\ m\ s^{-1}$) or more over any period of 10 minutes) per year. The prevailing wind directions in this area of England are southerly and north-westerly (Met Office, 2019). The average climatic data collected during 1981–2010 for Wattisham weather station, 32 km away from the Ardleigh catchment, are listed in Table 2.1.

Table 2. 1 Climatic data collected from Wattisham weather station, located 32 km from Colchester, Essex (average for 1981-2010) (Met Office, 2019).

Month	Max. temp. (°C)	Min. temp. (°C)	Days of air frost (days)	Precipitation (mm)	Days of precipitation ≥ 1 mm (days)	Monthly mean wind speed at 10 m ($m\ s^{-1}$)
Jan	6.6	1	10.8	49.2	11.2	5.6
Feb	6.8	0.8	11.3	40.7	9.5	5.4
Mar	9.8	2.6	6.3	44.4	10.4	5.4
Apr	12.7	4.1	3.1	41.1	9.3	4.8
May	16.2	7.2	0.4	50.9	8.7	4.5
Jun	19.1	9.9	0	52.6	9.1	4.2
Jul	21.9	12.2	0	50.1	8.7	4.1
Aug	21.8	12.2	0	56.2	8.4	4.2
Sep	18.6	10.2	0	51.9	8.8	4.4
Oct	14.2	7.5	0.6	64.8	10.1	4.7
Nov	9.7	3.9	4.6	59.9	10.9	4.9
Dec	6.9	1.6	10.3	52	10.6	5
Annual	13.7	6.1	47.4	613.7	115.8	4.8

2.4 Land use

2.4.1 Colne catchment

A large proportion of the Colne catchment area ($242\ km^2$) consists of agricultural/horticultural land (62.9% of the total catchment area), with grassland and woodland equal to 18.9 and 7%, respectively, and minor classes of freshwater, fens and marshes of >1%. The area under urban/suburban land use makes 2.5 and 8.3% of the total area of the catchment. The major settlements include Toppesfield and Finchingfield located at the head of the catchment, Halstead in the central area of the catchment, and Colchester at the bottom of the catchment (Figures 2.1, 2.4).

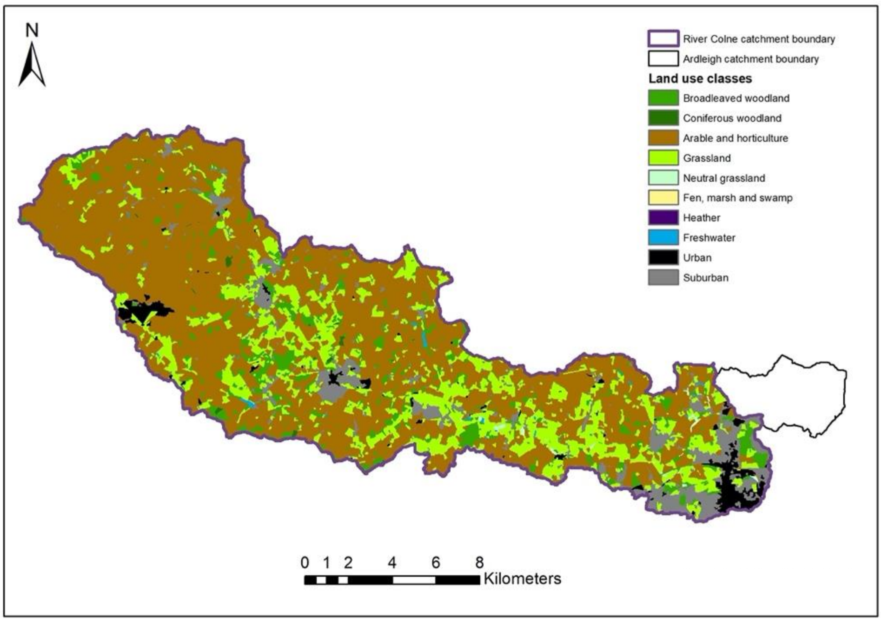


Figure 2. 4 Map showing land use classes present within the River Colne catchment. The map is based on Land Cover Map 2015 (LCM2015) with 25m spatial resolution (UKCEH, 2017).

2.4.2 Ardleigh catchment

As with the River Colne catchment, the Ardleigh catchment area consists of predominantly agricultural/horticultural land and grassland with some woodland. Together these classes contribute up to 85% of the total catchment area of 14 km^2. The urban/suburban land use classes (approximately 15%) are minor land use classes (Figure 2.5).

The major urban area is located in the south-eastern part of the catchment, with industry and business infrastructure and active residential development near the A12 dual-carriage way, as well as mainly residential areas further south. Runoff from urban areas enters the Eastern Salary brook, where the watercourse is located in close proximity to this urban cluster.

Suburban areas comprise households across the catchment situated in the agricultural setting (e.g. along the Hart's Lane and minor roads).

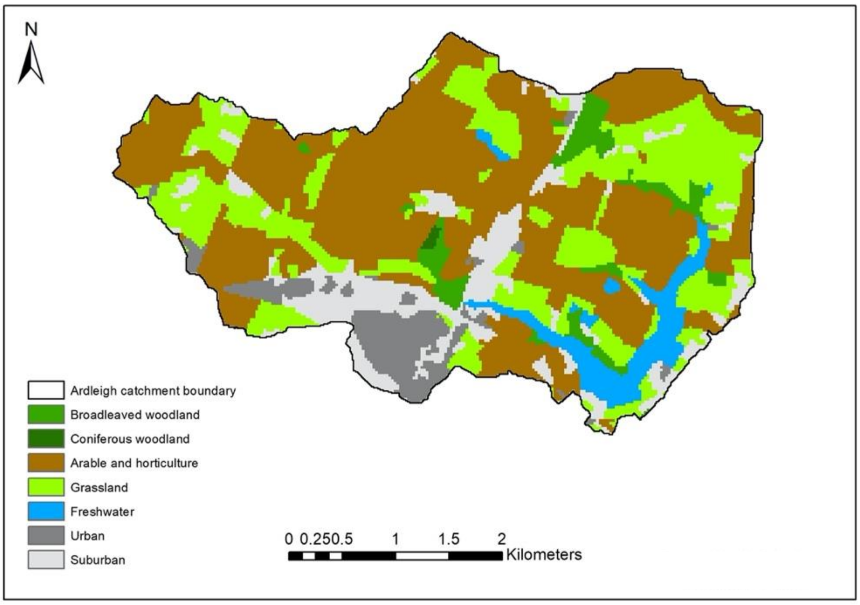


Figure 2. 5 Map showing land use classes present within the Ardleigh catchment. The map is based on Land Cover Map 2015 (LCM2015) with the 25m spatial resolution (UKCEH, 2017).

2.5 Crops

The total arable area in the Colne and the Ardleigh catchments is 189.1 km^2. The predominant arable crop types are cereals and oilseed rape (Figure 2.6, Table 2.2).

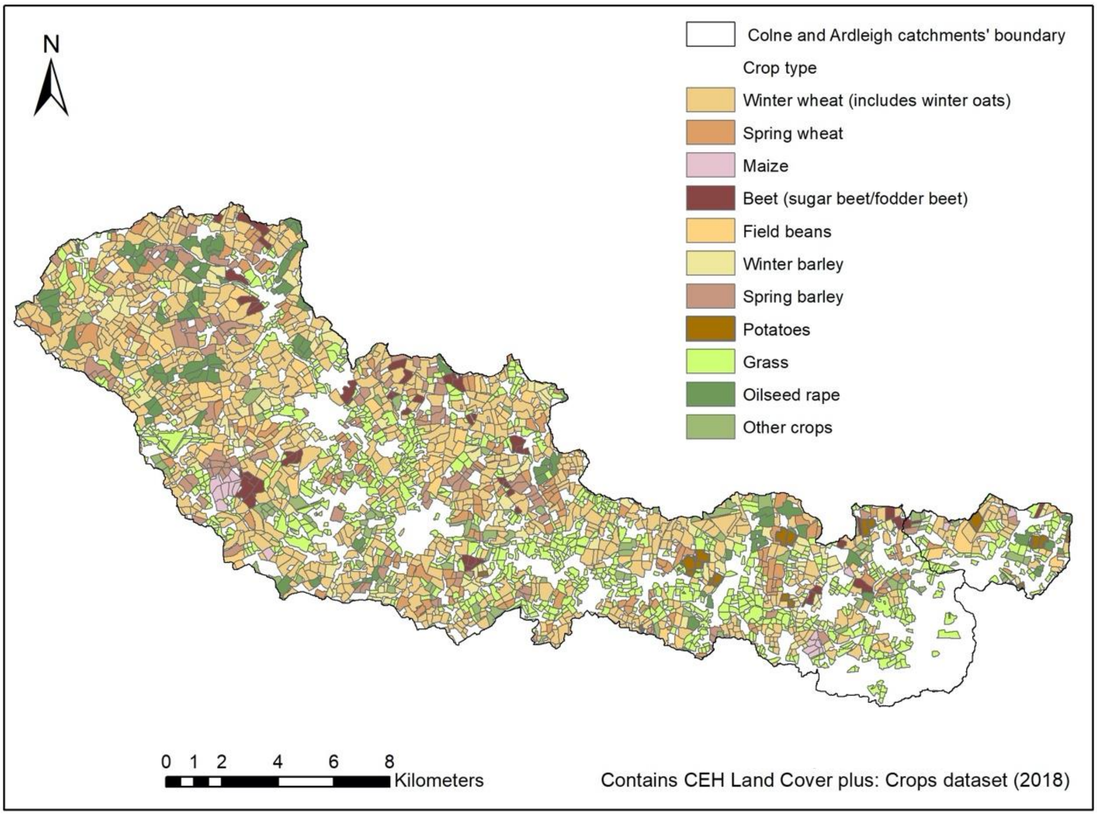


Figure 2. 6 Crop map of the Colne and the Ardleigh catchments. The map is based on the Land Cover Plus: Crops dataset (UKCEH, 2018).

Table 2. 2 Crop coverage (km^2) and percentage of the total arable area within the Colne and Ardleigh catchments. Statistics are derived from the Land Cover Plus: Crops dataset (UKCEH, 2018).

Crop	Area (km^2)	% of total arable area
Winter wheat	66.6	35.2
Spring wheat	13.5	7.1
Maize	1.7	0.9
Beet	5.2	2.8
Beans	11.9	6.3
Winter barley	14.8	7.9
Spring barley	12.1	6.4
Potatoes	2.0	1.0
Grass	42.0	22.2
Oilseed rape	11.7	6.2
Other crops	7.6	4.0

2.6 Hydrology

2.6.1 Colne catchment

The River Colne catchment includes the River Colne, Stambourne Brook, Toppesfield Brook, Pebmarsh Brook, Bourne Brook and St. Botolph's Brook. The length of the stream network within the Colne catchment is 50 km with the average streamflow increasing downstream from 0.29 $m^3\ s^{-1}$ and 0.73 $m^3\ s^{-1}$ at the upper and middle sub-catchment gauging stations (37012 and 37024) to 1.07 $m^3\ s^{-1}$ at the lower sub-catchment gauging station (37005) near Lexden and Colchester for the period 1959–2017.

Base Flow Index (BFI) values gradually increase from 0.28 in the upper part of the catchment (station 37012) to 0.43 and 0.52 (stations 37024 and 37005, respectively) in the middle and the lower parts of the study area (Figure 2.7; NRFA, 2019 a, b, c). Average runoff ratios calculated for the period 2009-2017 varied from 58% at the upper sub-catchment (station 37012) to 22% and 23% at the middle and the bottom parts of the Colne catchment (stations 37024 and 37005, respectively).

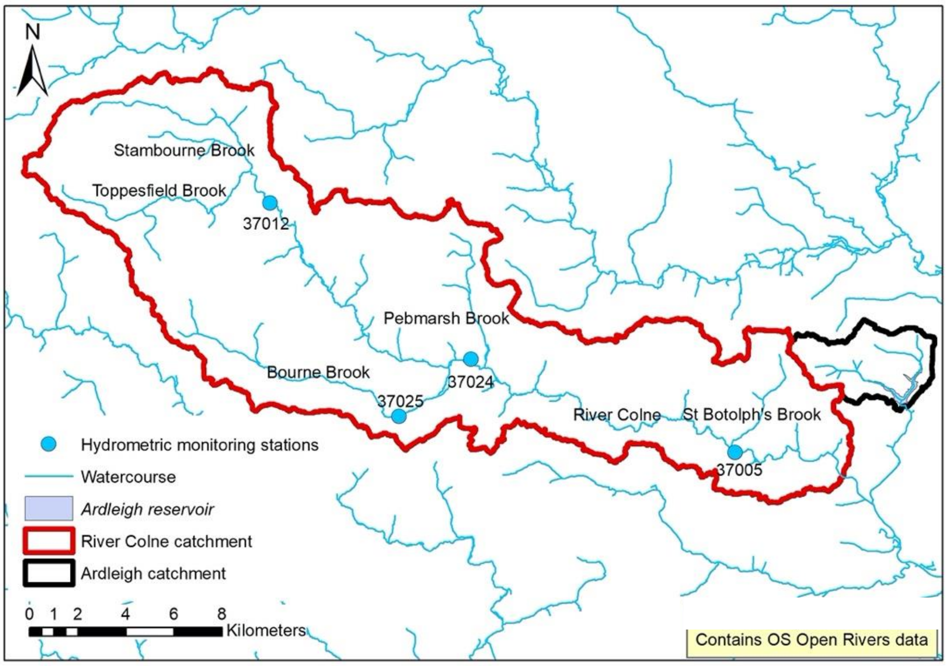


Figure 2. 7 Hydrological network of the river Colne catchment. Contains OS Open Rivers raster data (1:30,000 scale) (OS, 2018).

The top part of the catchment incorporates the section of the river Colne upstream of Great Yeldham. The watercourse length in this sub-catchment is 4 km (EA, 2019). Stambourne Brook and Toppesfield Brook flow from the top of the catchment into the middle section (from Great Yeldham to Doe's Corner). The length of the watercourses in this sub-catchment is 10.2 km. These brooks flow primarily through rural areas with agricultural land use (EA, 2019).

Pebmarsh and Bourne Brooks (downstream of Doe's Corner) flow into the downstream section, which is adjacent to the Ardleigh catchment. The total length of the watercourses is 31.8 km. (EA, 2019). The River Colne has a number of surface abstractions along the stretch used for irrigation in arable farming. The water from the river is also abstracted and pumped into Ardleigh Reservoir for drinking water supply (EA, 2019).

2.6.2 Ardleigh catchment

The Ardleigh Reservoir is a water storage body located at the Ardleigh catchment at the north-east boundary of Colchester (Figure 8). It was constructed in 1969 through flooding the valleys of the Northern Salary Brook (NSB) and the Western Salary Brook (WSB) (Abdul-Hussein & Mason, 1988). The reservoir is considerably shallow; its depth varies from 3.9 m to a maximum depth of 13 m and a maximum volume of 2,190,000 m^3 (Redshaw et al., 1988).

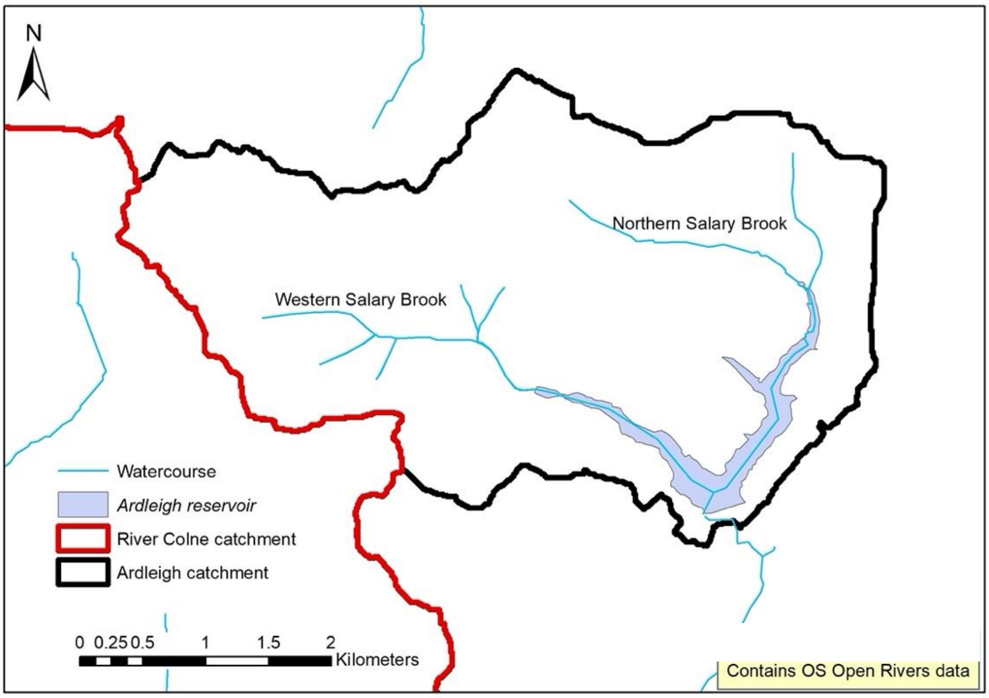


Figure 2. 8 Hydrological network of the Ardleigh catchment. Contains OS Open Rivers raster data (1:30,000 scale) (OS, 2018).

Both the Western and Northern Salary Brooks are shallow (up to 0.5 m deep) and fairly narrow (with widths varying between 0.5 and up to 1.5 m along the tributaries). These small streams constitute two natural (gravity flow-fed) sub-catchments (areas of 7.5 and 6.5 km^2, respectively) of the Ardleigh catchment with a total catchment area 14 km^2 (Figure 2.8, Table 2.3). Water enters the Ardleigh Reservoir from the Northern Salary Brook and the Eastern Salary Brook.

When necessary, additional water is abstracted from the River Colne and pumped into the reservoir. Precipitation and minor runoff are additional sources of water supply for the reservoir. Water leaves the reservoir by evaporation, abstractions to the treatment works (UK National Grid reference TM019238) and compensation flow to the Western Salary Brook (Redshaw et al., 1988).

Table 2. 3 General characteristics of the Ardleigh Reservoir (Environment Agency Catchment Data Explorer, 2018)

Characteristic	Value
Hydromorphological designation	Artificial
Easting	603190
Northing	228294
Mean depth	4.158 m
Altitude	34 m
Catchment area	14 km^2
Surface area	0.57 km^2

2.7 Soils

2.7.1 Colne catchment

The catchment includes nine soil associations of predominantly loamy and clayey soils, with slightly impeded drainage capacity. The top part of the catchment includes slowly permeable lime-rich clayey and loamy soils of the Hanslope Association, and the minor Ashley Association of fine loamy over clayey soils with slowly permeable subsoils (Figure 2.9; Cranfield University, 2019). Land use for crops includes mainly winter cereals and some other arable crops and grassland.

The central part of the catchment contains the Ludford Association, surrounded by the Hornbeam 3 and the Oak 2 Associations (Figure 9; Cranfield University, 2019). Ludford soils are fine and coarse loamy soils with high drainage capacity. The Hornbeam 3 and the Oak 2 Associations include fine loamy over clayey, and fine silty over clayey (the Oak 2 Association) soils that have subsoils with low permeability, subject to seasonal waterlogging. Ludford and Hornbeam 3 soils are used for a wide range of pasture and woodland types; whilst cropping land use for the Oak 2 Association includes winter wheat and other arable crops (Figure 2.9; Cranfield Soil and Agrifood Institute Soilscapes (CSAI), 2019).

The southeast part of the catchment around Colchester area includes coarse loamy soils of the Tendring (upper part of the area) and the Wix Associations (central to southern part), used for pasture and woodland. Soils of the Wix association are affected by groundwater in this area, as well as a the minor Fladbury 3 soil association. These loamy and clayey soils are located on the floodplain with naturally high groundwater levels (Figure 9; CSAI, 2019).

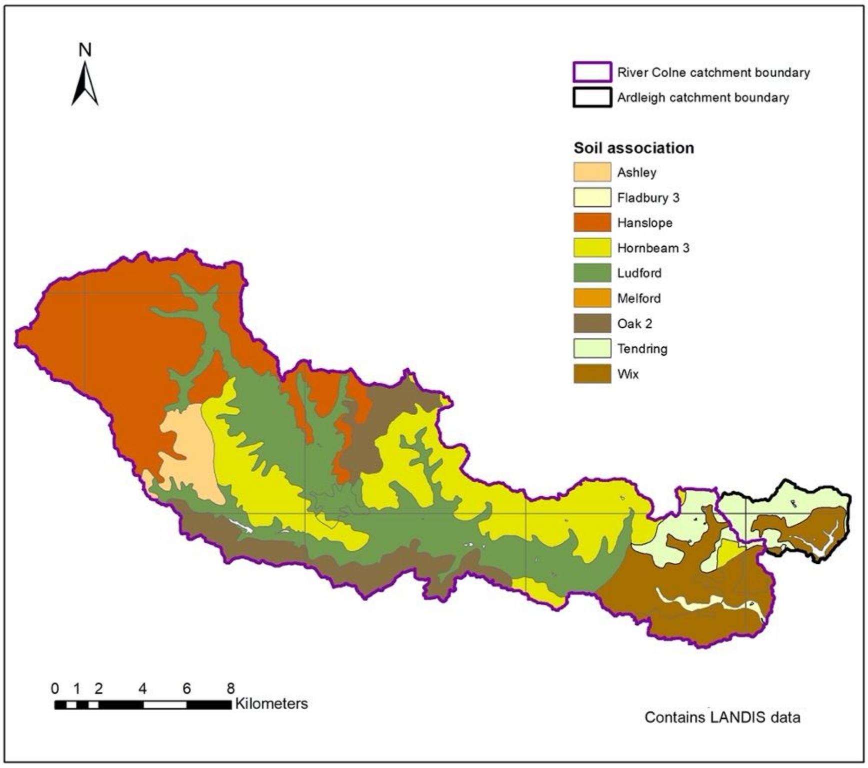


Figure 2. 9 Soil map of the River Colne and the Ardleigh catchments. Contains 1:250,000 national soil data from LandIS (CSAI, 2019).

2.7.2 Ardleigh catchment

Soils in the Ardleigh catchment are loamy and clayey, slightly acidic with impeded drainage. These include the Tendring and the Wix soil associations (Figure 9; LandIS, 2019). Tendring soils are located across the upper half of the catchment, whilst the Wix Association is found primarily in the south-eastern area around the Ardleigh Reservoir. These soil types allow flexible conditions for crops. However, they are more suitable for autumn-sown crops (CSAI, 2019).

2.8 Geology

The soil parent material of the River Colne and Ardleigh catchments is represented by Quaternary superficial deposits of clay, silt and chalk-rich diamicton, as well as sand and gravel deposits of glacial origin. These deposits were formed during the Pleistocene epoch, which lasted from 2.6 million to 11,700 years ago (Figure 2.10). An aeolian depositional environment of medium to fine grained sediments had led to the formation of beds and lenses across the area (British Geological Survey (BGS), 2019 a). These deposits contain water and produce spring seepages at their base, and have generally high permeability.

A small fraction of parent material includes bedrock deposits of clay, silt and sand formed in a marine environment (Paleogene period, 66–23 million years ago), as well as chalk deposits (Cretaceous period, 145.5–66 million years ago) (Figure 2.10).

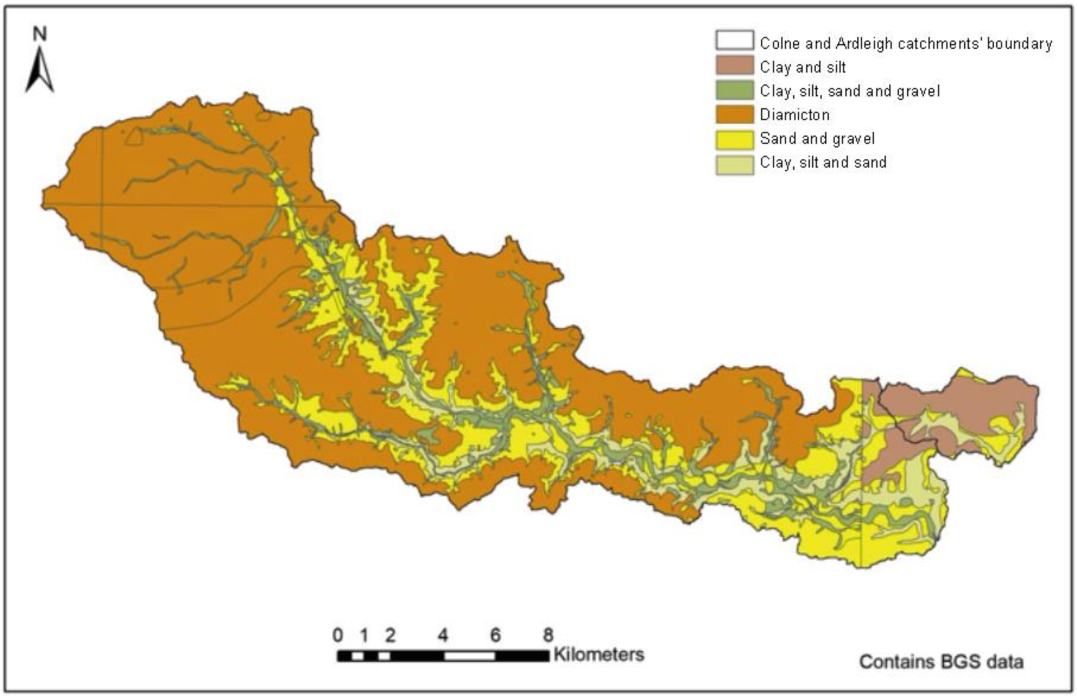


Figure 2. 10 Parent material map of the River Colne and the Ardleigh catchments. Contains 1:50,000 Soil Parent Material data from BGS (2019).

Bedrock material of the catchment area consists of silt, silty and sandy clay that belong to the London Clay Formation of the Thames Group, formed during the Paleogene period between 56 and 33.9 million years ago followed by clay, silt, sand and gravel bedrock material of the Lamberth Group (56 to 66 million years) (Figure 2.11). Bedrock deposits were formed in a shallow marine environment and marginal coastal plains with predominantly siliclastic sediments. The maximum thickness of clays near Colchester is 26 m (BGS, 2019 b). Having unfavourable infiltration potential, clays can confine water in underlying beds. The bedrock permeability class is very low, and generally there is no accessible groundwater.

In the top part of the Colne catchment, the underlying deposits include Chalk of the Sussex White Chalk formation formed in the Late Cretaceous period between 100.5 and 66 million years ago (Figure 2.11). The thickness of Chalk varies depending on the degree of post-Cretaceous erosion (BGS, 2019 c) and forms an aquifer yielding groundwater supplies.

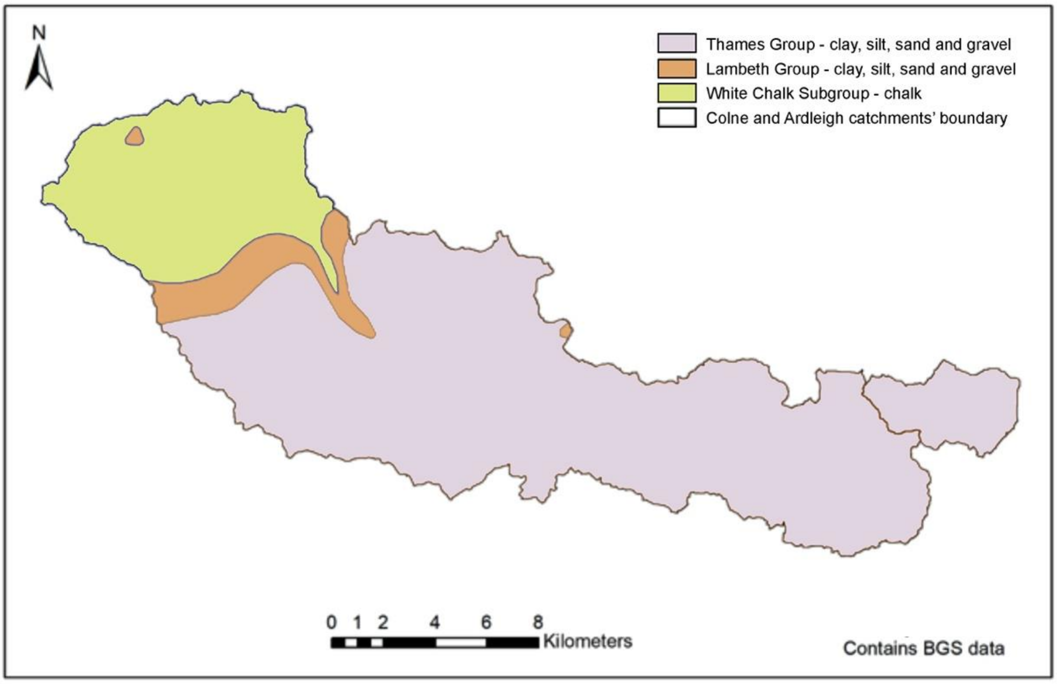


Figure 2. 11 Bedrock geology map of the River Colne and Ardleigh catchment. Contains 1:50,000 bedrock geology data from BGS.

Chapter 3 Ubiquity of microbial capacity to degrade metaldehyde in dissimilar agricultural, allotment and garden soils

This research was published in 2020:

Balashova, N., Wilderspin, S., Cai, C., Reid, B. J. (2020). Ubiquity of microbial capacity to degrade metaldehyde in dissimilar agricultural, garden and allotment soils. *Science of Total Environment*, 704, 1-9.

3.1 Chapter summary

Despite the extensive use of metaldehyde, very little is known about the capacity of soil microbial communities to degrade this chemical. This research provides a synopsis of the latent capacity of soil microbial communities, present in agricultural (n = 14), allotment (n = 4) and garden (n = 10) soils, to degrade metaldehyde.

Extents of ^{14}C-metaldehyde mineralisation across all soils ranged from 17.7 to 60.0%. Pre-exposure (*in situ*, in the field) to metaldehyde was not observed to consistently increase extents of metaldehyde mineralisation. Where soils were augmented, (*ex situ*, in the laboratory) with metaldehyde (28 mg kg^{-1}), the mineralisation capacity was increased in some, but not all, soils (uplift ranged from +0.10 to +16.9%). Results indicated that catabolic competence to degrade metaldehyde was evident in both surface (16.7–52.8 %) and in sub-surface (30.0–66.4%) soil horizons. Collectively, the results suggest that catabolic competence to degrade metaldehyde was ubiquitous across a diverse range of soil environments; that varied in texture (from sand to silty clay loam), pH (6.15–8.20) and soil organic matter (SOM) content (1.2–52.1%). Lighter texture soils, in general, were observed to have higher capacity to mineralise metaldehyde. Weak correlations between catabolic competence and soil pH and soil organic matter content were observed; it was noted that above a SOM threshold of 12% metaldehyde mineralisation was always >34%.

It was concluded that the common occurrence of metaldehyde in EU waters is unlikely the consequence of low potential for this chemical to be degraded in soil. It is more likely that application regimes (quantities/timings) and meteorological drivers facilitate the transport of metaldehyde from point of application into water resources.

3.2 Introduction

Slugs, snails and other gastropods are significant pests to a range of crops, including agricultural, horticultural and garden plants (Rae et al., 2009). Metaldehyde (2,4,6,8-tetramethyl-1,3,5,7-tetraoxcane) is a widely used molluscicide in agriculture and domestic settings globally (including the UK, Europe, the United States and China (EPA, 2011; Gavin et al., 2012; Ma et al., 2012; Zhongguo et al., 2013; EC, 2019)).

This pesticide is normally applied to crops in autumn and winter (Environment Agency, 2009). The maximum recommended application rate of metaldehyde in the UK is currently 210 g active substance/ha (from 1st August to 31st December); 700 g active substance/ha is the maximum total dose per calendar year (Metaldehyde Stewardship Group (MSG), 2019). Similar application rates are evident across Europe; allowing a maximum of 350 g active substance/ha per single treatment, with up to two treatments per year (EFSA, 2010). In the United States the recommended single application rate should not exceed 2240 g active substance/ha with a maximum of 6 applications per year (EPA, 2011).

Bait pellets release metaldehyde, under moderately moist conditions, for approximately 10 days (Puschner, 2006). Metaldehyde is relatively water soluble (190 mg L^{-1}; PPDB, 2017) and has as low K_{OW} value (0.12; Hall, 2010). Owing to, i) its physicochemical properties, ii) application times that often coincide with wetter periods (when molluscs are more prevalent, compared to dry weather conditions) and, iii) the prevailing wet autumn/winter weather in the UK and northern EU countries, metaldehyde is mobile in the environment. This mobility serves to transfer metaldehyde from soil to both ground- and surface waters. Thus, metaldehyde presence in surface water and groundwater has been reported with high frequency (Busquets et al., 2014; Hillocks, 2012).

Kay and Grayson (2014) reported peak concentrations of metaldehyde in the range 0.4–0.6 µg L^{-1} and highlighted that metaldehyde has been detected above the maximum allowable concentration for drinking water of 0.1 µg L^{-1} (EC, 2000) during the October–December periods, when slug pellets are typically applied. These findings agree with metaldehyde concentration trends, observed by Castle et al. (2018), who reported peak concentrations of metaldehyde in the stream water of the River Thames Catchment to vary between 0.1 and 0.35 µg L^{-1} during September – January 2017. The maximum concentration of 5 µg L^{-1} was recorded in November, and no metaldehyde concentrations above 0.1 μg L^{-1} were recorded during the February – August period (Castle et al., 2018). Concentrations up to 1.5 μg L^{-1} were reported in stream water of the same catchment by Lu et al. (2017). Metaldehyde concentrations up to 2.2 μg L^{-1} were reported in a UK chalk aquifer by (Bullock, 2014), with peak concentrations observed in January and February. Metaldehyde presence in the aquatic environment has been reported in other countries. Calumpang et al. (1995) reported maximum metaldehyde concentrations of 1.57 mg L^{-1}, in rice paddy water in the Philippines, following application and that concentrations fell to below the detection limit within nine days (Calumpang et al., 1995). Metaldehyde concentrations up to 6.98 μg L^{-1} were observed in run-off water from fish farming ponds in northern France within the Moselle River Basin (Lazartigues et al., 2012).

A key factor underpinning metaldehyde fate and mitigating its transport is the latent capacity of soil microbial communities to degrade this pesticide. Yet, literature relating to microorganisms capable of metaldehyde degradation is limited to three studies. Thomas et al. (2013, 2017) reported several metaldehyde-degrading bacterial strains that were isolated from domestic soils (liquid cultures contained 100 mg L^{-1} metaldehyde); *acinetobacter* E1 was reported to degraded metaldehyde present in solution at concentrations less than 1 nM (0.16 μg L^{-1}), other *acinetobacter* strains were reported to be unable to degrade the pesticide. A laboratory study (EFSA, 2010), reported metaldehyde to be mineralised (50–78%) by soil microbial communities under aerobic conditions; while under anaerobic conditions metaldehyde was observed to be stable.

However, to date, no reports have been published that account the capacity (assessed using ^{14}C-respirometry) of dissimilar soils from contrasting settings, to degrade metaldehyde. Thus, this current research sought to establish the level of catabolic competence of soil microbial communities to degrade metaldehyde (i.e. the competence of the microbial community to break down metaldehyde molecules into smaller units that are subsequently oxidised/mineralised to carbon dioxide).

The current research considered soils obtained from three contrasting settings: agricultural fields, allotments and gardens (and both surface and sub-surface regimes). The research sought to establish intrinsic metaldehyde mineralisation potential of the microbial community within these soils and the directing influence of metaldehyde augmentation in terms of inducing metaldehyde degradation. Furthermore, it was hypothesised that soil attributes, include texture, SOM and pH would have a shaping influence upon levels of metaldehyde catabolic competence. These original lines of enquiry provide a synopsis of metaldehyde biodegradation in dissimilar soils from contrasting settings.

3.3 Materials and Methods

3.3.1 Chemicals

Metaldehyde pellets (1.5% active ingredient) were manufactured by Bayer. ^{14}C-metaldehyde (UL-^{14}C; 5.1 mCi mmol^{-1}) was obtained from American Radiolabelled Chemicals Inc. St Louis, USA. Ultima Gold and Ultima Gold XR liquid scintillation fluids were purchased from Perkin Elmer, UK. Calcium chloride, ethanol, methanol and sodium hydroxide were supplied by Fisher Scientific, UK; and dichloromethane provided by Sigma Aldrich, UK. Mineral Basal Salt (MBS) components (namely: NaCl, $(NH_4)_2SO_4$, KNO_3, KH_2PO_4, K_2HPO_4 and $MgSO_4.7H_2O$) were obtained from BDH, UK.

3.3.2 Soils

Soil was collected from three contrasting settings: agricultural fields, allotments and gardens. Soils were collected in Norfolk and Essex, UK (Table 3.1). Soil samples (200 g) were collected using a Dutch auger (0–10 cm for top soil; and, 40–50 cm for sub-soil samples); four auger heads were combined to produce a single composite sample at each sampling point and a given location was sampled in triplicate (within 5 m of each other). Between sampling the auger head was thoroughly cleaned (washed with water and tissue, then sprayed with 70% ethanol solution that was allowed to evaporate). Soils were transported to the laboratory and stored (4 °C) in sealed plastic bags, for no more than 2 days, prior to assessment of catabolic competence.

Soils were characterised in terms of their: SOM content (mass loss on ignition in a muffle furnace (450 °C) for 12 h; 10 g (n = 3)) (Ghabbour et al., 2014); pH (samples (3 g, n = 3)) were combined with 30 mL of distilled water in a centrifuge tube, tubes were then shaken (reciprocal shaker IKA Labortechnik KS501) at 100 r.p.m for 14 h and the soil water pH was measured using an electrode (Jenway) and meter (Mettler Toledo FE20

Five Easy Benchtop pH Meter), and texture (samples of soil were moistened and kneaded into a ball and texture determined following the hand-texture framework of McDonald et al. (1998)). Soil characteristics are listed in Table 3.1.

Table 3. 1 Field, Allotment and Garden soil properties.

Soil Code	Setting	Soil horizon	Coordinates (Lat., Lon.)	Texture	Metaldehyde application	OM (%)	pH
FT(n)1	Field 1	Topsoil	51.9749, 1.1308	Sand	>4 years ago	3.49 ± 0.1	6.68 ± 0.23
FT(n)2	Field 2	Topsoil	51.9730, 1.1459	Loamy Sand	>4 years ago	3.08 ± 0.2	7.55 ± 0.5
FS(n)2	Field 2	Subsoil	51.9730, 1.1459	Sand	>4 years ago	1.82 ± 0.4	7.55 ± 0.2
FT(n)3	Field 3	Topsoil	52.0231, 1.0825	Sandy Loam	>4 years ago	2.53 ± 0.1	6.57 ± 0.1
FT(n)4	Field 4	Topsoil	51.9370, 0.9752	Sandy Loam	>4 years ago	3.85 ± 0.03	6.35 ± 0.1
FS(n)4	Field 4	Subsoil	51.9370, 0.9752	Sand	>4 years ago	2.38 ± 0.1	7.21 ± 0.4
FT(n)5	Field 5	Topsoil	51.9180, 0.9740	Sandy Loam	>4 years ago	4.52 ± 0.3	7.19 ± 0.3
FT(p)6	Field 6	Topsoil	52.5198, 1.5466	Sandy Loam	Seasonal (ongoing)*	2.79 ± 0.2	8.2 ± 0.1
FT(p)7	Field 7	Topsoil	52.5079, 1.5366	Silty Loam	Seasonal (ongoing)	3.89 ± 0.1	7.24 ± 0.1
FT(n)8	Field 8	Topsoil	51.9340, 0.9221	Loam	>4 years ago	4.02 ± 0.3	6.15 ± 0.1
FT(p)9	Field 9	Topsoil	52.5082, 1.5390	Loam	Seasonal (ongoing)	3.4 ± 0.1	7.11 ± 0.2
FT(p)10	Field 10	Topsoil	52.5190, 1.5440	Loam	Seasonal (ongoing)	2.67 ± 0.1	7.73 ± 0.2
FT(p)11	Field 11	Topsoil	52.5084, 1.5423	Sandy Clay Loam	Seasonal (ongoing)	3.96 ± 0.3	6.44 ± 0.02
FT(p)12	Field 12	Topsoil	52.5089, 1.5266	Silty Clay Loam	Seasonal (ongoing)	4.02 ± 3.9	7.29 ± 0.2
AT(n)1	Allotment 1	Topsoil	52.6268, 1.2552	Loamy Sand	No previous application	7.91 ± 0.4	7.58 ± 0.01
AS(n)1	Allotment 1	Subsoil	52.6268, 1.2552	Sand	No previous application	1.36 ± 0.3	7.05 ± 0.2
AT(p)2	Allotment 2	Topsoil	52.6276, 1.2539	Loamy Sand	Seasonal (ongoing)[$]	5.24 ± 0.1	7.44 ± 0.5
AS(p)2	Allotment 2	Subsoil	52.6276, 1.2539	Sand	Seasonal (ongoing)	1.17 ± 0.1	7.18 ± 0.1
GT(n)1	Garden 1	Topsoil	52.7049, 0.9694	Sandy Loam	>6 years ago	52.1 ± 1.0	7.1 ± 0.03
GT(n)2	Garden 2	Topsoil	52.5090, 0.8789	Loamy Sand	>6 years ago	7.2 ± 0.2	7.54 ± 0.03

GT(n)3	Garden 3	Topsoil	52.6514, 1.0481	Loamy Sand	>6 years ago	25.3 ± 0.2	6.92 ± 0.02
GT(n)4	Garden 4	Topsoil	52.6803, 1.1930	Loamy Sand	>6 years ago	16.2 ± 0.3	7.49 ± 0.04
GT(n)5	Garden 5	Topsoil	52.5542, 1.2367	Loamy Sand	>6 years ago	11.8 ± 0.5	8.02 ± 0.02
GT(n)6	Garden 6	Topsoil	52.6207, 1.2457	Loamy Sand	>6 years ago	11.4 ± 0.4	8.01 ± 0.01
GT(n)7	Garden 7	Topsoil	52.7777, 0.9809	Sandy Clay Loam	>6 years ago	10.2 ± 0.1	7.65 ± 0.01
GT(n)8	Garden 8	Topsoil	52.5725, 0.9822	Sandy Clay Loam	>6 years ago	12.4 ± 0.4	7.52 ± 0.01
GT(n)9	Garden 9	Topsoil	52.5310, 0.8733	Sandy Clay Loam	>6 years ago	5.5 ± 0.1	8.15 ± 0.01
GT(n)10	Garden 10	Topsoil	52.6284, 0.9922	Sandy Clay	>6 years ago	8.6 ± 0.3	7.7 ± 0.02

3.3.3 ^{14}C-radiorespirometry assessment of intrinsic and induced catabolic competence

Prior to undertaking the respirometry, soils were transferred to the laboratory incubator for 24 h to bring them back to a temperature of 18 °C. Soil samples (10 g) were added to sterile Duran Schott bottles (250 mL) containing sterile MBS (30 mL) (0.3 g NaCl, 0.6 g $(NH_4)_2SO_4$, 0.6 g KNO_3, 0.25 g KH_2PO_4, 0.75 g K_2HPO_4 and 0.15 g $MgSO_4.7H_2O$ dissolved in 1 L of deionised water) (Hickman et al., 2008). To each bottle ^{14}C-metaldehyde was added (100 Bq in 100 µL of ethanol). To capture $^{14}CO_2$ generated from the mineralisation of ^{14}C-metaldehyde, a glass scintillation vial (7 mL) containing 1M NaOH (1 mL) was suspended (using a stainless-steel clip) from the top of a Teflon^{TM} lined respirometer lid. Bottles were continuously shaken on an orbital shaker (IKA Labortechnik KS501) at 100 r.p.m and the vials were removed and replaced periodically over the 120 h (5 d) assay time (the total time of the experiment). Removed vials were wiped with a tissue, and Ultima Gold scintillation fluid (6 mL) added. Vials were sealed, shaken and stored in the dark (for a minimum of 24 h) and then analysed by liquid scintillation counting (Perkin-Elmer TriCarb 2900TR liquid scintillation analyser; count time 10 mins). Results were corrected for background radiation using un-spiked respirometers (Reid et al., 2001). The respirometer system was previously validated by Reid et al. (2001), who reported that up to 400 µmol CO_2 could be accommodated in a single trap and a ^{14}C activity balance of 101 $\pm$ 8.9%.

In order to assess the inducible capacity of soil microbial communities in response to metaldehyde augmentation the above procedure was repeated with the addition of a metaldehyde pellet to each respirometer bottle. Each pellet had a mass of 0.028 g and a metaldehyde content of 1.5%. Thus, each respirometer was dosed with the equivalent of 28 mg metaldehyde kg^{-1} soil. Sterile respirometers, containing MBS (30ml), were spiked with ^{14}C-metaldehyde to evaluate abiotic degradation and volatilisation of ^{14}C-metaldehyde. All respirometer assays were run in triplicate.

3.3.4 Sample codes

Samples have been coded to indicate: land use regime, Field (F), Allotment (A) and Garden (G); the location qualifier (1-10; see Table 3.1); if samples were top soil (T) or subsoil (S); if the *in situ* regime had metaldehyde application (p) or no metaldehyde application for at least the last 4 years (n), and; if the *ex situ* laboratory assay was conducted in the presence of a slug pellet (+) or its absence (-). For example, F2Tp+ corresponds to Field 2, a topsoil sample that was exposed to metaldehyde *in situ* and was screened for catabolic competence in the presence of a metaldehyde pellet. In presenting the data, soils have been organised with lighter (sandier) textures presented first and heavier (clay) textures presented last.

3.3.5 Statistics

Significant differences between intrinsic and induced mineralisation levels were established using ANOVA post hoc Tukey Tests (SPSS Statistics 22); a significance level of 0.05 (95% level of confidence). Pearson's correlation test was applied to determine linear correlation between mineralisation and pH/SOM values, a significance level of 0.05.

3.4 Results

3.4.1 Control flasks and blanks

Abiotic degradation/volatilisation of ^{14}C-metaldehyde was evident at a modest level (7.8 $\pm$ 3.9%). This value was commensurate with a fugacity (Mackay, 2001) driven pseudo-equilibrium (theoretical value = 9.5 %), where: the respirometer MBS media volume was 30ml, the trap volume was 1 mL and the trap was changed three times over the assay period. Background ^{14}C-radiation was negligible (0.06% of the activity delivered in the respirometer spike).

3.4.2 Agricultural Field Soils (FT, FS)

Intinsic catabolic competence (i.e. in samples with no metaldehyde pellet added (-)) was ubiquitous across all agricultural field soils; mineralisation varied between 17.6% (FT(p)7) and 31.0% (FT(n)1) (Figure 3.1).

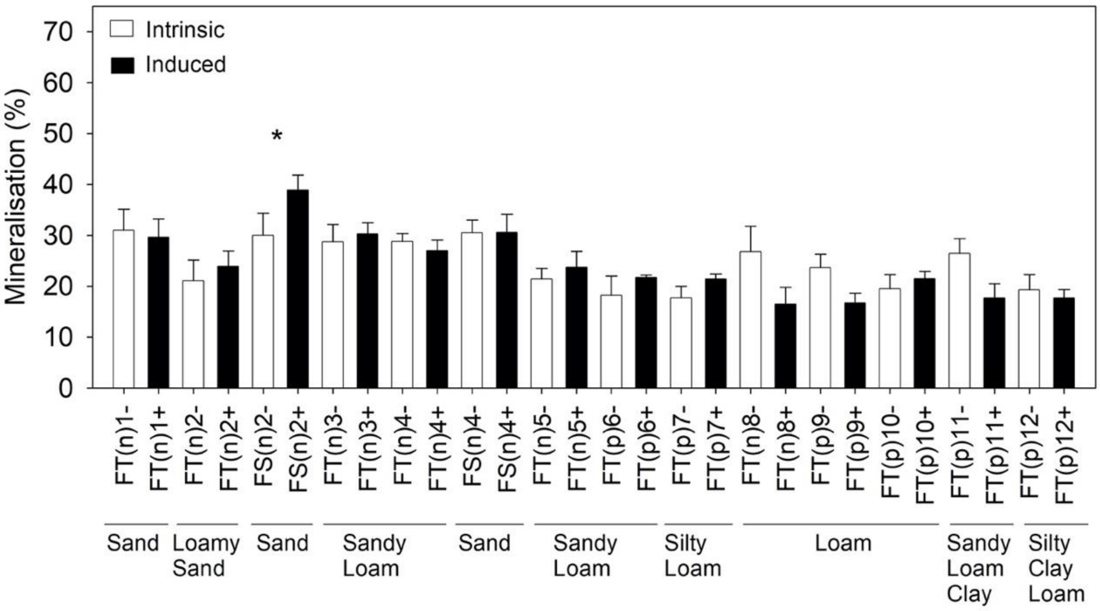


Figure 3. 1 Catabolic competence (^{14}C-metaldehyde mineralisation (%) after 5 days assay time) in Field topsoil (FT(n)1-FT(p)12) and Field subsoil (FS(n)2, FS(n)4): soil only treatments (white bars) and soil with metaldehyde addition (black bars). Soil types are ordered by texture and then by mineralisation (%) for each texture class. Error bars are standard error of the mean (n = 3). A star indicates significant difference ($p < 0.05$) between soil only (-) and soil with metaldehyde (+) couplets.

In most instances soils with light texture (FT(n)1, FS(n)2, FS(n)4 – sand, FT(n)2 – loamy sand, FT(n)3 – FT(p)6 – sandy loam, FT(p)7 – silty loam), were observed to have higher intrinsic capacites to mineralise ^{14}C-metaldehyde. Soils with heavier texture (FT(n)8, FT(p)9 and FT(p)10 – loam, FT(p)11 – sandy loam clay, FT(p)12 – silty clay loam) were observed to have lower intinsic catabolic competence (Figure 3.1).

Similarly, induced (with pellet present (+)) catabolic competence was observed to be higher in lighter textured soils (FT(n)1 – FT(p)7) than in heavier textured soils (FT(n)8 – FT(p)12). This was also the case for the Field Subsoil samples (FS(n)2, FS(n)4 – sandy texture), where an uplift in induced mineralisation was observed (+8.9% and +0.1%) (Figure 1). The extent of induced mineralisation in FT (where a pellet was added to the respirometer) varied from 16.5% (FT(n)8) to 30.3% (FT(n)3) (Figure 3.1); this range was almost identical to the intrinsic catabolic competence range, suggesting that catabolism of metaldehyde was operating at its maximum capacity before the pellet was added.

With the exception of FT(n)1 (light sandy texture) and FT(n)8 (medium loamy texture), all agricultural soils that were not exposed to metaldehyde *in situ* (n) were observed to show an uplift of catabolic competnce following the addition of a metaldehyde pellet (+) (FS(n)2 – FT(n)5). Lighter FT soil textures included sand (FS(n)2, FS(n)4), loamy sand (FT(n)2), sandy loam (FT(n)3 – FT(n)5). The same outcome was observed for light soils where metaldehyde was used *in situ* (p) (FT(p)6 – sandy loam, FT(p)7 – silty loam).

FS(n)2 was the only sample among all agricultural Field soils in which a significant difference between intrinsic and induced mineralisation was observed ($P < 0.05$) (+8.9%) (Figure 1). The maximum level of observed catabolic activity did not exceed 38.9% (induced mineralisation in FS(n)2 sample) in the Agricultural Field soils (Figure 3.1).

3.4.3 Allotment Soils (AT, AS)

Intinsic (-) catabolic competence was ubiquitous across all Allotment soils; mineralisation varied between 34.3% (AT(p)2) and 60.0% (AS(n)1) (Figure 3.2). Similar to the Field soils, Allotment soils with lighter texture (sand) exhibited higher intrinsic mineralisation capacities when compared to soils with slightly heavier texture (loamy sand) (Figure 3.2).

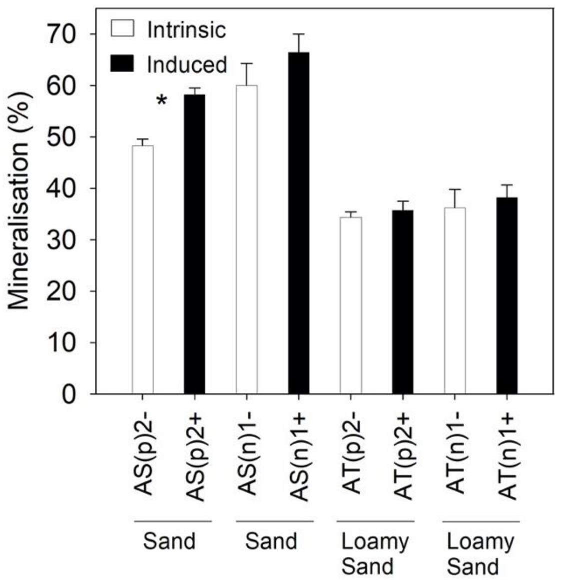


Figure 3. 2 Catabolic activity (^{14}C-metaldehyde mineralisation (%) after 5 days assay time) in Allotment soils (AT – Allotment topsoil, AS – Allotment subsoil): soil only treatments (white bars) and soil with metaldehyde addition (black bars). Soil types are ordered by texture and then by mineralisation (%) for each class. Error bars are standard error of the mean (n = 3). A star indicates significant difference ($p < 0.05$) between soil only (-) and soil with metaldehyde (+) couplets.

Relative difference between intrinsic (-) and induced (+) mineralisation in lighter textured subsoils were also higher, particularly in soil with previous *in situ* metaldehyde application history (p) (AS(p)2) (Figure 3.2). Sandy Subsoil sample (AS(n)1) with no previous metaldehyde application had the highest metaldehyde mineralisation (both induced and intrinsic).

Like Field soils, Allotment soils exhibited elevated mineralisation levels in the presence of metaldehyde (Figure 2). In the presence of metaldehyde, the extent of mineralisation varied from 35.7% (AT(p)2) to 66.4% (AS(n)1) (Figure 3.2).

Only in the case of AS(p)2, intrinsic and induced levels of ^{14}C-metaldehyde mineralisation were significantly different ($P<0.05$) (a +9.9 % uplift in mineralisation was observed). The maximum level of observed catabolic activity did not exceed 66.4% (induced mineralisation in AS(n)1 sample) (Figure 3.2).

3.4.4 Garden soils (GT)

As observed for Field and Allotment soils, competence to degrade metaldehyde in garden soils was ubiquitous across soil types (Figure 3.3). In the absence of a metaldehyde pellet, the extent of intrinsic metaldehyde mineralisation varied from 28.9% (GT(n)7) to 52.8% (GT(n)6) (Figure 3.3).

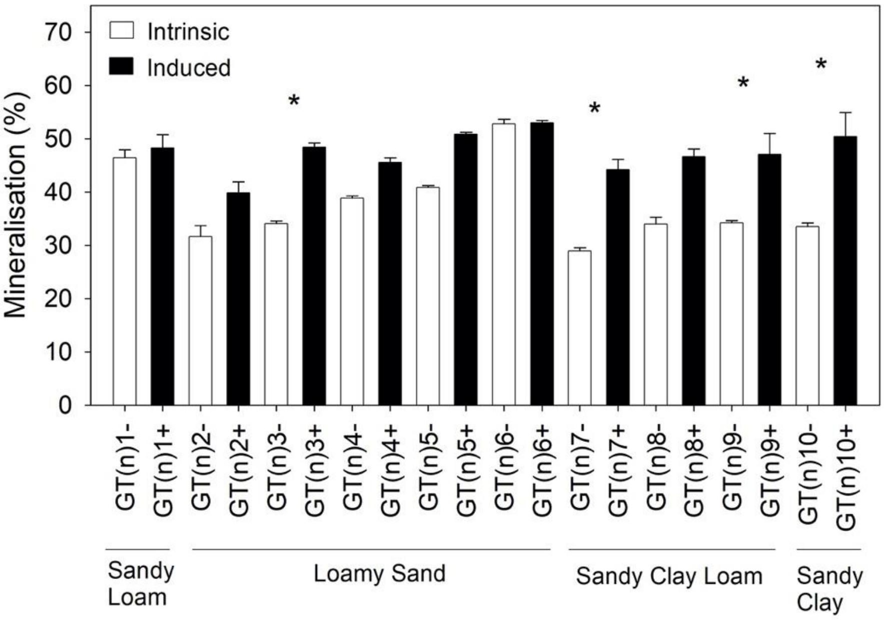


Figure 3. 3 Catabolic activity (^{14}C-metaldehyde mineralisation (%) after 5 days assay time) in Garden soils (GT(n)1-GT(n)10): soil only treatments (white bars) and soil with metaldehyde addition (black bars). Soil types are ordered by texture and then by mineralisation (%) for each class. Error bars are standard error of the mean (n = 3). Stars indicate significant difference ($p < 0.05$) between soil only (-) and soil with metaldehyde (+) couplets.

In general, as was the case with Field soils (Figure 3), lighter textures (sandy loam and loamy sand); GT(n)1 through GT(n)6) indicated higher levels of catabolic competence to mineralise metaldehyde when compared to heavier textures (sandy clay loam and sandy clay) (Figure 3.3).

In the presence of metaldehyde all soils showed elevated levels of mineralisation (Figure 3.3); the extent of mineralisation varied from 39.9% (GT(n)2) to 53.0% (GT(n)6). Uplift in mineralisation, in the presence of a metaldehyde pellet (+), was greatest for soils observed to have lower intrinsic catabolic competence; conversely, where soils were observed to already have high catabolic competence only small increases (a few %) in mineralisation were observed following metaldehyde augmentation (e.g. GT(n)1 and GT(n)6; Figure 3.3).

In several instances the augmentation resulted in significant ($P < 0.05$) increases in mineralisation GT(n)3, GT(n)7, GT(n)9 and GT(n)10; +14.4%, +15.3%, +12.8% and +16.9%, respectively). Again, as observed for Field and Allotment soils, the maximum catabolic capacity of 50–55% appeared to be a ceiling beyond, which catabolic capacity was not exceeded.

3.5 Discussion

The degradation of any pesticide depends upon its physical and chemical characteristics, e.g. aqueous solubility and inherent recalcitrance (Semple et al., 2003) and the physical, chemical and biological properties of the soil (Rao et al., 1983), such as pH, redox conditions, matrix attributes, carbon:nitrogen:phosphorus (C:N:P) elemental ratio, temperature, moisture content (Arias-Estévez et al., 2007). Presence/absence/activity of catabolic enzymes in soils affect pesticide degradation directly (Deng et al., 2016) while pesticide bioavailability/bioaccessibility indirectly influence pesticide degradation (Arias-Estévez et al., 2007). Additionally, pesticide transport, biological degradation and chemical transformation processes are affected by application regime (rates/methods and timing), as well as hydrological and weather conditions (Borgesen et al., 2015). Thus, site-specific physical, chemical and biological properties control the fate and transport of pesticides in the environment and determine the variation in spatial distribution of pollutants.

3.5.1 Soil microbe response to chemicals inputs

The ability of microbial communities to respond to organic compounds (e.g. pesticides) presence/augmentation is well documented for a range of compound classes, including: several semi-volatile hydrocarbon pollutants (Kelsey and Alexander 1997; Reid et al., 2002; Springael and Top, 2004; Hickman et al., 2008), pesticides (Duah-Yentumi and Johnson, 1986; Reid et al., 2005; Bending et al., 2006; Posen et al., 2006; Trinh et al., 2012; Reid et al., 2013) and antibiotics (Islas-spinosa et al., 2012; Bennet et al., 2017).

These studies confirm the capacity of microbial communities to respond to organic compound input by becoming more catabolically competent (Reid et al., 2005; Bending et al., 2006; Posen et al., 2006; Reid et al., 2013). For example, Reid et al. (2005) reported soil microbial communities, of initially low catabolic competence, to degrade the herbicide isoproturon, (mineralisation C. 5%) to increase in their competence following the incubation of soil with a low (0.05 μg kg^{-1}) application of the herbicide (mineralisation increased to C. 40 %). In column studies, Trinh et al. (2012) reported three phases of attenuation/degradation of these herbicides isoproturon and MCPA: an initial sorption phase, followed by an acclimatisation/adaptation phase and a final rapid degradation phase (resulting in complete removal of the herbicides).

Several studies on biodegradation of metaldehyde have been reported, for example, Thomas et al. (2013, 2017) isolated and characterised metaldehyde-degrading bacteria in domestic soils. They reported Acinobacter E1 strain to be able to degraded metaldehyde to a concentration below 1 nM. However, to date, the response of soil microbial communities, present in agricultural, allotment and garden soils, to metaldehyde augmentation has not been reported. Thus, our results confirm the potential for soil microbial communities to increase in their competence to degrade metaldehyde following exposure. In keeping with observations for other compounds, metaldehyde catabolic competence was observed to increase significantly, following slug pellet addition (in some cases increasing by a factor of 2). Largest increases in catabolic competence following metaldehyde augmentation were observed for FS(n)2 (+8.9%), AS(p)2 (+9.9%), GT(n)3, GT(n)7, GT(n)9 and GT(n)10 (+14.4%, +15.3%, +12.8% and + 16.9%, respectively).

In contrast to other pesticides, where low catabolic competence is exhibited in unexposed soils, high levels of intrinsic catabolic competence to degrade metaldehyde were observed (up to 66.0 %). Metaldehyde is a cyclic tetramer of sub-units that can depolymerise, through microbial activity, into acetaldehyde (Castle et al., 2017; Tomlin, 2003). High levels of metaldehyde degradation in the soil environment have been reported in the literature. For example, Bieri (2003) reported fast degradation rates of metaldehyde in agricultural soils in Germany; with, DT_{50} values ranging from 5.3 to 9.9 days. Coloso et al. (1998) reported metaldehyde concentration in pond sediment to rapidly decrease from an initial concentration of 80 mg kg^{-1} to 1 mg kg^{-1} after 15 days. Ma et al. (2012) studied metaldehyde residues in agricultural soils in China and reported metaldehyde residue of up 9 mg kg^{-1} to decrease below 0.3 mg kg^{-1} over 7 days. While Calumpang et al. (1995) reported metaldehyde concentrations in paddy soil to fall from 0.13 mg kg^{-1} to below the analytical detection level within 22 days.

We suggest the ubiquity of high levels of catabolic competence observed in our research are likely due to the degradation of the simple metaldehyde molecule to acetaldehyde (the primary degradation product), and the subsequent degradation of acetaldehyde to acetate; this being assimilated into Krebs tricarboxylic acid (TCA) Cycle (Tomlin, 2003) and respired as carbon dioxide.

3.5.2 Catabolic competence and its relationship with soil properties

All soil types, drawn from all settings (Field, Allotment and Garden), were observed to exhibit significant levels of catabolic competence. As already highlighted, soil texture had a shaping influence on the extent of ^{14}C-metaldehyde mineralisation; with sandy soils supporting, in general, higher level of catabolic competence. It is widely recognised that soil texture has a substantial influence on the soil environment. It controls soil porosity, and thus, has a directing influence on soil hydrology (Luna et al., 2017) and soil atmosphere (Pagliai et al., 2004). In turn, these drivers exert a shaping influence on soil microbial community structure (Fierer, 2017). Schroll et al. (2006) reported optimum pesticide mineralisation at a soil water potential of -0.015 MPa; pesticide mineralisation was markedly reduced when soil moisture approached soil water holding capacity.

Acknowledging the considerable influence soil texture has on soil moisture conditions, it is unsurprising that levels of catabolic competence observed have been influenced by soil texture. We suggest that the higher levels of catabolic competence for metaldehyde, observed in the lighter soil textures, could be linked to a higher redox potential in these more freely drained soils (Voroney and Heck, 2015). These conditions would, putatively, support a more active microbial community with greater capacity to degrade organic substrates (including metaldehyde). In general, pesticide degradation (Fenner et al., 2013), and metaldehyde degradation specifically (EFSA, 2010), have been reported to be faster under aerobic conditions.

Beyond its influence on soil, physical, hydrological and biological attributes soil texture also controls pesticide bioavailability (Gavrilescu, 2005). Numerous studies have sustained the general trend that lighter sandy soil textures assist biodegradation by maintaining high pesticide bioavailability and, in contrast, heavier clay textures tend to facilitate greater sorption and entrapment of pesticide (e.g. Reid et al., 2000; Gavrilescu, 2005). Thus, heavier clay textures tend to decrease the potential for degradation though stronger sorption. These strong interactions have been reported to preclude the opportunity for pesticides to induce catabolic competence (Reid et al., 2013).

In addition to their texture, the dissimilar soils also varied in their SOM content. SOM has been reported to influence the fate, behaviour and biodegradation of pesticides (Hatzinger and Alexander, 1995). However, to date, there have been no reports accounting how soil properties (specifically, SOM and pH) influence the biodegradation of metaldehyde by soil microbial communities. To elucidate any such relationships, SOM and soil pH were correlated with ^{14}C-metaldehyde mineralisation under intrinsic and induced regimes and across all settings (Figure 3.4).

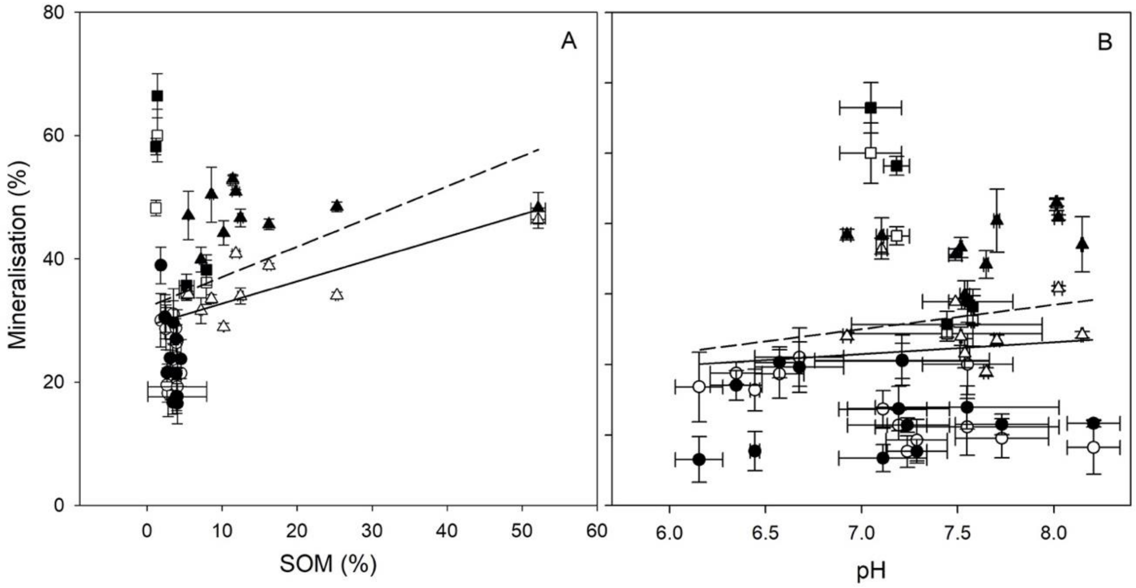


Figure 3. 4 Correlation of intrinsic (black), and induced (white), catabolic activity (mineralisation, %) with: SOM (A) and pH (B); for, Field soils (○), Allotment soils (☐) and Garden soils (△). Errors bars are ± 1 standard deviation (n = 3). Lines of best fit indicates correlations between intrinsic (solid) and induced (dashed) mineralisation capacity and SOM (A) and pH (B).

SOM varied (from 1.17% to 52.14%) across the dissimilar soil types obtained from contrasting settings (Table 3.1) and extent of mineralisation in these soils also varied greatly (from 16.51% to 66.44%). Considering all soils, ^{14}C-metaldehyde mineralised was observed to increase with increasing SOM for both intrinsic and induced assessment (Figure 3.4A). While the correlations between mineralisation extent and SOM were not significant ($r = 0.34$, $p = 0.08$; intrinsic and induced mineralisation vs. SOM); the data supports the conclusions that i) beyond a SOM content of 12% metaldehyde mineralisation was consistently > 34%, and, ii) where SOM content was less than 12% metaldehyde mineralisation was observed across a very broad range (from 16.5 to 60%) (Figure 3.4A). These results suggest that efforts to sustain SOM levels in soil could assist in promoting higher levels of metaldehyde degradation, and thus, reduce the opportunity for metaldehyde to transfer to water resources.

On one hand, SOM controls sorption of pesticides in soil (Chiou et al., 1983). Sorption is responsible for retention of pesticides in soil, preventing leaching and decreases pesticide bioavailability (Singh, 2008). While, on the other hand, SOM is the cornerstone of soil food webs, and its amount and quality underpins microbial diversity and its capacity to utilise a broad range of substrates (Neumann et al., 2014). With regards to metaldehyde, as a relatively water soluble compound (190 mg L^{-1}) and as a labile carbon source (Bieri, 2003; EFSA, 2010), we suggest sorption onto SOM is unlikely to be a significant influence on biodegradation. It more likely that SOM has a synergistic influence on metaldehyde biodegradation as it acts as a primer for microbial activity. The higher levels of catabolic competence observed to be synonymous with SOM content of >12% (Figure 3.4A) support this linkage.

Where pH was correlated with mineralisation across all soil types and regimes, no relationship was observed for intrinsic mineralisation ($r = 0.19$, $p = 0.34$) (Figure 3.4B). A slightly positive correlation was observed between increasing pH and induced mineralisation ($r = 0.44$, $p = 0.02$) (Figure 3.4B). More useful, perhaps, is the observable distinction between soils of pH lower than 6.9, where mineralisation never exceeded 30%, and soils where pH was greater than 6.9, and mineralisation was more often observed to be greater than 35% (Figure 3.4B). Thus, while pH influence on pesticide degradation has been reported for other compounds (e.g. atrazine (Houot et al., 2000) and pirimicarb and metsulfuron-methyl (Kah et al., 2007)), its influence upon metaldehyde mineralisation was inconsistent.

3.5.3 Wider Context

The results reported herein highlight soil microbial communities, in dissimilar soils under Agriculture, Allotment and Garden regimes, to all have a considerable latent capacity to degrade metaldehyde (Figures 3.1–3.3). Our results suggest that soil microbial communities across these regimes, and present in both top-soil and sub-soil, are well predisposed to degrade metaldehyde. We suggest that it is unlikely that the, at times, high levels of metaldehyde detected in water (Castle et al., 2017; Kay and Grayson, 2014) are due to low degradation capacity in the soil system. It is more likely that runoff and fast leaching of metaldehyde is the main driver underpinning the high incidence and high concentrations of metaldehyde sometimes reported in water resources (Calampung et al., 1995; Coloso et al., 1998; EC, 2000; Bieri, 2003; Hillocks, 2012; Ma et al., 2012; Busquets et al., 2014; Lu et al., 2017).

With metaldehyde being mainly applied in autumn and winter, when slug populations are higher due to wet weather (and when young crops are most vulnerable), the opportunity for metaldehyde transport is increased. The situation is further antagonised by metaldehyde having a relatively high aqueous solubility (190 mg L^{-1}). In support of this view there is considerable evidence that pesticides applied to the soil surface can be transported rapidly, bypassing the unsaturated soil zone, to groundwater (Arias-Estévez et al., 2007; Johnson et al., 1995; Lopez-Perez et al., 2006). Indeed, metaldehyde has frequently been detected in groundwater at levels higher than the EU Drinking Water Framework Directive limit (0.1 µg L^{-1}) (EC, 1998); in some cases, concentrations of metaldehyde of up to ten times this limit have been reported (UKWIR, 2013).

Given its ubiquity in water resources, metaldehyde has been subject to scrutiny, voluntary initiatives and evolving regulation. Specifically, in the UK the Get Pelletwise campaign of the Metaldehyde Stewardship Group (MSG, formed in 2008), aimed to promote sustainable use of metaldehyde by applying principles of Integrated Pest Management and introducing guidelines for metaldehyde application (MSG, 2020). However, metaldehyde is still regularly detected at the concentrations above the DWD limit of 0.1 µg L^{-1} (Castle et al., 2017; Lu et al., 2017). Thus, in order to mitigate metaldehyde transfer still further a reduction in the nominal loading of metaldehyde in pellets (e.g. from 3% to 1.5% active ingredient) and the development of pellets that afford stronger metaldehyde attenuation might offer further opportunity for improvements.

We highlight that soil itself is likely to be a significant reservoir of metaldehyde. With respect to this soil burden, the results reported herein suggest that there is good prospect that, given time, the indigenous soil microbial communities will degrade this reservoir of metaldehyde. However, further research regarding the levels of microbial catabolic activity, specifically under lower substrate concentrations, should be undertaken.

3.6 Conclusions

Results indicate substantial catabolic competence to degrade metaldehyde in soils with various texture (from sand to silty clay loam), pH (6.15–8.20) and organic matter content (1.2–52.1%). Ubiquitous catabolic competence was observed in both topsoil (16.7–52.8%) and subsoil horizons (30.0–66.4%). In general, soils with lighter texture (sand, sandy loam and loamy sand; average mineralisation 37.3%) had higher levels of ^{14}C-metaldehyde mineralisation when compared to soils with heavier texture (sandy clay, sandy clay loam and silty clay loam; average mineralisation 33.3%). When soils were augmented with metaldehyde (in the laboratory) an increase in mineralisation was observed in some, but not all soils (up to 16.9% increase in the Garden Soil GT(n)10 (sandy clay)).

Overall, pH and organic matter content were weakly correlated with ^{14}C-metaldehyde mineralisation. However, soils with higher SOM (>12%) were, in general, observed to support higher levels of metaldehyde mineralisation. It is suggested that the higher SOM status of these soils exerted a beneficial shaping influence upon soil microbial communities and their capacity to degrade metaldehyde. Collectively, results suggest that the concentrations of metaldehyde (that are at times high), detected in water, are unlikely due to insufficient microbial capacity to degrade this pesticide. It is suggested that application regime (rate and timing), the high mobility of metaldehyde and its loss to the watercourses via runoff and leaching are the driving factors underpinning the ubiquity of metaldehyde in surface and ground water resources.

To reduce metaldehyde runoff to watercourses, this molluscicide should not be applied outdoors when it is raining or rain is due. The use of pellets with reduced concentrations of metaldehyde and development of the pellet products with stronger attenuation capacity, as well as following the MSG guidelines (MSG, 2020) could further assist in the effort to reduce metaldehyde transfer to the aquatic environment.

Chapter 4 Long-term and seasonal trends in metaldehyde concentrations and fluxes in lowland semi-agricultural catchments in Essex, UK

This research was published in 2021:

Balashova, N., Hiscock, K. M., Reid, B. J. and Reynolds, R. (2021). Trends in metaldehyde concentrations and fluxes in a lowland, semi-agricultural catchment in the UK (2008-2018). *Science of Total Environment*, 795, 1-13.

4.1 Chapter summary

Metaldehyde, a widely used molluscicide, is one of the most commonly detected pesticides in aquatic environments in the UK. In this study, metaldehyde concentrations and fluxes in stream water over a ten-year period (2008–2018) are reported for the River Colne and the Ardleigh catchments (Essex, southeast England), and the influence of hydrological conditions and application regimes are assessed.

In general, peaks in metaldehyde concentration in river water occasionally exceeded 0.25 µg L^{-1}, but concentrations did not typically exceed the European Union Drinking Water Directive (EU DWD) regulatory limit of 0.1 µg L^{-1}. Metaldehyde concentration peaks displayed a seasonal pattern. Metaldehyde concentrations during periods when the molluscicide was not applied to agricultural land (January, July) and during the spring-summer application period (February to June) were generally low (0.01–0.03 µg L^{-1}). Peaks in metaldehyde concentration mainly occurred during the autumn-winter application season (August to December), and were typically associated with high intensity hydrological regimes (daily precipitation ≥10 mm; streamflow up to 18 m^3 s^{-1}). Where metaldehyde concentrations exceeded the EU DWD regulatory limit, this was short-lived.

The annual flux at the top of the Colne catchment (0.2–0.6 kg a^{-1}) tended to be lower than in the middle of the catchment (0.3–1.4 kg a^{-1}), with maximum flux values observed

at the bottom of the catchment (0.5–25.8 kg a^{-1}). Metaldehyde losses from point of application to surface water varied between 0.01 and 0.25%, with a maximum of 1.18% (2012). Annual flux was primarily controlled by the annual precipitation and streamflow ($R^2 = 0.9$) rather than annual metaldehyde use (kg active applied). Precipitation explained 37% and 81% of variability in metaldehyde concentration and flux, respectively.

Annual ranges in metaldehyde concentration were greater in the years 2012 and 2014 with an overall reduction in the range of metaldehyde concentrations evident over the period 2015–2018. It is the expectation that metaldehyde concentrations in stream water will continue to decrease following the withdrawal of metaldehyde for outdoor use in the UK in March 2022.

4.2 Introduction

Pesticides are widely present in surface water (e.g. Sandin et al., 2018; Metcalfe et al., 2019), affecting ecological status of water bodies (Palma et al., 2004). Pesticide presence in watercourses is a challenge for environmental risk regulators tasked with achieving good water quality status (Holvoet et al., 2007) under the European Union Drinking Water Directive (EU DWD) (Directive 98/83/EC; EC, 1998) and the European Union Water Framework Directive (Directive 2000/60/EC; EC, 2000).

These pollutants enter aquatic environments via diffuse pathways (runoff, drain and groundwater flow, and atmospheric deposition), and point sources, often associated with pesticide handling procedures (Fait et al., 2007). The amount of pesticide loss to surface water depends on a number of factors, including topography, land use, hydrological conditions, pesticides application regime (timing of application and the amounts applied), as well as physio-chemical properties of the substance (Morvan et al., 2006; Gevaert et al., 2008; Villamizar and Brown, 2017).

Metaldehyde, the cyclic tetramer of acetaldehyde with the formula $(CH_3CHO)_4$, has regularly been detected in water supplies in the UK over the past decade (Stuart et al., 2012). This molluscicide is commonly used in agriculture to control populations of snails and slugs, and is widely applied in the months August–December to protect winter cereals and winter oilseed rape crops (EA, 2016). Wet weather conditions typical for the autumn period create a favourable environment for slugs, and slug control becomes a priority. With increased precipitation and runoff during the application season, exceedances of metaldehyde concentrations above the EU DWD limit of 0.1 μg L^{-1} (EC, 1998) have been regularly recorded (Castle et al., 2017) since 2008, when intensive regulatory monitoring of metaldehyde began nationwide. Overland and subsurface runoff is known to be a major input pathway for pesticides found in watercourses (Huber et al., 1998; Larsbo et al., 2016). Coupled with the physio-chemical characteristics of metaldehyde, a relatively water-soluble substance (188–190 mg L^{-1} at 20 °C) with low adsorption potential (K_{oc} of 35 L kg^{-1}) (PAN, 2020; PPDB, 2020), there is a high potential of increased mobility of metaldehyde in the environment (Lu et al., 2017; Asfaw et al., 2018). Due to its physico-chemical properties, metaldehyde is susceptible to surface runoff during precipitation events. It is likely to be mobile in the soil zone (Castle et al., 2017) and transported rapidly to groundwater (Balashova et al., 2020).

Furthermore, due to its physico-chemical properties, metaldehyde cannot be removed from water using conventional methods of water treatment works, including granular activated carbon, chlorination and ozonation (Kay and Grayson, 2014). Water companies rely on catchment management approaches to manage metaldehyde presence in drinking water supplies. One such initiative, the Slug It Out campaign, started by Anglian Water Services in 2015 is focused on controlling metaldehyde in seven trial catchments (surrounding reservoirs) before it enters watercourse networks in East Anglia, eastern England. Farmers that participate in the campaign (all farms within the trial catchments) are incentivised to follow sustainable pesticide management practices, as described in Chapter 1, Section 1.4.6.1, and to replace metaldehyde use on their land with an alternative method of slug control, such as use of ferric phosphate (Anglian Water, 2020). However, participation in the campaign did not oblige farmers to stop using metaldehyde, and metaldehyde concentration spikes in stream water occurred in several trial catchments (Mohamad Ibrahim et al., 2019).

Not only do the increasing amounts of metaldehyde contamination in surface waters give cause for concern, the adverse effects of metaldehyde on aquatic ecosystems and non-target organisms are also problematic, and non-target effects of metaldehyde on aquatic organisms and small mammals have been reported (Moreau et al., 2015; Hallet et al., 2016; De Roma et al., 2017). Due to the risk that metaldehyde poses to wildlife, the outdoor use of metaldehyde will be withdrawn from March 2022 in the UK (DEFRA, 2020).

In light of these recent changes in UK policy, research regarding temporal trends in metaldehyde concentrations in aquatic systems is particularly important, not least as a benchmark for the pre-withdrawal situation. Yet, peer-reviewed studies of metaldehyde levels in surface water are limited (e.g. Calumpang et al., 1995; Coloso et al., 1998), and only a few studies are available on patterns of metaldehyde concentrations at the catchment scale. For example, Kay and Grayson (2014) quantified metaldehyde levels in surface water of the River Ouse catchment in Yorkshire, UK using concentration data collected over a period of 2.5 years (2008–2011). Kay and Grayson (2014) also studied the effect of catchment characteristics (slope, soil type and crop coverage) on metaldehyde levels in rivers and found no significant relationships and concluded that the metaldehyde application regime at the individual farm level (such as application rate, timing and technique; although data were not available) may be the driving factor transporting metaldehyde to surface water. Lu et al. (2017) used metaldehyde concentration data collected over a period of 5 years (2011–2015) in the River Thames catchment as input data to a process–based hydrobiochemical transport model (INCA). Their results highlighted that increased metaldehyde concentrations in the watercourse network were directly linked to excessive application (Lu et al., 2017). Asfaw et al. (2018) developed a surface runoff transport model to describe short-term metaldehyde dynamics in the River Leam catchment (central England, UK) using high resolution metaldehyde concentration data and precipitation data for four separate precipitation events (9–35 h duration). Castle et al. (2018) compared metaldehyde levels in surface water using two monitoring approaches (automated passive and spot sampling) in the River Dee and the River Thames catchments during a 1-year period (January 2016–January 2017). Additionally, metaldehyde concentrations in surface water samples were examined in the Mimmshall Brook catchment (Hertfordshire, UK) using similar approaches, with samples collected during a 3-month period (October–December 2017) (Castle et al., 2019).

Most of these studies are short-term, and there is currently a knowledge gap when it comes to understanding metaldehyde trends over longer time periods. There is currently no published peer-reviewed research that explores temporal and spatial patterns of metaldehyde by considering the effect of: (i) hydrological conditions (flow and precipitation), and (ii) application regime on metaldehyde levels over a longer term time period of the order of a decade.

The aim of the current research was to review long-term and seasonal trends in metaldehyde concentrations and fluxes in two lowland, semi-agricultural UK catchments (the River Colne and the Ardleigh catchments). To meet this aim, the first objective was to quantify and evaluate long-term and seasonal metaldehyde concentration and flux patterns using metaldehyde concentration data collected over a period of 10 years and 7 months (June 2008–December 2018). Seasonal trends are defined from i) meteorological seasons, and ii) typical application season of metaldehyde in England (the August-December period).

The second objective was to evaluate the impact of hydrological conditions (stream discharge (flow) and precipitation) and metaldehyde application regime (application timing and annual application rates) on concentrations of metaldehyde in the watercourse network of the study catchments. The final objective was to achieve a better understanding of metaldehyde pathways/sources and their scale within the study catchments. Collectively, these objectives are aimed to provide a prognosis regarding long-term levels and persistency of metaldehyde in the environment. Such a prognosis will help support informed design of water quality policy.

4.3 Materials and Methods

4.3.1 Study area

The study area is located in southeast Essex in East Anglia and incorporates the River Colne and Ardleigh catchments (Figure 4.1).

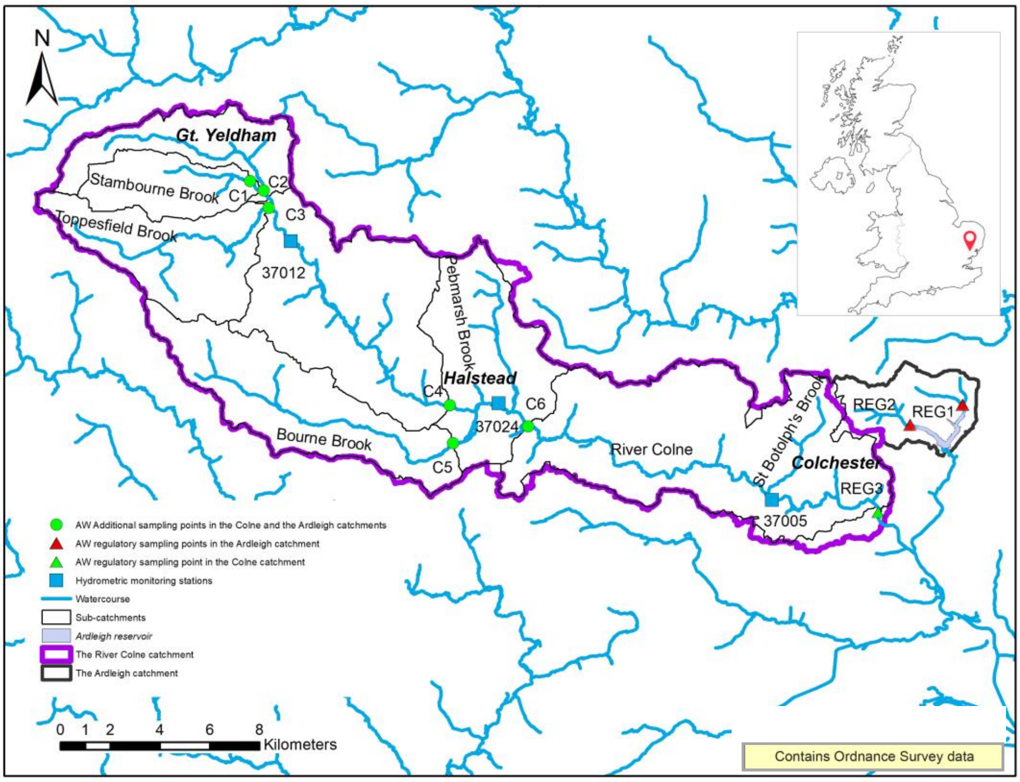


Figure 4. 1 Geographical location of the study sites indicating major settlements and road networks. The hydrological network of the study area includes the locations of sampling points and gauging stations.

The River Colne has a catchment area of 242 km^2, comprising six sub-catchments and the catchment outlet: Stambourne Brook and River Colne at Nuns Walk, Great Yeldham (C1, 14 km^2); River Colne at Highfields Close, Great Yeldham (C2, 17 km^2); Toppesfield Brook (C3, 26 km^2); River Colne at Langley Mill, Earls Colne (C4, 49 km^2); Bourne Brook (C5, 35 km^2); Pebmarsh Brook and River Colne at Earls Colne Road (C6, 31 km^2); and the River Colne outlet at Eastmill (REG3, 70 km^2) (Figure 4.1). The length of the stream network within the Colne catchment is 50 km with the average streamflow increasing downstream from 0.29 m^3 s^{-1} and 0.73 m^3 s^{-1} at the upper and middle sub-catchment gauging stations (37012 and 37024) to 1.07 m^3 s^{-1} at the lower sub-catchment gauging station (37005) near Lexden and Colchester for the period 1959–2017. Base Flow Index (BFI) values gradually increase from 0.28 in the upper part of the catchment (station 37012) to 0.43 and 0.52 (stations 37024 and 37005, respectively) in the middle and the lower parts of the study area (Figure 1; NRFA, 2019 a, b, c).

The River Colne has a number of abstractions along its reach for irrigation use in arable farming. The water from the river is also abstracted and pumped into the Ardleigh Reservoir in the adjacent catchment for drinking water supply (EA, 2019).

The Ardleigh catchment is comprised of the Ardleigh Reservoir and the Northern and Western Salary Brooks. The reservoir is considerably shallow; its depth varies from 3.9 m to a maximum depth of 13 m and a maximum volume of 2.19 x 10^6 m^3 (Redshaw et al., 1988).

Both the Western and Northern Salary Brooks are also shallow (up to 0.5 m deep) and fairly narrow (width varies between 0.5 to 1.5 m along the tributaries). These small streams constitute two natural sub-catchments (areas 6.5 and 7.5 km^2, respectively) of the Ardleigh catchment with a total catchment area of 14 km^2. A mean flow of 1.07 m^3 s^{-1} (1959-2017 time period) is recorded at gauging station 37005 (Colne at Lexden), the closest station to the Ardleigh catchment (NRFA, 2019 c). Water enters the Ardleigh Reservoir from the Northern Salary Brook and the Eastern Salary Brook. When necessary, additional water is abstracted from the River Colne and pumped into the reservoir. Precipitation and minor runoff are additional sources of water supply for the reservoir. Water leaves the reservoir by evaporation, abstractions to the treatment works and compensation flow to the Western Salary Brook (Redshaw et al., 1988).

The area is characterised by a temperate maritime climate with the mean annual temperature ranging between 9.5 °C to 10.5 °C. The mean annual precipitation for 1981–2010 is less than 700 mm; with the lowest and the highest mean monthly precipitation occurring in February (40.7 mm) and October (64.8 mm), respectively (Met Office, 2019).

Approximately 61% and 65% of the catchments (the River Colne and Ardleigh) is arable land, with more residential and industrial land use in the lower part of both catchments. Urban land use in the Colne and the Ardleigh catchments comprise 11% and 15% of the total catchment area, respectively.

4.3.2 Data collection and analyses

4.3.2.1 Water sampling and analytical procedure

Water sampling and analysis were conducted by Anglian Water Services. Non-composite water samples were collected manually on a weekly basis from the watercourse network during the period June 2008–December 2018 at the regulatory points REG1–REG2 in the Ardleigh catchment, and at the point REG3 at the Colne catchment outlet. Additionally, in the period July 2015–December 2018, samples were collected at monitoring points C1–C6 in the Colne catchment, giving a total of nine monitoring points (Figure 1). Samples were collected in 500 mL brown plastic bottles (these were flushed with sample before being sealed) and refrigerated at 4° C (within 24 h of collection). Determination of the metaldehyde concentration in water samples was conducted within 7 days of sample collection using liquid chromatography with mass spectrometric detection in line with the Drinking Water Testing Specification (method No CL/TO/046; UKAS, 2019). In liquid chromatography mass spectrometry (LC-MS) method, compounds are separated from a sample prior to analysis based on the interaction of the compounds with the stationary and mobile phases (LC stage). Separated compounds are then eluted off, desolvated into the gas phase and ionized. Following these steps, compounds 'mass analysis is conducted using the mass spectrometer (MS stage) (Thermo Fisher Scientific, 2022). The method's limit of detection of metaldehyde is 0.004 µg L^{-1}. All data entries in the dataset are above the detection limit.

4.3.2.2 Hydrological parameters

Daily streamflow data (m^3 s^{-1}) recorded during the investigation period at three gauging stations (37012, 37024 and 37005 (FGS 1, 2 and 3) with UK National Grid references TL771364, TL855297 and TL962261, respectively) across the Colne catchment (Figure 4.1) were obtained from the National River Flow Archive (NRFA, 2019 a, b, c) and the Environment Agency. Daily precipitation (mm) data were retrieved from the UK Climate Projections (UKCP09) dataset covering the period June 2008–December 2016 for a weather station located in the Ardleigh Catchment, northeast of Colchester (TM025275), 6.5 km at 80 degrees from the FGS3 location (Met Office et al., 2017). Daily precipitation data recorded at the West Bergholt station (TL960267, 0.6 km at 343 degrees from the FGS3 location) during January 2017–February 2019 were provided by the Environment Agency. The collected data were used to calculate monthly and annual average precipitation and flow for the investigation period.

The Northern and Western Salary Brooks are ungauged watercourses; therefore, daily streamflow estimation at these sites was required. Daily streamflow was modelled using the Area-Ratio based method, as described by Shu and Ouarda (2012):

$$Qy = \frac{Ay}{Ax} Qx \qquad \text{equation (1)}$$

where Q_y is estimated streamflow at an ungauged site, Q_x is recorded streamflow at a gauged site, and A_y and A_x are the drainage areas of the ungauged and gauged areas, respectively.

Flow data collected from FGS3 were used to model streamflow at sites REG1 and REG2.

4.3.2.3 Catchment delineation

The Colne catchment was delineated into separate sub–catchments focused on the location of sampling points, with the outlets defined using the Hydrology Toolset in ArcGIS. Flow direction and accumulation were generated from the 50-m grid Digital Terrain Model (OS, 2019) to determine the contributing area following the application of the Watershed tool to define sub-catchments draining to individual sampling points. The total area of sub-catchments draining to the C2, C4, C6 and REG3 sampling points incorporated the area of sub-catchments located upstream. For example, the sub-catchment draining to point C4 incorporated the area of sub-catchments with outlets at the C1, C2, and C3 sampling points (Figure 4.1).

4.3.2.4 Calculations

The monthly metaldehyde fluxes (monthly load, ML) were calculated using the formula:

$$ML\ (\mu g) = Q\, C_i\, t_i \qquad \text{equation (2)}$$

where Q is average monthly streamflow during period t_i (L s^{-1}), C_i is average metaldehyde concentration in water samples collected within a month period (µg L^{-1}), and t_i is the time of the considered period (s in a month), i represents the time period of one month. The sum of ML values within each year represents the annual load of metaldehyde (kg a^{-1}) (Kreuger, 1998; Rabiet, 2010).

Annual metaldehyde application rates (active applied, kg ha^{-1}) were obtained from the Pesticide Usage Survey for the period 2008–2018 (FERA, 2018). Crop coverage area (ha) was retrieved from the UKCEH Land Cover plus Crop map (UKCEH, 2018). The total arable area (all crops excluding grassland) and the area of cereals and oilseed rape crops were estimated for the entire Colne catchment and its sub-catchments. To calculate the amount of metaldehyde applied annually in the Colne catchment (annual application (AA), kg a^{-1}), metaldehyde application rates were multiplied by the crop area within the catchment, as follows:

$$AA = r\,A_i \qquad \text{equation (3)}$$

where r is metaldehyde application rate (kg ha^{-1}) for a given year, and A_i is the area of arable crops (ha). Annual application of metaldehyde was estimated for: (i) total arable area (all crops excluding grassland) to reflect applications during the February–June months to protect rooted vegetables, maize and other spring/summer crops; and (ii) the area of cereals and oilseed rape crops in each sub-catchment. Winter cereals and oilseed rape crops are the predominant type of crops within the study area, with metaldehyde applied during the August-December period to protect these crops.

Metaldehyde transport from the point of application to the stream network was calculated using two methods: (i) loss per hectare (g ha^{-1}) of arable crop, by dividing annual metaldehyde load (AL) by crop area; and (ii) loss of metaldehyde as a percentage of the amount applied in a sub-catchment annually:

$$Annual\ Loss = \frac{AL}{AA}100 \qquad \text{equation (4)}$$

The loss values from the total crop area (excluding grassland) and from cereals and oilseed rape crops were established separately.

The t-test, with a significance value of 0.05, was applied to establish the level of difference between the averages of quarterly metaldehyde concentrations before the Slug it Out campaign (2009, 2010) in the Ardleigh catchment and in 2016, the second year of the campaign. Simple and multiple stepwise linear regression models were completed to estimate the relationship between metaldehyde concentration, flux, precipitation, flow and metaldehyde use. Multiple stepwise regression model performs multiple regression a number of times, each time the weakest correlated variable is removed. JASP and Microsoft Excel software were used for the statistical analysis, including data visualisation.

4.4 Results

4.4.1 Annual trends in metaldehyde levels

4.4.1.1 Spatial trends

Metaldehyde concentrations were observed to vary between monitoring points within the Colne and Ardleigh catchments on an annual basis (Figure 4.2, Tables 4.1, 4.2).

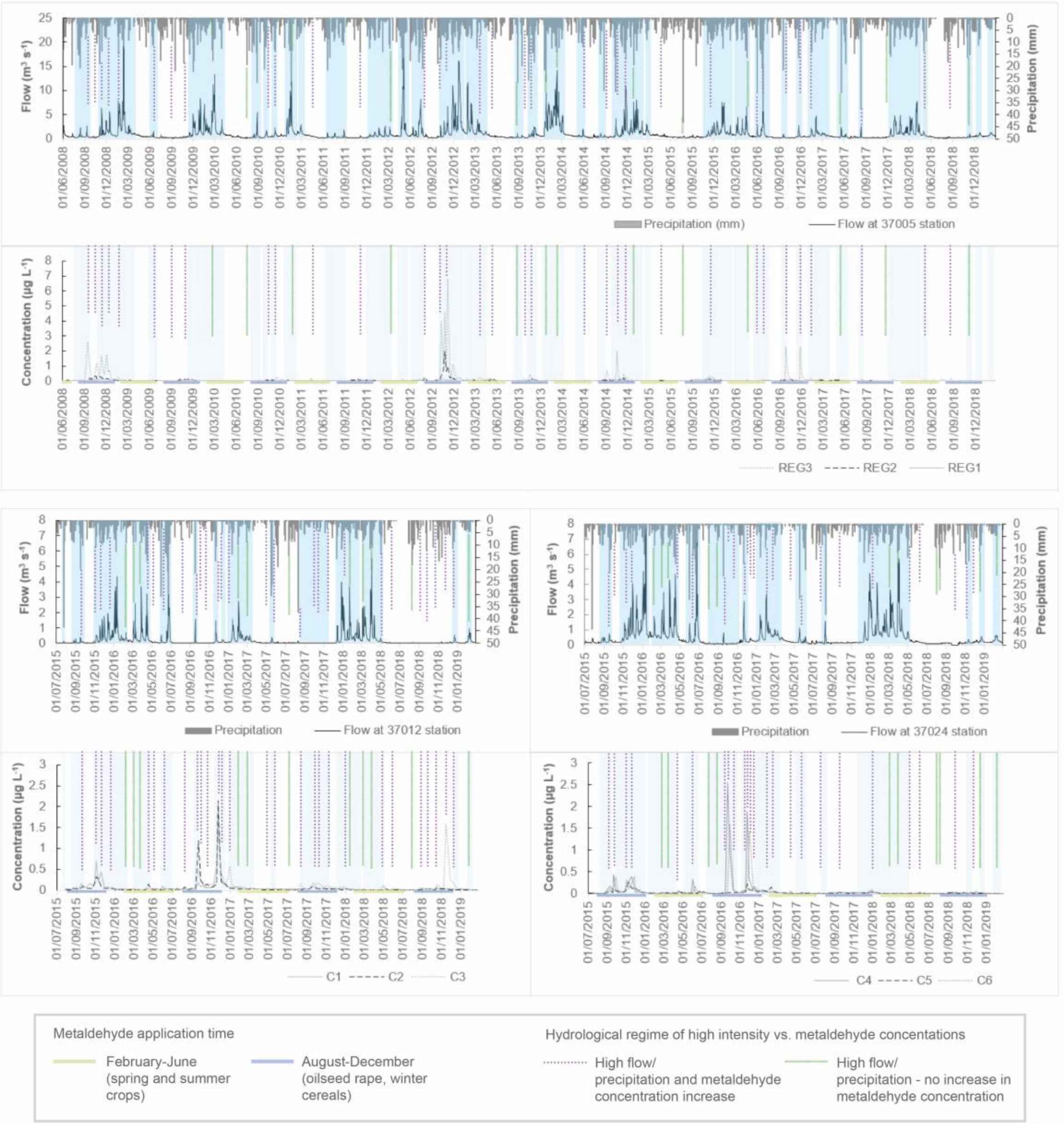


Figure 4. 2 Daily precipitation (mm), streamflow (m^3 s^{-1}) and metaldehyde concentration (µg L^{-1}) at the sampling locations during the period 2008 to 2018. REG1-REG3 and C1-C6 represent metaldehyde concentrations in the corresponding monitoring points. Colour shaded areas indicate periods of increase flow and/or precipitation.

Table 4. 1 Summary of historic metaldehyde concentration (μg L^{-1}) data in the Colne (REG3) and the Ardleigh catchments (REG1, REG2) during the period 2008 to 2018.

Site	Year	Total number of samples	Metaldehyde concentration (μg L^{-1})			Number of samples above the EU DWD limit	Percentile of samples above the EU DWD limit
			Minimum	Median	Maximum		
REG1	2008*	23	0.01	0.08	0.12	6	26
REG2		24	0.03	0.14	0.31	15	63
REG3**		22	0.03	0.52	2.63	18	82
REG1	2009	52	0.01	0.02	0.07	0	0
REG2		52	0.01	0.03	0.11	1	2
REG3**		52	0.01	0.03	0.26	3	6
REG1	2010	52	0.01	0.01	0.04	0	0
REG2		52	0.01	0.02	0.07	0	0
REG3**		52	0.01	0.02	0.24	3	6
REG1	2011	51	0.01	0.01	0.05	0	0
REG2		51	0.01	0.01	0.09	0	0
REG3**		51	0.01	0.02	0.19	1	2
REG1	2012*	52	0.01	0.02	0.11	1	2
REG2		52	<0.01	0.02	2.00	11	21
REG3**		58	0.01	0.04	6.78	16	28
REG1	2013*	49	0.02	0.03	0.18	1	2
REG2		50	0.02	0.03	0.16	3	6
REG3**		106	0.01	0.04	0.45	21	20
REG1	2014	50	0.01	0.02	0.09	0	0
REG2		50	0.01	0.02	0.18	2	4
REG3**		77	0.01	0.04	2.02	26	34
REG1	2015*	79	0.01	0.02	0.14	1	1
REG2		84	0.01	0.02	0.23	5	6
REG3**		80	0.01	0.03	0.35	9	11
REG1	2016*	81	0.01	0.03	0.11	1	1
REG2		81	0.01	0.03	0.19	3	4
REG3**		112	0.01	0.05	2.28	25	22
REG1	2017	78	0.01	0.03	0.06	0	0
REG2		78	0.01	0.02	0.09	0	0
REG3**		136	0.01	0.03	0.18	6	4
REG1	2018	87	0.01	0.01	0.04	0	0
REG2		87	0.01	0.01	0.08	0	0
REG3**		148	0.01	0.02	0.21	4	3

* Year when all sampling sites had samples above the EU DWD limit (0.1 μg L^{-1})

** Site with samples above the EU DWD limit in 2015–2018 time period

Table 4. 2 Summary of historic metaldehyde concentration (µg L^{-1}) data in the Colne catchment for the period during 2015 to 2018.

Site	Year	Total number of samples	Metaldehyde concentration (µg L^{-1})			Number of samples above the EU DWD limit	Percentile of samples above the EU DWD limit
			Minimum	Median	Maximum		
C1*	2015*	23	0.02	0.07	0.70	8	35
C2		23	0.01	0.04	0.32	3	13
C4		37	0.01	0.03	0.44	7	19
C5		37	<0.01	0.02	0.25	6	16
C6		38	0.02	0.03	0.40	8	21
C1*	2016*	53	0.01	0.03	1.91	7	13
C2		53	0.01	0.02	2.14	11	21
C3**		53	<0.01	0.02	1.48	13	25
C4		53	0.01	0.02	2.55	7	13
C5		53	0.01	0.02	0.22	7	13
C6		53	0.01	0.02	1.16	8	15
C1*	2017	52	0.02	0.03	0.11	1	2
C2		52	0.01	0.02	0.08	0	0
C3**		52	<0.01	0.03	0.19	7	13
C4		52	0.01	0.02	0.09	0	0
C5		52	<0.01	0.02	0.16	1	2
C6		52	0.01	0.02	0.09	0	0
C1*	2018	52	0.01	0.02	0.12	1	2
C2		52	<0.01	0.01	0.05	0	0
C3**		52	<0.01	0.01	1.57	6	12
C4		52	<0.01	0.01	0.05	0	0
C5		52	<0.01	0.01	0.03	0	0
C6		52	0.01	0.02	0.09	0	0

* Site with samples above DWD limit (0.1 µg L^{-1}) in the period 2015–2018

** Site with the largest number of samples above DWD limit in the period 2016–2018

Lowest median concentrations and a minimum number of concentrations exceeding the EU DWD limit (0.1 µg L^{-1}) in the Ardleigh catchment were registered at the Northern Salary Brook (inlet to the Ardleigh Reservoir, REG1), followed by more frequent exceedances of the regulatory standard at REG2 on the Western Salary Brook at the inlet to the Ardleigh Reservoir. Median concentrations varied between 0.01 and 0.07 µg L^{-1} for the Northern Salary Brook, and from 0.01 µg L^{-1} to 0.14 µg L^{-1} for the Western Salary Brook. The percentile of samples above the EU DWD limit varied between 0 and

2% (REG1) and 0–21% (REG2) during 2008–2018 (Table 4.1). Median concentrations at the REG1 and REG2 sites were below 0.1 µg L^{-1} during 2008–2018, except for the median concentration value at REG2 in 2016 (0.14 µg L^{-1}) (Table 4.1).

Median concentrations recorded in the stream network of the Colne catchment tended to be lower at the C4–C6 monitoring points situated in the middle part of the catchment compared to values at sites C1–C3 in the upper part of the catchment (up to 0.07 µg L^{-1} at monitoring point C1 in 2015) (Table 4.2; Figures 4.3, 4.4). Metaldehyde concentrations above 0.1 µg L^{-1} were detected each year during 2015–2018 at sites C1 and C3 (Figures 4.2–4.4).

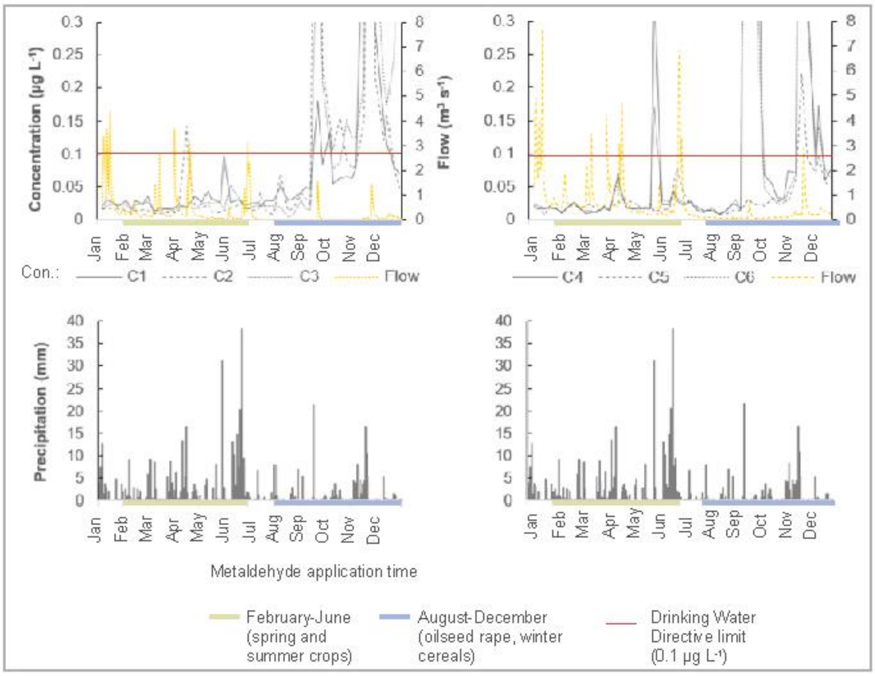


Figure 4. 3 Streamflow, precipitation and metaldehyde concentration for sampling points C1–3 (top panel) and points C4–6 (bottom panel) in the Colne catchment in 2016.

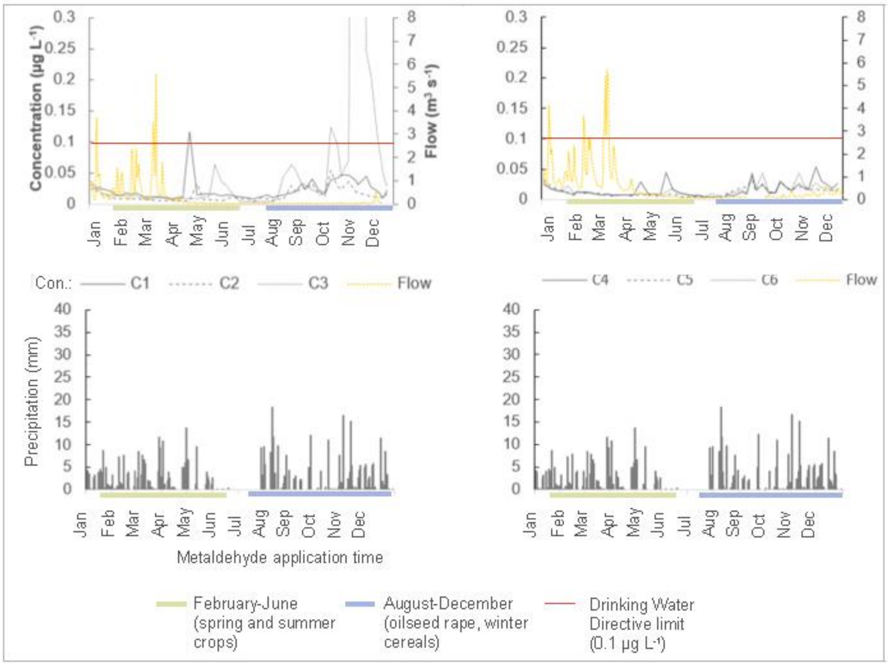


Figure 4. 4 Streamflow, precipitation and metaldehyde concentration for sampling points C1–3 (top panel) and points C4–6 (bottom panel) in the Colne catchment in 2018.

During the years 2016–2018, 2–13% and 12–25% of samples collected at C1 and C3, respectively, contained metaldehyde concentrations above the EU DWD limit. At the sub-catchment level, higher metaldehyde concentrations were observed at sites C1 and C3 at the top of the Colne catchment and also in the middle section of the catchment (points C4 and C6) during 2015–2018 (Table 4.2).

Highest concentrations and proportion of samples exceeding the EU DWD were observed at site REG3 within the same time period (percentile range 2–34% of samples collected). Median concentrations at site REG3 were consistently higher than at the monitoring points within the catchment, and varied between 0.02 and 0.52 µg L^{-1} during 2008–2018 (Figure 4.2, Table 4.1).

Similar to metaldehyde concentrations, metaldehyde flux at site REG3 was consistently the highest among all monitoring points in each year during the period 2015–2018, and the flux values were highest in 2016 across all monitoring points, except at site C5. Collectively, the annual flux at the top of the Colne catchment (sites C1–C3) tended to be lower than in the middle part of the catchment (C4–C6), where metaldehyde fluxes at C2 were comparable to the values at points REG1 and REG2 in the Ardleigh catchment (Figure 4.5). For example, in 2017 metaldehyde flux within the range 0.1–0.2 kg a^{-1} and

0.4–0.5 kg a^{-1} were recorded in C1–C3 and C4–C6 sites, respectively, with a maximum flux of 0.7 kg a^{-1} observed at REG3 (Figure 4.5).

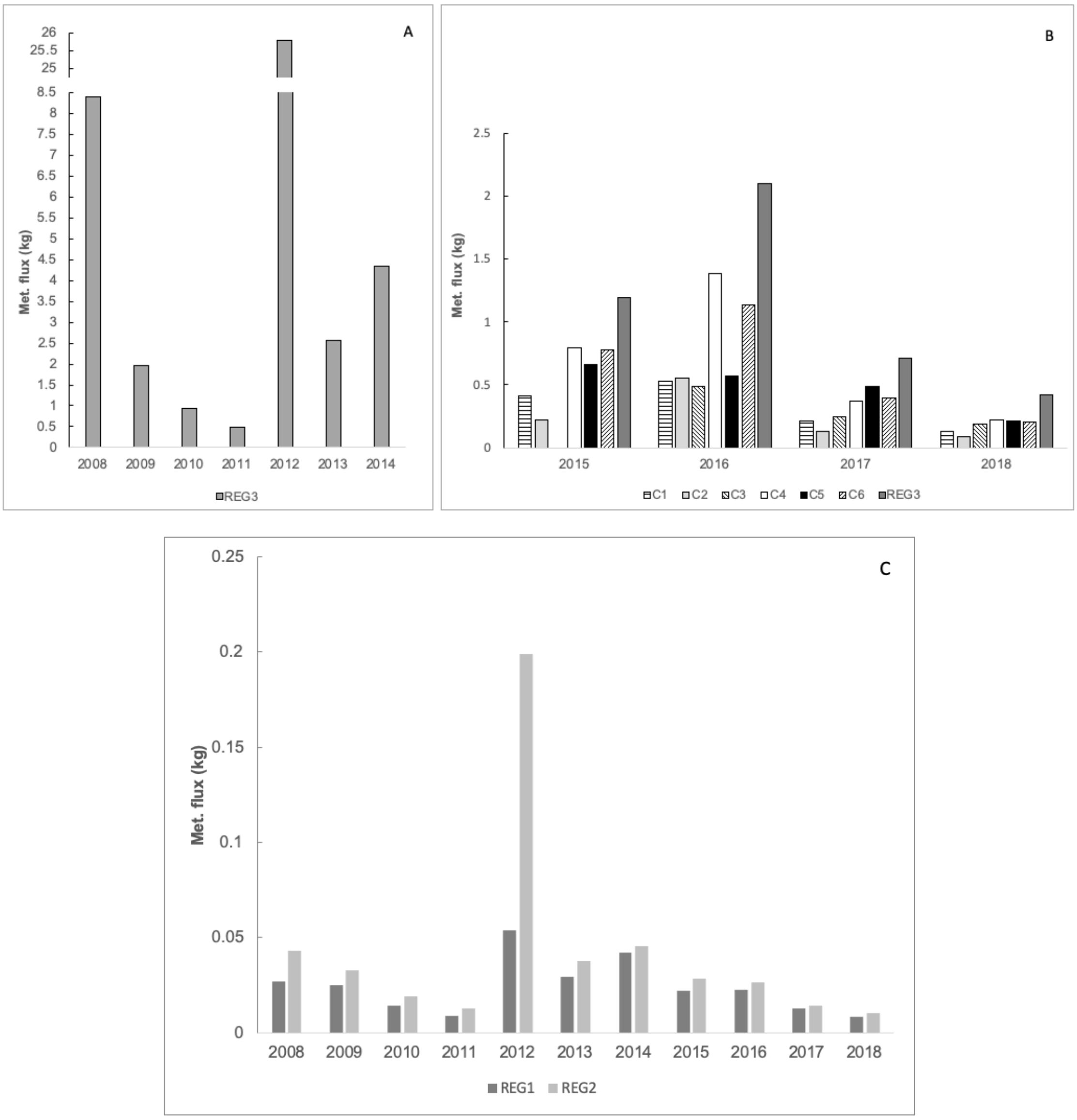


Figure 4. 5 Time series of annual metaldehyde flux (kg) during the period 2008 to 2018.

4.4.1.2 Temporal trends

Metaldehyde concentrations above the EU DWD regulatory limit (0.1 µg L^{-1}) were detected at all monitoring points in 2008, 2012, 2013, 2015 and 2016 in the study area. The highest percentile of all samples with a metaldehyde concentration above 0.1 µg L^{-1}

was in 2008 (82%), followed by 28% and 34% in 2012 and 2014, respectively (Tables 4.1, 4.2).

Maximum concentrations did not exceed 0.5 µg L^{-1} in all years except 2008, 2012, 2014 and 2016 (except at site C1 November 2015 (concentrations up to 1.57 µg L^{-1}) and at C3 in November 2018 (up to 1.57 µg L^{-1})). Concentration levels up to 2.63 µg L^{-1} were recorded in 2008, 2014 and 2016, with highest levels in 2012 (6.78 µg L^{-1}) at monitoring point REG3 (Figure 4.2, Table 4.1). The highest mean annual concentrations and variability in metaldehyde concentrations were observed in 2012, followed by the 2014 and 2016 time series at REG3 when mean concentrations were above the EU DWD limit in these periods (Figure 4.6). In 2016, the maximum concentration at the Colne catchment reached 2.28 µg L^{-1} (Figures 4.2, 4.6, 4.7).

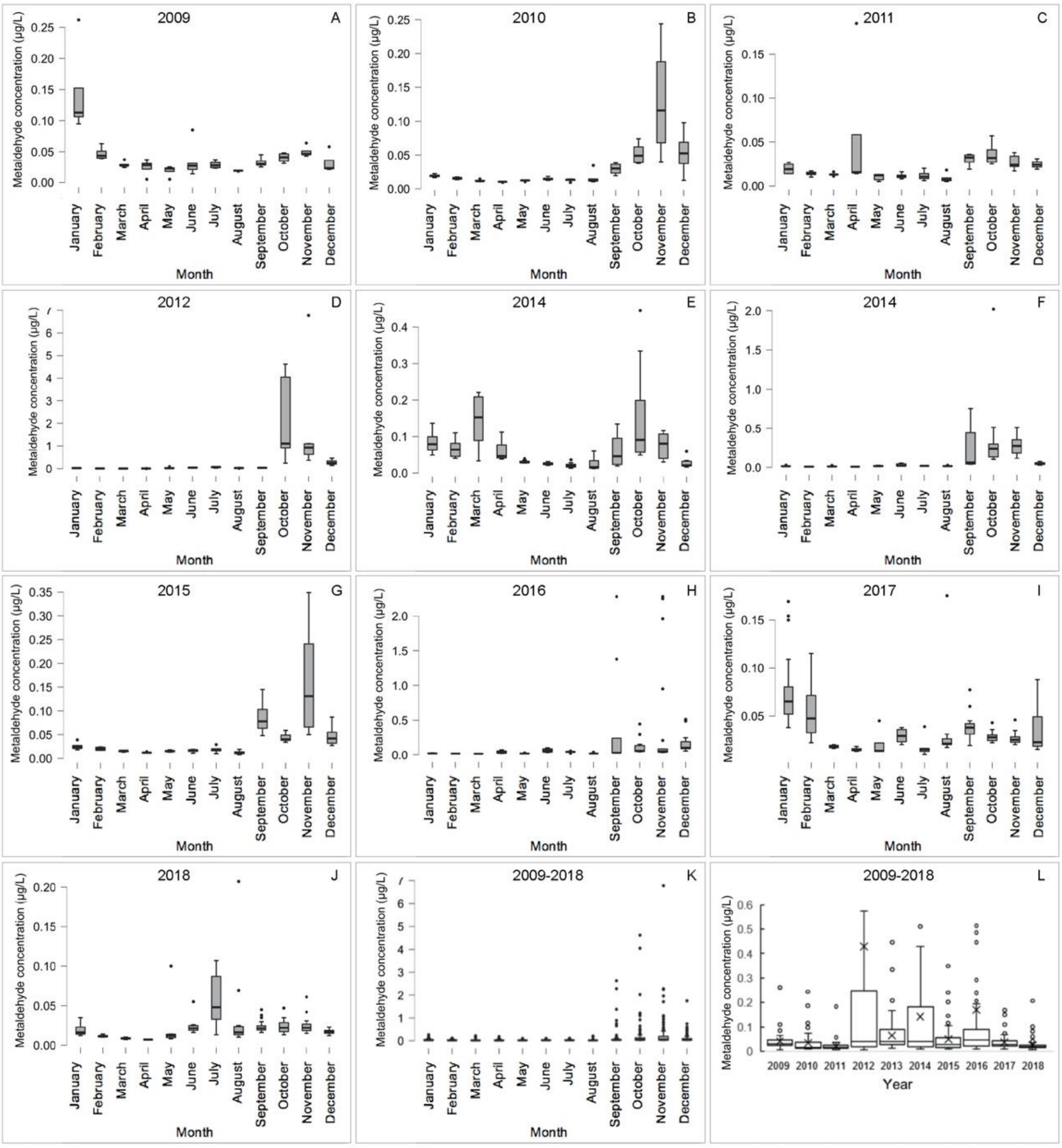


Figure 4. 6 Box plots representing the range in metaldehyde concentrations (µg L^{-1}) in the Colne catchment outlet (REG3)) during the period 2009 to 2018. Panels A-J show monthly range in metaldehyde concentrations for individual years. Panels K and L represent monthly range and annual range in concentrations over the period 2009-2018. Circles represent outliers that are not included in the range data. Crosses and lines in each box indicate mean and median values, respectively; error bars display one standard deviation of the sample range. Whiskers (A-K) represent minimum and maximum values.

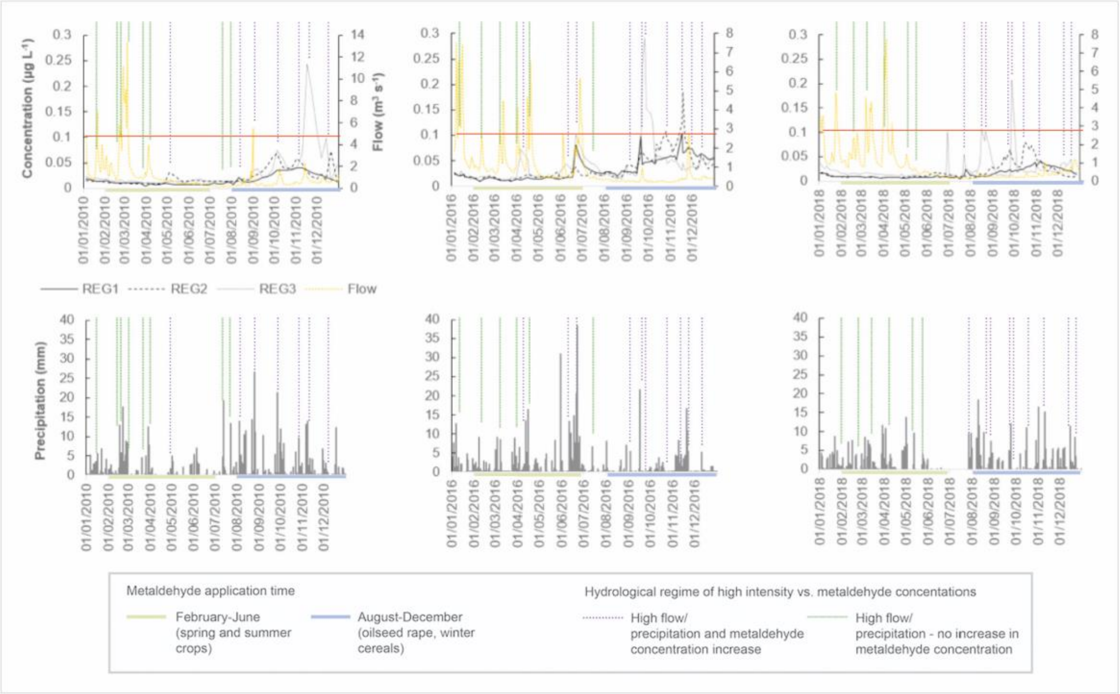


Figure 4. 7 Streamflow, precipitation and metaldehyde concentration in the Ardleigh catchment (points REG1 and REG2) and the abstraction point in the Colne catchment (REG3) in 2010, 2016 and 2018.

To a lesser extent, this trend (highest mean annual concentrations and variability) was recorded at points REG1 and REG2 in 2012 and 2016. Peak concentrations up to 2.0 and 6.78 µg L^{-1} were recorded in 2012 at sites REG2 and REG3. In 2016, maximum concentrations at these monitoring points in the Ardleigh and the Colne catchments reached 0.19 µg L^{-1} and 2.28 µg L^{-1} (Figures 4.2, 4.6, 4.7). Noticeable decreases in metaldehyde concentrations above the EU DWD limit took place in 2017 and 2018, when compared with concentration statistics for the 2015 and 2016 time series (Figures 4.2, 4.6, 4.7, Tables 4.1, 4.2). Annual ranges in metaldehyde concentration were greater in the years 2012 and 2014 with an overall reduction in the range of metaldehyde concentrations evident over the period 2015-2018 (Figure 4.6).

Annual time series of metaldehyde fluxes were similar to overall trends in annual metaldehyde concentrations during the study period 2008–2018 (Figure 4.5). When mean annual concentration values were compared to annual flux at REG3, the data showed a strong positive relationship ($R^2 = 0.9$, $r = 0.7$, $p = 0.02$, $n = 22$). Maximum flux values at monitoring points REG1–REG3 were recorded in 2012 with up to 25.78 kg at REG3, followed by flux values of 8.37 kg in 2008 and 4.35 kg in 2014, with both values again recorded at REG3.

Metaldehyde loss to the stream network in g ha^{-1} varied across the Colne catchment and was highest downstream to the C1 and C5 monitoring points, with up to 1.13 and 0.34 g ha^{-1} metaldehyde loss from cereal and oilseed rape crops in 2016, respectively (Table 3). Metaldehyde loss from cereal and oilseed rape crops in the Colne catchment recorded at REG3 reached a maximum of 2.39 g ha^{-1} in 2012, followed by losses of 0.78 and 0.40 g ha^{-1} in 2008 and 2014, respectively. The lowest losses of metaldehyde were observed in 2011 and 2018 with 0.04 g ha^{-1} recorded at REG3 (Table 4.3).

Table 4. 3 Metaldehyde loss to the watercourse network (g ha^{-1}) from the River Colne sub–catchments C1–C6 and the catchment outlet REG3.

	Metaldehyde loss (g ha^{-1})					
	C1	C2	C3	C4	C5	C6
Year	All crops					
2015	0.33	0.09		0.11	0.25	0.07
2016	0.42	0.23	0.23	0.20	0.21	0.10
2017	0.17	0.05	0.11	0.05	0.18	0.03
2018	0.10	0.03	0.09	0.03	0.08	0.02

	C1	C2	C3	C4	C5	C6
Year	Cereals and oilseed rape crops					
2015	0.88	0.14	N/A	0.14	0.40	0.09
2016	1.13	0.35	0.26	0.25	0.34	0.13
2017	0.46	0.08	0.13	0.07	0.30	0.05
2018	0.28	0.05	0.10	0.04	0.13	0.02

Metaldehyde loss (g ha^{-1})		
	REG3	
Year	All crops	Cereals and oilseed rape crops
2008	0.58	0.78
2009	0.14	0.18
2010	0.06	0.09
2011	0.03	0.04
2012	1.79	2.39
2013	0.18	0.24
2014	0.30	0.40
2015	0.08	0.11
2016	0.15	0.19
2017	0.07	0.07
2018	0.03	0.04

Similar trends were observed when metaldehyde loss was expressed as a percentage of annual metaldehyde application in the period 2008–2018. Highest levels of metaldehyde loss from cereal and oilseed rape crops in the Colne catchment were equal to 1.57%, 0.33% and 0.24% in 2012, 2014 and 2008, respectively, at monitoring point REG3. Metaldehyde losses to surface water from all crops varied between 0.01 and 0.25%, with a maximum of 1.18% in 2012 (Table 4.4).

Table 4. 4 Summary of metaldehyde use (kg) and loss to the streamflow network (%, based on the cumulative flux) in the Colne catchment during the period 2008–2018.

Year	Metaldehyde use (active applied, kg)	Metaldehyde use (active applied, kg)	Metaldehyde flux (kg)	Metaldehyde loss (%)	
	All crops	Cereal and oilseed rape crops		All crops	Cereal and oilseed rape crops
2008	4680	3510	8.39	0.18	0.24
2009	4680	3510	1.95	0.04	0.06
2010	3326	2495	0.93	0.03	0.04
2011	3240	2430	0.48	0.01	0.02
2012	2189	1642	25.8	1.18	1.57
2013	2189	1642	2.55	0.12	0.16
2014	1757	1318	4.35	0.25	0.33
2015	1757	1318	1.19	0.07	0.09
2016	1526	1145	2.10	0.14	0.18
2017	2246	1711	0.71	0.03	0.04
2018	1435	1077	0.42	0.03	0.04

Metaldehyde use (kg a^{-1}) in the Colne catchment showed a decline from 4680 kg in 2008/2009 to 3326 kg in 2010 and 2189 kg in each of 2012 and 2013. Although the application of metaldehyde in 2012 and 2013 was similar to the metaldehyde use in 2014 and 2015 (1757 kg a^{-1}), a substantial increase of metaldehyde flux was observed in 2012 and 2014 (25.78 and 4.35 kg, respectively, at REG3). Consequently, no relationship between application rates and metaldehyde concentration/flux was observed (Figure 4.8). Results of multiple linear stepwise regression demonstrated that precipitation and streamflow are the main factors controlling flux (R^2=0.9), while the precipitation variable explains 37% and 81% of variability in metaldehyde concentration and flux, respectively (Figure 4.9)

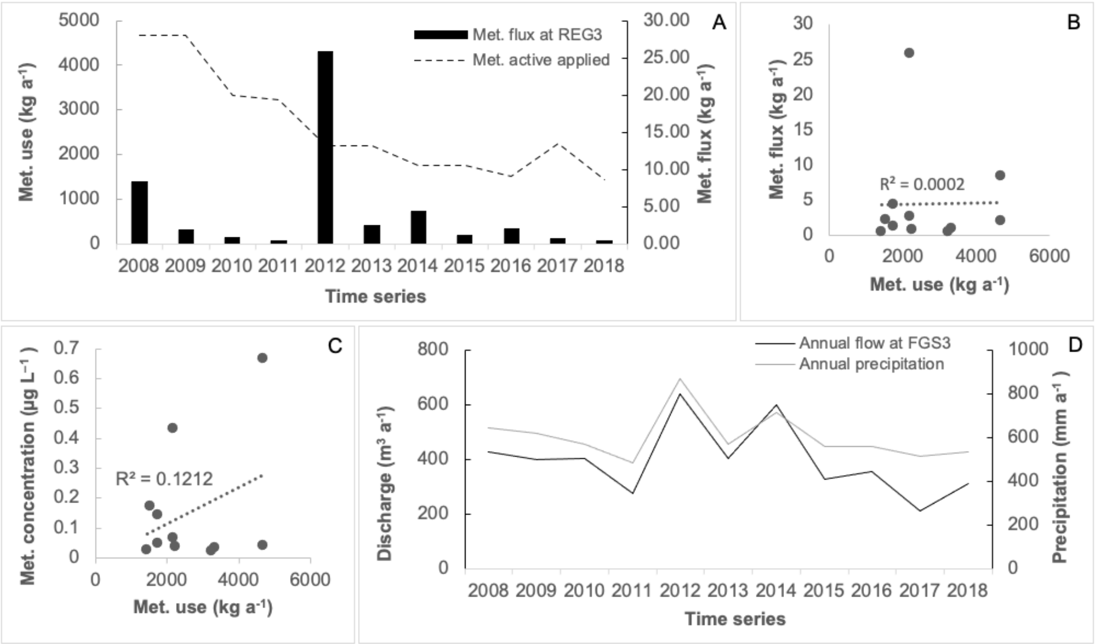


Figure 4. 8 Relationship between annual metaldehyde use (active applied in the study area, kg a^{-1}) and: i) annual metaldehyde flux (kg a^{-1}) (A, B) and ii) mean metaldehyde concentration (µg L^{-1}) for the period 2008–2018 (C). D: total annual discharge (m^3 a^{-1}) and annual precipitation (mm a^{-1}) in the Colne catchment for the period 2008–2018.

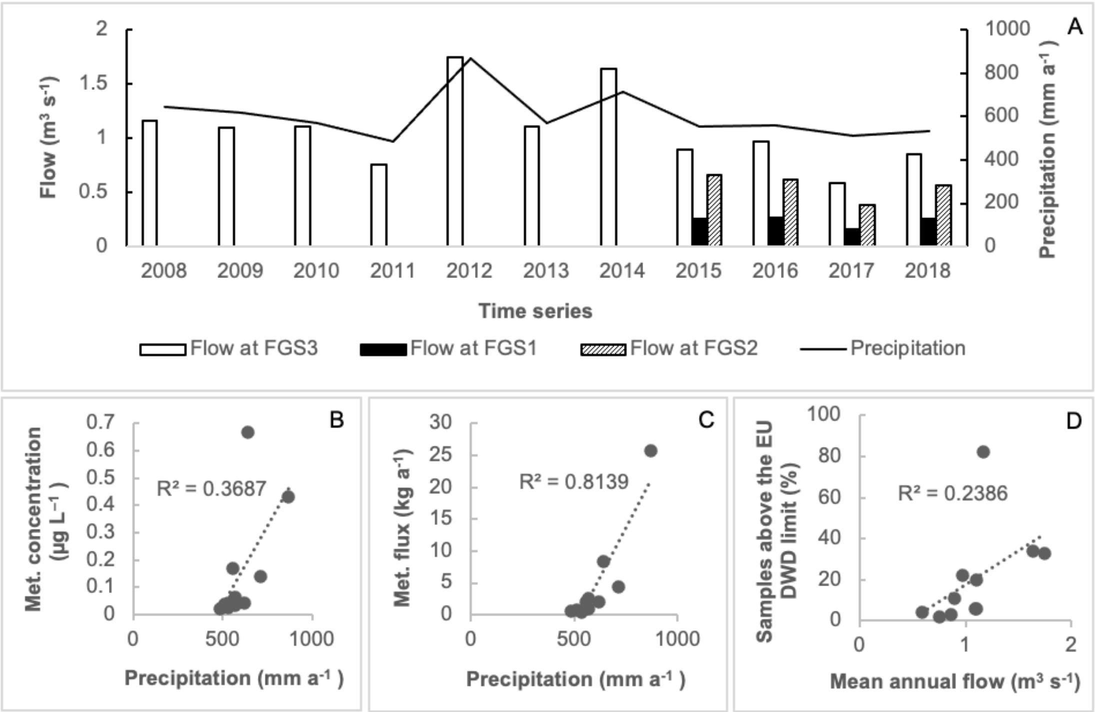


Figure 4. 9 Top panel (A): annual precipitation (mm a^{-1}) and average streamflow (m^3 s^{-1}) at gauging stations in the Colne catchment during the period 2008–2018. Bottom panel: i) relationship between annual precipitation and metaldehyde concentration and flux (B, C); ii) relationship between samples above the EU DWD limit (%) and mean annual flow (m^3 s^{-1}) (D).

Table 4. 5 Multiple forward stepwise linear regression results.

Model Summary - Met. flux (kg)	Variable/ Intercept	R	R	Adjusted R	RMSE	Standard Error	t	p
1	(Intercept)	0	0	0	7.449	2.246	1.977	0.076
2	(Intercept)	0.902	0.814	0.793	3.388	6.038	-5.446	< .001
	Precipitation (mm a^{-1})					0.01	6.272	< .001
3	(Intercept)	0.944	0.891	0.864	2.748	6.957	-6.42	< .001
	Precipitation (mm)					0.022	5.029	0.001
	Average annual flow (m^3 s^{-1})					6.866	-2.383	0.044
Model Summary - Met. concentration (µg/L)	(Intercept)					0.063	2.431	0.035
1	(Intercept)	0	0	0	0.208	0.311	-1.768	0.111
2	Precipitation (mm a^{-1})	0.607	0.369	0.299	0.174	5.084e - 4	2.293	0.048

Note. The following covariates were considered but not included: i) Flux regression model: Metaldehyde use (active applied, kg a^{-1}), Average metaldehyde concentration (µg L^{-1}), Annual discharge (m^3 a^{-1}); ii) Metaldehyde concentration regression model: Average annual flow (m^3 s^{-1}), Annual discharge (m^3 a^{-1}), Metaldehyde use (active applied, kg a^{-1}).

4.4.2. Seasonal variations in metaldehyde levels: comparison with hydrological conditions and application regime

4.4.2.1. Hydrological conditions

Concentration displayed a seasonal pattern with concentrations rising during September–December each year across all monitoring points. Such elevated levels often coincided with high–intensity precipitation events followed by increased stream discharge during

September–December annually (Figures 4.2-4.4, 4.7). Highest metaldehyde concentrations frequently occurred following precipitation events with daily precipitation above 10 mm. For example, in 2012, concentrations within the 4.05–6.78 μg L^{-1} range were associated with 15-30 mm cumulative precipitation (4 days before the concentration peak was detected). 63% of all samples above the EU DWD limit (0.1 μg L^{-1}) were recorded when 4-day cumulative precipitation was ≥ 10 mm. During the metaldehyde application period from August–December, elevated levels were also associated with precipitation events of lower intensity (up to 5 mm of daily precipitation) and under baseflow conditions (below 0.5 m^3 s^{-1}). For example, in October–November 2016, metaldehyde levels above the EU DWD limit were recorded. A significant positive relationship ($p = <0.001$) between average quarterly metaldehyde concentration and average flow during the 2009–2018 period was observed.

When average quarterly concentrations at site REG3 are compared for the periods January–March, April–June, July–September and October–December in 2009, 2010 (dry years) and 2016 (a wet year), average metaldehyde concentrations across all seasons remained below the EU DWD limit across all seasons in 2009 and 2010. Average concentrations of metaldehyde at REG3 were below 0.2 μg L^{-1} when an average flow of 2.7 m^3 s^{-1} (January–March) and cumulative precipitation of 210 mm (July–September) were recorded in 2010. A significant positive relationship ($R^2 = 0.76$, $r = 0.87$, $p = <0.001$, $n = 10$) between average metaldehyde concentration and streamflow was observed in the months October–December in 2009–2018 (Figure 4.10).

In a similar way to the Colne catchment, average metaldehyde concentrations for the Northern and Western Salary Brooks (REG1 and REG2) in the Ardleigh catchment in 2016 are shown to be higher than when compared with analogous concentrations at these points in 2009 and 2010 (Figure 4.10). In the case of the 2009 time series, average metaldehyde concentrations in January–March (REG2), July–September and October-December (REG1) were significantly lower than in 2016. The concentrations were significantly lower ($p <0.05$) in 2010 than in 2016 in all instances apart from the time series in July–September at REG2 (Figure 4.10).

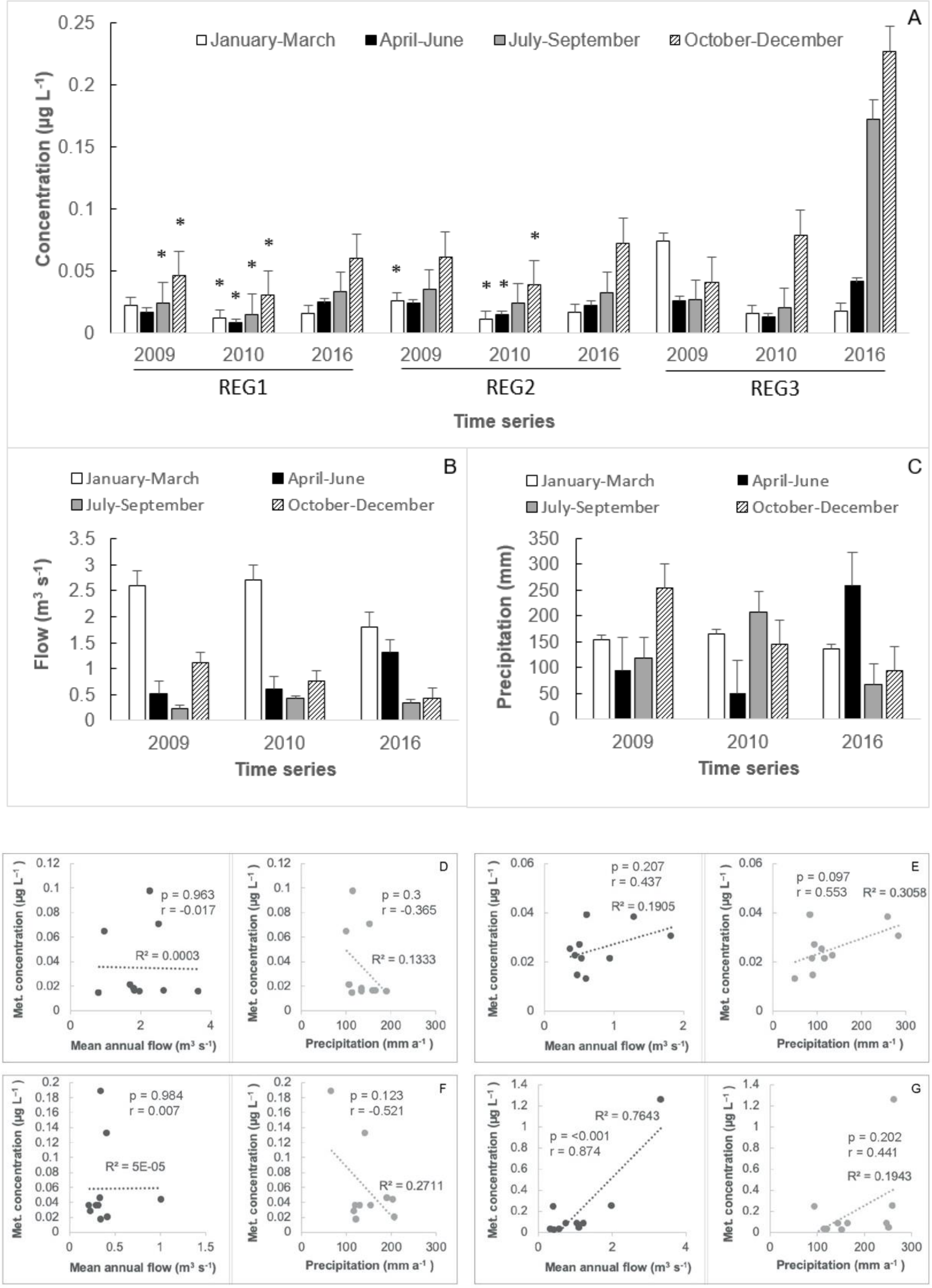


Figure 4. 9 Panel A shows average metaldehyde concentrations at the REG1–REG3 monitoring points in the periods 2009, 2010 and 2016. Asterisks indicate a statistically significant difference between mean metaldehyde concentration in 2009 vs. 2016, and in 2010 vs. 2016 at points REG1 and REG2. Panel B represents mean flow ($m^3\ s^{-1}$) and Panel C represents cumulative precipitation (mm). Error bars are standard error of the mean. Panels D-G: relationship between average quarterly metaldehyde concentration and average flow/precipitation during the period 2009–2018 (n = 10; D: January–March, E: April–June, F: July–September, G: October–December).

Hydrological conditions of high intensity with daily precipitation ranging between 10 and 20 mm (for example, daily precipitation within the range 10–18 mm day^{-1} on 7, 8, 12 and 13 July 2012), and within 30–43 mm on several occasions (43 mm on 24 July 2015; 31 and 38 mm on 30 May and 22 June 2016, respectively; see Figures 4.2, 4.3, 4.7), and maximum daily flow up to 16 m^3 s^{-1} (FGS3) during February–July were not associated with metaldehyde levels above 0.1 µg L^{-1}, except for those occasions in 2009, 2013 and 2017.

Three instances of EU DWD limit exceedance were recorded at REG3 in January 2009 (Table 4.6); elevated but below the regulatory limit metaldehyde concentrations, up to 0.06 µg L^{-1}, were observed in February of the same year. Eight instances of regulatory limit exceedance (observed concentrations up to 0.22 µg L^{-1}) occurred in February–April 2013 and a rise in metaldehyde concentrations in February 2017 (up to 0.12 µg L^{-1}) (Tables 4.6-4.8) Streamflows recorded at FGS3 during these time periods varied between 1 and 7 m^3 s^{-1}. Additionally, one instance of the EU DWD limit exceedance (0.16 µg L^{-1}) was recorded at site C5 on 9 February 2017 (Figure 4.2, Table 4.8).

Table 4. 6 Statistics of metaldehyde concentrations above the EU DWD limit for August–December (autumn/winter application period), February–June (spring/summer application period), and January and July (no application) during the period 2008 to 2018 at the catchment outlet REG3.

Site	Year	Total number of samples			Number of samples above the EU DWD limit			Percentile of samples above the EU DWD limit		
		August–December	February–June	January, July	August–December	February–June	January, July	August–December	February–June	January, July
REG3	2008*	19	2	1	18	0	0	95	0	0
	2009	22	22	8	0	0	3 (January)	0	0	38
	2010	22	22	8	3	0	0	14	0	0
	2011	21	22	8	0	1 (April)	0	0	5	0
	2012*	27	21	10	19	0	0	70	0	0
	2013	46	42	18	11	8 (including 1 in February, 6 in March, and 1 in April)	2 (January)	24	19	11
	2014*	46	21	10	26	0	0	57	0	0
	2015	49	21	10	9	0	0	18	0	0
	2016*	76	24	12	24	1 (June)	0	32	4	0
	2017	90	22	24	1	1 (February)	3 (January)	1	5	13
	2018	93	26	29	1	1 (May)	2 (July)	1	4	7

*Year with >30% of samples above the EU DWD limit (0.1 μg L^{-1}) collected in August–December.

Table 4. 7 Instances of increase in metaldehyde concentrations during the spring/summer application period (February–June) and no application period (January, July) in the Colne catchment at site REG3 in years 2009–2018.

Year	Month	Number of metaldehyde concentrations in the range of 0.05–0.09 µg L^{-1} at REG3	Number of metaldehyde concentrations above 0.1 µg L^{-1} at REG3
2009	February–March	1	
	April–June	1	
	January, July	0	3 (January)
2010	February–March	0	
	April–June	0	
	January, July	0	
2011	February–March	0	
	April–June	0	1 (April, 0.19 µg L^{-1})
	January, July	0	
2012	February–March	0	
	April–June	3 (in June)	
	January, July	3 (July)	
2013	February–March	4	7 (up to 0.22 µg L^{-1})
	April–June	3	1 (0.11 µg L^{-1} in April)
	January, July	5 (January)	2 (January)
2014	February–March	0	
	April–June	2	
	January, July	0	
2015	February–March	0	
	April–June	0	
	January, July	0	
2016	February–March	0	
	April–June	4	1 (0.1 µg L^{-1})
	January, July	1 (July)	
2017	February–March	2	1 (0.12 µg L^{-1})
	April–June	0	
	January, July	12 (January)	3 (January)
2018	February–March	0	
	April–June	1	1 (0.1 µg L^{-1} in May)
	January, July	2 (July)	2 (up to 0.11µg L^{-1} in July)

Table 4. 8 Instances of increase in metaldehyde concentrations during the spring/summer application period (February–June) and no application period (July) in the Colne catchment (sites C1–C6) in years 2015–2018.

	Month	Number of metaldehyde concentrations in the range of 0.05–0.09 µg L^{-1}					
		C1	C2	C3	C4	C5	C6
2015	April–June	N/A	N/A	N/A	0	0	0
	July	N/A	N/A	N/A	0	0	0
2016	February–March	0	0	0	0	0	0
	April–June	1	1 (and 0.14 µg L^{-1} in 1 instance in April)	1	2 (and 0.35 µg L^{-1} in 1 instance in April)	2	1 (and 0.17 µg L^{-1} in 1 instance in May)
	July	1	1	0	0	0	0
2017	February–March	3	0	0	0	1 (and 0.16 µg L^{-1} in 1 instance in February)	2
	April–June	0	0	0	1	0	0
	July	0	0	0	0	0	0
2018	February–March	0	0	0	0	0	0
	April–June	0 (and 0.12 µg L^{-1} in 1 instance in May)	0	0	0	0	0
	July	0	0	0	0	0	0

Occasional increases up to 0.04 µg L^{-1} and rare instances of concentrations in the range 0.05–0.09 µg L^{-1} on four occasions in the Ardleigh catchment were observed over a 10-year period during February–July. One instance of regulatory limit exceedance, with an observed metaldehyde concentration of 0.2 µg L^{-1}, was recorded on 17 July 2012 at point REG2. Prior to this date, the daily precipitation recorded on 12 and 13 July 2012 was 12.3 and 10.6 mm, respectively (Figure 4.2). The total precipitation and average flow recorded at the bottom part of the Colne catchment on 17 July 2012 were 38.4 mm and 2.27 m^3 s^{-1}, respectively (Figure 4.2). On 22 June 2016, concentrations increased at all monitoring points to varying extent, with peak concentrations ranging between 0.05 µg L^{-1} (C5) and 0.1 µg L^{-1} (REG3) across the Colne catchment. In the Ardleigh catchment, peak concentrations reached 0.08 µg L^{-1} at REG1 (Figures 4.3, 4.7).

In those instances when metaldehyde levels above the regulatory limit were detected during baseflow conditions during February–July, regulatory limit exceedances were localised and shortlived. These circumstances support probable point source pollution as the cause. For example, a metaldehyde concentration of 0.19 µg L^{-1} was recorded at REG3 in April 2011 when only 3 mm of monthly precipitation and an average daily flow of 0.5 m^3 s^{-1} were recorded. Also, metaldehyde concentrations up to 0.1 µg L^{-1} were detected at REG3 in the first two weeks of July 2018 when no precipitation fell and an average daily flow of 0.18 m^3 s^{-1} was recorded at FGS3 (Figure 4.7). No increase in metaldehyde concentrations was observed elsewhere across the catchment during July 2018 (Figure 4.4).

4.4.2.2 Application regime

When periods of no metaldehyde application (January, July) were assessed, metaldehyde concentrations were typically in the range of 0.01–0.03 µg L^{-1} across all years observed. Elevated concentrations within the range 0.05–0.09 µg L^{-1} were observed on 23 instances at REG3 in January (n = 17) and July (n = 6) during 2008–2018, accounting for 17% of samples collected during no-application months (Table 4.7).

Metaldehyde concentrations above 0.1 µg L^{-1} were observed on eight occasions in January from 2008–2018 and on two occasions in July from 2008–2018, representing 7% of all samples collected in these two months (Table 4.6).

Concentrations during metaldehyde application periods to protect spring and summer crops (February–June) were within a similar range to concentration values observed during no application time periods, generally not exceeding 0.03 μg L^{-1}. Concentrations within the range 0.05–0.09 μg L^{-1} were observed on seven and 14 instances at REG3 in February–March and April–June 2008–2018, respectively (9% of all samples collected in February–June 2008–2018) (Table S2). Twelve instances (5% of all samples) occurred when metaldehyde concentrations above 0.1 μg L^{-1} were observed at REG3 during the spring/summer application period (Table 4.6).

At the sub-catchment level, only five instances of metaldehyde concentrations above 0.1 μg L^{-1} were recorded during February–June in 2015–2018 across monitoring points C1–C6 in the Colne catchment. For comparison, 101 instances of regulatory limit exceedance were recorded during the whole period 2015–2018 at these monitoring points (C1–C6, Table 4.2).

In the autumn/winter application period (August–December) 2008–2018, 64% of samples collected during these months had metaldehyde concentrations within the range 0.01–0.04 μg L^{-1}. At REG3, elevated levels of metaldehyde within the range 0.05–0.09 μg L^{-1} were observed in 14% of samples collected between August–December 2008–2018. The autumn/winter application period was associated with the highest number of concentrations above 0.1 μg L^{-1}, with 22% of all samples collected in August–December 2008–2018 (112 out of 511) containing metaldehyde above the EU DWD limit. More than 50% of samples collected in August–December 2008, 2012 and 2014 had metaldehyde concentrations above 0.1 μg L^{-1} (Table 4.6).

Cumulative fluxes in dry (2010, 2018) and wet years (2016) at the catchment outlet were compared across metaldehyde application seasons (Table 4.9). In dry years, cumulative flux during January and July (no metaldehyde application) was equal to 0.1 kg (2010, 2018) and up to 0.3 kg during the spring/summer application period (February–June) in 2010. In the autumn/winter period of these dry years, metaldehyde flux was 0.5 and 0.1 kg (2010, 2018, respectively). Maximum fluxes across all application seasons were observed in 2016 when 0.2, 0.6 and 1.3 kg (no application, spring/summer and autumn/winter application periods, respectively) (Table 4.9) were recorded.

Table 4. 9 Summary of monthly metaldehyde flux (kg) at site REG3 in 2010, 2016 and 2018. Monthly values >0.2 kg are highlighted in bold.

Month	Monthly Flux (kg)		
	2010	2016	2018
January	0.12	**0.16**	0.10
February	0.15	0.04	0.04
March	0.07	0.06	0.05
April	0.03	**0.18**	0.04
May	0.02	0.03	0.04
June	0.01	**0.28**	0.02
July	0.01	0.05	0.03
August	0.03	0.02	0.03
September	0.02	**0.38**	0.01
October	0.08	0.07	0.02
November	**0.26**	**0.65**	0.03
December	0.13	**0.19**	0.03

While variability in metaldehyde concentrations in the Ardleigh catchment remained relatively stable in dry years during the period 2009-2016 (August–December application period), a gradual decrease in levels and variability was observed in the subsequent years of the Slug It Out campaign. Similar trends were observed in the Colne catchment in 2017 and 2018; however, in 2019 and 2020 the variability (range) in concentrations increased and a noticeably higher number of DWD exceedances were recorded (Figure 4.11).

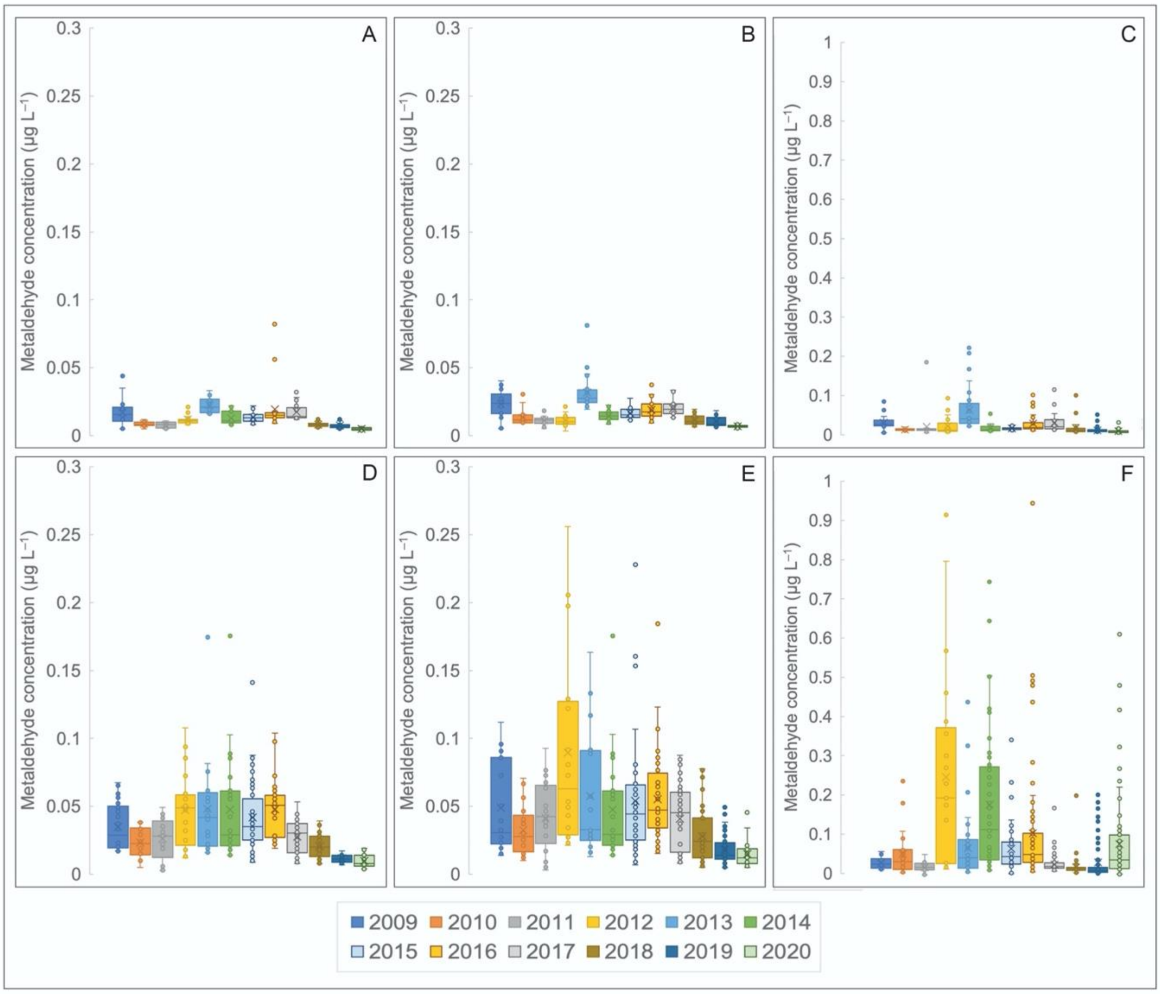


Figure 4. 10 A–C: variability in metaldehyde concentrations (µg L^{-1}) in the spring-summer application period (February–June) at REG1 (A), REG2 (B) and REG3 (C) during the period 2009–2020. D–F: variability in metaldehyde concentrations in the autumn-winter application period (August–December) at REG1 (D), REG2 (E) and REG3 (F) during the period 2009-2020. Crosses and lines in each box indicate mean and median values, respectively; error bars display one standard deviation of the sample range.

Water companies continuously work towards the reduction of metaldehyde concentrations in water supplies, and these efforts cause a consistent decline in metaldehyde concentrations detected in samples (Table 4.10; Drinking Water Inspectorate, 2021).

Table 4. 10 An overview of metaldehyde concentrations above the EU DWD limit detected in water samples from water companies in England (Drinking Water Inspectorate, 2021) in the context of changes in molluscicide product use (Pesticide Usage Survey, 2021).

Year	Number of samples above the EU DWD limit	Area of arable crops treated in the UK (ha)	Molluscicide
2013	325		
2014	134	74,426	Ferric phosphate
		920,317	Metaldehyde
2015	65		
2016	47	186,208	Ferric phosphate
		1,223,746	Metaldehyde
2017	29		
2018	4	480,531	Ferric phosphate
		1,023,281	Metaldehyde
2019	3		

4.5 Discussion

4.5.1 Temporal and spatial trends in metaldehyde concentrations and fluxes

Time series analysis of metaldehyde presence in the study area revealed that the molluscicide is consistently present in stream networks at concentrations that generally do not exceed the EU DWD limit of 0.1 μg L^{-1}. Peak concentrations, with frequent increases in concentrations by an order of magnitude, regularly occurred during the application periods in September–December each year. Noticeably smaller increases in metaldehyde, when concentrations tended to rise occasionally from 0.01 to 0.03 μg L^{-1}, and up to 0.09 μg L^{-1} on rare occasions, were observed during the spring–summer application period from April–June. These trends agree with observations of metaldehyde time series in other studies. Peak concentrations of a similar order of magnitude were reported by Kay and Grayson (2014), Lu et al. (2017) and Castle et al. (2018).

The increase in metaldehyde concentrations and frequent exceedance of the regulatory limit during the months September–December are linked to land use in the study area: 49% of all crops in the Colne catchment comprise winter cereals and oilseed rape. Applications of metaldehyde are made to protect these crops during the months August–December. Higher amounts of the metaldehyde are applied in the autumn (up to 210 g ha^{-1} active substance from a permitted maximum total of 700 g ha^{-1} active substance per calendar year) during August–December (MSG, 2020), compared to applications made to protect crops in the spring and summer. However, several exceptions were observed, for example in February–March 2013 and 2017, when metaldehyde applications to protect spring crops commenced and wet antecedent soil moisture conditions caused an increase in surface runoff, metaldehyde concentrations were in the range 0.03–0.1 µg L^{-1}.

Compared to the upper catchment reaches, higher fluxes of metaldehyde were identified in the mid-section and lower part of the Colne catchment due to higher stream discharge, particularly during the application period September–December when flowing field drains provide greater hydrological connectivity. Streamflow at site REG3 receives metaldehyde delivered to the river network from upstream, resulting in an elevated flux of the molluscicide, particularly during wet years such as 2012. The peak concentration of 6.78 µg L^{-1} at site REG3 in 2012 was the highest recorded in the Colne catchment in the period 2008–2018 (Figure 4.2, Table 4.1).

This finding compares with Lu et al. (2017) who reported increased metaldehyde concentrations of up to 1.6 µg L^{-1} recorded at several sites along the River Thames under high flow conditions in 2012. Lu et al. (2017) suggested that in years such as 2012, when a warm winter was followed by wet summer and autumn months, farmers tend to apply metaldehyde at maximum allowable rates to control slug populations. In this study, median and maximum concentrations of metaldehyde (up to 0.04 µg L^{-1}and 6.78 µg L^{-1}, respectively, in 2012) recorded at monitoring point REG3 at the bottom of the Colne catchment were consistently the highest in comparison with levels recorded at other monitoring points during the period 2008–2018. A peak concentration of 6.78 µg L^{-1} at point REG3 in 2012 was the highest concentration recorded in the Colne catchment over the period 2008–2018 (Figure 4.2, Table 4.1).

Metaldehyde losses to surface water were similar to the values reported for other pesticides, varying between 0.01% and 0.5% of application amounts in studies by Brown et al. (1995), Kreuger et al. (1998) and Rabiet et al. (2010). Pesticide concentrations were generally higher under high flow conditions during the application period and following months (Rabiet et al., 2010, Perez et al., 2017). The highest percentile of samples above 0.1 µg L^{-1} (33% and 34% in 2012 and 2014, respectively) corresponded with high values of annual precipitation and average discharge recorded in 2012 and 2014 (Figures 4.8, 4.11).

Increased concentrations of metaldehyde were observed in the smaller sub-catchments, for example in the Stambourne and Toppesfield Brooks (C1, C3). In these areas, horticultural land use, the relatively small size of the sub-catchments and the lack of metaldehyde dilution, compared to the river Colne, make these areas especially responsive to changes in metaldehyde applications.

In the Ardleigh catchment, metaldehyde concentrations in the Western Salary Brook tended to be higher compared to the Northern Salary Brook sub-catchment, which has a larger percentage of grassland. However, elevated concentrations of metaldehyde during September–December in both sub-catchments, including the years of the Slug It Out trial (from 2015 onward), suggest an agricultural source of the pollutant. Although it is difficult to identify the precise location where metaldehyde loss occurs, the higher risk area within the catchment is the Western Salary Brook sub-catchment based on higher metaldehyde levels in comparison to the Eastern Salary Brook sub-catchment. These findings suggest that metaldehyde originates from either metaldehyde applications on agricultural land within the Ardleigh catchment, and/or from farmed areas within close proximity to the catchment. An additional source of metaldehyde could also be associated with equipment which might have retained metaldehyde product from previous use outside the Ardleigh catchment.

On the other hand, in 2019 and 2020, the range in metaldehyde concentrations at REG1 and REG2 were the lowest on record, yet an increased metaldehyde concentration range and a number of EU DWD exceedances were recorded at REG3. This observation coincided with changes in metaldehyde use policy, when in December 2018 DEFRA first announced metaldehyde outdoor use withdrawal from 2020 (DEFRA, 2018). This decision was overturned in 2019 and reinstated in September 2020. The uncertainty around metaldehyde use policy and changes in policy in 2019–2020 are factors that may have influenced farmers within the Colne catchment to opt for use of their existing metaldehyde stock, making this molluscicide a slug control of choice. A contrast in metaldehyde concentrations recorded in the Ardleigh and Colne catchments in the period 2019-2020 highlights that shifts in farmer behaviour takes time to achieve.

4.5.2 Relationship between metaldehyde concentrations, hydrological regime and application rates

The results indicate that metaldehyde concentration peaks were detected during metaldehyde application periods in the autumn and winter periods. These months coincide with increased precipitation and stream discharge, and highest peaks in metaldehyde levels were often, but not always, associated with periods of wet weather. Precipitation events following pesticide application play an important role in pesticide transport and loss to the stream network, and peaks in pesticide concentrations, including metaldehyde, are associated with periods of high flow and periods of increased precipitation (Tediosi et al., 2012; Bloodworth et al., 2014).

Additionally, duration, frequency and amount of precipitation control runoff generation, amount and rate (Holvoet et al., 2007). Increased frequency and larger, high-intensity precipitation events are likely to cause larger amounts of pesticides being transported to watercourses from land (Banks et al., 2005; Sandin et al., 2018) in the autumn and winter when soils are often at or near field capacity. When soils with low permeability are subject to seasonal waterlogging, such as soils of the Tendring and Wix soil associations in the lower part of the Colne and Ardleigh catchments (CSAI, 2019) that are developed on silt, silty and sandy clay superficial deposits (BGS, 2019), it is more likely that pesticides could be mobilised via sediment runoff and also be transported via runoff in dissolved form. Surface and subsurface runoff in field drainage is likely to be a predominant mode of metaldehyde transport in the Colne catchment due to the physical characteristics of the soil and sub-soil.

Similarly, Castle et al. (2018) reported elevated metaldehyde concentrations following intensive precipitation events in early June 2016 in the River Dee catchment, North West

England, and suggested that a spike in metaldehyde was caused by a possible use of metaldehyde in the summer growing season or from the washout of residual molluscicide in the soil. A further factor in metaldehyde transport is overspreading due to poor application techniques that can lead to the risk of residual pesticide loss during precipitation events.

In the study by Asfaw et al. (2018), when metaldehyde concentrations were monitored and compared with high-resolution precipitation event data, short-lived metaldehyde peaks occurred with a duration of 12–48 hours. In this study, peaks in metaldehyde concentration occurred up to 5–7 days following high precipitation events (daily precipitation $\geq$10 mm), which indicates a relatively short time period for the pollutant to reach the stream network.

In this study, the regulatory limit exceedances of metaldehyde concentrations were associated with a series of precipitation events and were rarely observed to occur outside of application periods. These results suggest that increased precipitation and streamflow outside the typical metaldehyde application periods would not lead to frequent metaldehyde concentration exceedances of the EU DWD limit (0.1 μg L^{-1}). Metaldehyde concentrations above the regulatory standard were more likely to occur when metaldehyde application coincided with precipitation events, as happened in 2012 when maximum concentrations and fluxes of metaldehyde in stream water were observed.

Frequent and prolonged precipitation events in the summer, as well as mild and wet conditions in the autumn and winter in England in 2012 promoted the increased application of metaldehyde under these conditions (Bloodworth et al., 2014; Lu et al., 2017). Metaldehyde concentrations of up to 1.5 μg L^{-1} were recorded in September 2012 in the River Thames catchment, when the maximum application rate should have been reduced to 33 g ha^{-1} a^{-1} to meet the drinking water standard limit, according to metaldehyde transport modelling conducted by Lu et al. (2017). Lu et al. (2017) concluded that precipitation coupled with application rates and soil hydraulic properties are the key factors controlling metaldehyde presence in streams (Lu et al., 2017). Similarly, Guo et al. (2004) found that pesticide use and precipitation amount were the two main factors controlling pesticide transport to surface water when regression analyses were undertaken for other pesticides (R^2 = 0.9 at the single basin scale).

Furthermore, Kreuger and Tornqvist (1998) established that the amount of pesticides applied to land was the most important predictor of pesticide fluxes and concentrations in stream water, explaining up to 85% of pesticide concentration variability in their multiple regression model. In this study, although precipitation and flow are the main factors controlling metaldehyde concentrations and flux, metaldehyde application amount was not a significant variable predicting metaldehyde levels in surface water. This could be due to several factors, including the sample size, difference in physio-chemical properties of pesticides, and the time period considered. For example, Kreuger and Tornqvist (1998) included between 16 and 21 pesticides in their analysis, where a separate regression model was used to evaluate the relationship between variables in individual years during the period May–September. The linear stepwise regression in the current study included a reduced sample size of variables, considered one pesticide, and compared annual values of variables, including the application rate.

In this study, low metaldehyde concentrations in a similar concentration range (0.01–0.03 $\mu g\ L^{-1}$) were recorded in 2009–2011 and during 2017–2018. A lower intensity hydrological regime was prevalent during these periods, particularly during the metaldehyde application season. Relatively dry weather conditions minimised slug population rates, reducing the inherent need for larger amounts of metaldehyde application to agricultural land. Furthermore, statutory requirements of an application limit of 700 $g\ a^{-1}$ and a 6-metre no-application buffer adjacent to a watercourse (EA, 2016), as well as metaldehyde application guidelines of the Metaldehyde Stewardship Group (for example, a maximum application rate of 210 g active substance ha^{-1} during August–December; MSG, 2020), were beneficial for controlling metaldehyde runoff from agriculture during these dry periods in the Colne catchment.

Spatio-temporal trends of metaldehyde levels in watercourses observed in this and other studies (Kay and Grayson, 2014; Lu et al., 2017; Asfaw et al., 2018; Castle et al., 2018; Castle et al., 2019) suggest that surface and subsurface runoff-driven transport of metaldehyde serves as a major pathway in explaining the presence of metaldehyde in surface water. Hydrological conditions of high intensity during and following metaldehyde application coincide with metaldehyde concentration spikes. At the same time, wet weather conditions during months associated with high flow (up to 18 $m^3\ s^{-1}$) and periods of increased precipitation ($\geq$10 mm day^{-1}) with no application of metaldehyde and metaldehyde application in spring and summer were not connected with an increase in metaldehyde concentrations >0.03 μg L^{-1}. These results suggest that metaldehyde at concentration levels above the EU DWD limit are short-lived in the aquatic environment.

Although elevated levels of metaldehyde have a seasonal nature and tend to occur in the autumn and winter seasons, metaldehyde is continuously present in streams at concentrations that are an order of magnitude lower than the EU DWD limit of 0.1 μg L^{-1}. The presence of metaldehyde in the stream network at background concentrations (0.01–0.03 μg L^{-1}) is likely to be associated with applications of the molluscicide during August–December and February–June, causing the pollutant to be present in the aquatic environment all year around. In addition, due to its physico-chemical properties (including its relatively high solubility and low sorption potential), metaldehyde legacy sources (e.g. in stream sediment and soil profiles) and groundwater recharge are potential contributing factors active during periods of low hydrological intensity and low/no application.

Collectively, the findings of this study suggest that metaldehyde concentrations in aquatic systems are likely to be below the EU DWD standard of 0.1 μg L^{-1} in areas with catchment characteristics and farming practices similar to the study area (East of England) following withdrawal of metaldehyde for outdoor use applied in the UK in March 2022. The remaining pool of metaldehyde residues from historic applications in soil profiles is likely to be degraded by soil microbial communities over time due to the high biodegradation potential of this chemical (Balashova et al., 2020).

4.6 Conclusions

This study is the first to examine long-term temporal trends of metaldehyde concentrations in surface water in a semi-agricultural catchment at both catchment and sub-catchment scales. Metaldehyde concentration and flux data for a ten-year period (2008–2018) were analysed and compared with hydrological parameters (streamflow and precipitation). Although metaldehyde levels varied on an annual basis, there were seasonal commonalities in metaldehyde presence in surface waters.

In each year, metaldehyde concentration peaks above the EU DWD limit (0.1 μg L^{-1}) occurred during September–December and coincided with periods of metaldehyde application and the onset of autumn precipitation and increased surface/subsurface runoff. An increase in metaldehyde concentrations were ubiquitously associated with metaldehyde application periods. The EU DWD limit exceedances of metaldehyde concentration were considerably lower during the application periods in 2009–2011 and 2017–2018 years, when hydrological conditions of lower intensity were prevalent, particularly in the autumn and winter months. The results of this study indicate the significance of the coincidence of the hydrological regime during periods of metaldehyde application, coupled with the rates of molluscicide applied, on metaldehyde concentrations in stream water. Metaldehyde levels varied spatially, with higher concentrations observed in the small headwater sub-catchments with predominantly agricultural land use, as well as at the regulatory point at the bottom of the Colne catchment.

Metaldehyde concentrations in stream water during months when metaldehyde is not normally applied to agricultural land in the East of England (January and July) and during application times to protect spring and summer crops (February–June) were in general an order of magnitude lower than the EU DWD limit of 0.1 $\mu g\ L^{-1}$. Periods of high intensity hydrological conditions during months with no metaldehyde applications were not associated with an increase in metaldehyde concentrations above 0.1 $\mu g\ L^{-1}$.

It is concluded that the presence of metaldehyde in stream runoff observed in the Colne catchment suggests that metaldehyde at concentrations above the EU DWD limit is short-lived in the aquatic environment. Therefore, the use of on-line monitoring systems, such as GC-MS on-line system (Castle et al., 2019) available for measuring metaldehyde can provide useful insight into monitoring for point sources. Furthermore, metaldehyde residues in soil and aquatic sediment mobilised during high flow conditions do not pose a long-term concern for meeting the EU DWD water quality standard. Collectively, the results of this study indicate that metaldehyde levels in surface water are likely to be consistently below the EU DWD limit once the withdrawal of metaldehyde for outdoor use is enforced in the UK in March 2022.

Chapter 5 Metaldehyde transport processes at a sub-catchment scale

5.1 Chapter summary

Building upon the findings presented in previous chapters, the motivation of Chapter 5 is to further advance understanding of metaldehyde transport within the Ardleigh catchment at a finer, sub-catchment scale during a 14-month period (January 2019–February 2020). Spatio-temporal variability in physico-chemical water quality parameters and nutrient concentrations was also examined. For the first time, a mass budget model of metaldehyde for a reservoir was applied and the contribution of atmospheric deposition to the mass balance of metaldehyde assessed.

Spatio-temporal trends in water quality parameters were linked to land use of the catchment. Heightened nitrate-N levels were observed in predominantly arable land areas (points 1, 3), while increased P concentrations were detected at point 2 (Northern Salary Brook) with a larger grassland area. When N and P temporal variability was considered, phosphorus displayed heightened levels in the summer months, similar to nitrite-N and ammonia. Total nitrogen reached its maximum levels in the winter months.

Variability in metaldehyde concentrations and fluxes displayed the same trends as observed in the catchment in previous years of observations. A rise in metaldehyde concentrations was observed at all monitoring points, to varying extents, in the months of seasonal applications. The highest increases in metaldehyde levels (concentrations up to 0.05 $\mu g\ L^{-1}$) across the catchment were observed in the autumn months and in December. These findings reinforce the mobile nature of the pesticide, with surface and field drain runoff likely to be the predominant mode of transfer to surface waters.

The scale of individual sources of metaldehyde influx and the highest contributions to the total flux input to the Ardleigh Reservoir were from the River Colne water abstraction. The lowest influx levels were observed in the Northern Salary Brook, followed by influx from the Western Salary Brook. Atmospheric deposition followed a similar seasonal pattern to that observed in metaldehyde levels in surface water and runoff, and in certain months accounted for a higher input than surface influx from the Salary Brooks (May, August–October 2019).

Monthly values of metaldehyde mass in the reservoir ranged from 27.7 to 47.4 g. An increase in mass was associated with elevated levels of flux from individual sources. Relatively stable levels of metaldehyde total mass in the Ardleigh Reservoir could be due to the high aqueous solubility and decreased degradation rates of metaldehyde in the aquatic environment (compared to those observed in soil; see Chapter 3).

5.2 Introduction

Following the analysis of long-term and seasonal spatio-temporal trends in metaldehyde concentrations and fluxes in stream water of the River Colne and the Ardleigh catchments (Chapter 4), a separate study was conducted to further explore environmental drivers that govern metaldehyde transport at a sub-catchment scale. This fieldwork-based study investigates metaldehyde levels at a finer spatial scale over the 14-month period January 2019–February 2020. An *in situ* sampling campaign enabled an extension of the existing regulatory monitoring network by including additional sampling points in the upstream parts of the Salary Brooks in order to improve understanding of metaldehyde transport at the finer sub-catchment scale. In addition to a surface water pathway of metaldehyde, this study also considers metaldehyde transport via field drain runoff and atmospheric deposition of the pesticide.

The aims of the chapter are twofold: i) to assess metaldehyde transport and the role of source-mobilisation-pathway-delivery mechanisms in metaldehyde exports in surface waters of the Ardleigh catchment; and ii) to quantify and evaluate the mass budget and dynamics of metaldehyde in the Ardleigh Reservoir. To meet these aims, the following objectives were identified:

i) To explore spatio-temporal variability in metaldehyde and nutrient levels in surface waters and field drain runoff.

ii) To assess the relationship between metaldehyde concentrations, water quality parameters and climatic/terrestrial system variables.

iii) To evaluate deposition of metaldehyde within the Ardleigh catchment from the atmosphere and field drain runoff.

iv) To estimate the impact of individual sources of metaldehyde on the metaldehyde budget of the Ardleigh Reservoir.

5.3 Materials and methods

5.3.1 Study area

The study area comprises the Ardleigh catchment, southeast England. The watercourse network includes the Northern and Western Salary Brooks (sub-catchment areas are 6.5 and 7.5 km^2, respectively) that drain to the Ardleigh Reservoir (Figure 5.1). The network of monitoring points included exploratory/*in situ* and regularity sampling locations. Exploratory sites (surface water sampling) were located at two distributary channels of the Northern Salary Brook (NSB points 1, 2) and across the stretch of the Western Salary Brook (WSB points 3, 4, 5). Field drain runoff sites were situated at the upstream and downstream areas of the Western Salary Brook sub-catchment. Additionally, rainwater samples were collected from two sites: a rural area site located near the Northern Salary Brook inlet to the Ardleigh Reservoir (Figure 5.1) and at an urban area site (8.5 km from the Ardleigh site at 216 degrees, south of Colchester, UK National Grid reference TL994222).

The regulatory monitoring network included sampling sites at the outlet of the Northern and Western Salary Brooks (REG1, REG2) and at the Ardleigh Reservoir (Draw off tower, Figure 5.1). The regulatory sampling site adjacent to the study area (point REG3) is at the Colne catchment outlet (TM007255), 8 km south of the Ardleigh catchment, where surface water is abstracted and transferred by pumping to the Ardleigh Reservoir.

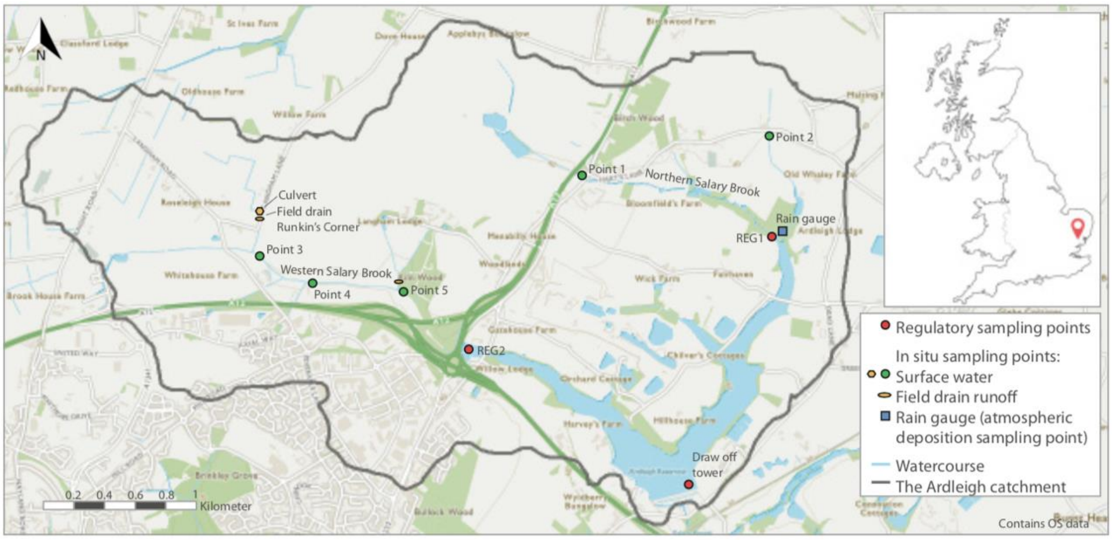


Figure 5. 1. Geographical location of the study site. The sampling points for surface water, field drain runoff and rain gauge (atmospheric deposition sampling point) are overlaid on OS Digimap (OS Digimap, 2021).

5.3.2 Sampling and *in situ* measurements

5.3.2.1 Stream water and field drain runoff sampling

Surface water sampling took place during the period January 2019–February 2020; a 14-month duration of the field work allowed to capture typical weather conditions in the study area over a hydrological year. Non-composite samples were collected at the exploratory sampling points 1–5 (Figure 5.1) monthly during March–September 2019 and more frequently, fortnightly, in January–February 2020 and October 2020–February 2020 (months of typical metaldehyde application when average hydrological condition is associated with increased discharge and precipitation). Two sampling points (points 1 and 2) located at the Northern Salary Brook were selected to monitor metaldehyde concentrations in both tributaries of the Northern Salary Brook at its' upstream parts. The sampling point locations at the Western Salary Brook were selected to monitor metaldehyde concentrations both upstream and downstream (points 3 and 5, respectively), as well as at its middle part, where the monitoring point 4 is adjacent to the outlet of the tributary that flows from Colchester. These exploratory sampling points were complementary to the regulatory sampling points REG1 and REG2 located at the inlets to the Reservoir. Weekly sampling was conducted by Anglian Water Services at the REG1–REG3 sites and from Ardleigh Reservoir (Draw off tower, Figure 5.1).

Field drain sampling sites were identified within the catchment in June 2019, and drain runoff sampling was conducted on a fortnightly basis in November 2019–February 2020 (the period when the drains were flowing). The field drain runoff sampling sites were located in the Western Salary Brook sub-catchment; no field drains were identified within the Northern Salary Brook sub-catchment.

All water samples were collected in 500 mL, previously unused, brown plastic bottles (these were flushed with sample before being sealed) and refrigerated at 4° C within 24 h of collection. A separate set of samples was collected in pre-cleaned 300 ml bottles for further nutrient analysis in the lab; the samples were stored at -18° C. Bottles were kept in a 5% HCl acid solution 24 h prior to sample collection in the field.

5.3.2.2 Rainwater sample collection and quality control procedure

Bulk precipitation samples including dry and wet deposition were collected monthly from February 2019 to February 2020. These samples were collected in an instrument made of a funnel connected to a glass bottle via a rubber hose. To prevent sample contamination, the funnel was located 180 cm above the ground level, and the bottle was stored in a stainless-steel container. The amount of precipitation was recorded in a plastic rain gauge tube to calculate metaldehyde atmospheric flux. Following rainwater sample collection, the equipment was rinsed with Type 1 ultrapure water (Merck Milli-Q Ultrapure Water Purification System).

To assess if metaldehyde was present in the equipment and to establish whether dry atmospheric deposition of metaldehyde occurred, a quality control procedure was implemented from September to November 2020. An ultrapure water sample (500 ml) was deposited in rainwater collectors and left for a period of one month. Instruments were situated under a 2 x 2 m waterproof gazebo with side panels to eliminate any wet deposition. The water samples were collected at the end of each month and refrigerated at 4° C prior to despatch for metaldehyde detection analysis within 24 h of collection.

5.3.3 Hydrological and climatic data

Streamflow (discharge) data used in this study were obtained from the Environment Agency via a Freedom of Information request. Streamflow was recorded at the gauging station 37005 at the bottom of the Colne Catchment (TL962261). Climatic data were recorded at the Agrii weather station located in the Ardleigh catchment (TM022306). These data included daily records of precipitation, air temperature and humidity, soil temperature and soil moisture. Data sets were collected for the period January 2019–February 2020.

5.3.4 Water quality parameters and measurement methods

5.3.4.1 Water quality characteristics measured *in situ*

Along with the water sampling at the *in situ* sampling locations (points 1–5), electrical conductivity, water temperature, pH and dissolved oxygen were measured during the period January 2019–February 2020. The following instruments were used to conduct measurements: Eutech Instruments Cyberscan CON 11 Conductivity/TDS/C Meter, HANNA HI 9025 pH meter and HANNA HI 9146 Microprocessor Dissolved Oxygen meter. Each instrument was calibrated in line with the manufacturers' instructions prior to the first measurement. Probes were rinsed with Milli-Q water following completion of measurements at each sampling point.

5.3.4.2 Laboratory analyses

Surface water and field drain runoff samples collected at *in situ* exploratory points (Figure 5.1) were analysed for the following nutrients: nitrite (NO_2^-), total nitrogen (the sum of nitrite and nitrate: $NO_2^- + NO_3^-$), phosphate (PO_4^{3-}), total phosphorus (TP) and ammonia (NH_3^+-N). Water samples (n = 134) were defrosted and stored at 4° C prior to analysis. Nitrite, total nitrogen, phosphate and ammonia were analysed simultaneously using the Skalar SAN ++ Continuous Flow Analyser (CFA). The CFA technique is based on automated spectrophotometry by measuring colours produced as a result of the chemical reaction of target analytes and reagents. Certified Reference Material standards (CRMs, n = 3 run for each analyte) were purchased from Sigma-Aldrich at the following certified values: 7050, 1990, 1460 and 14,300 $\mu g\ L^{-1}$ for nitrate, nitrite, phosphate and ammonia, respectively. Deionised distilled water was used for blank samples. To produce analytical standards and bring samples within the instrument and sample range, CRM standards were diluted with deionised distilled water at the 1:100 (nitrate and ammonium) and 1:20 (nitrite and phosphate) ratios. The limits of detection of the methods were equal to 1 µg L^{-1} (phosphate) and 2 µg L^{-1} (nitrate, nitrite and ammonia).

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to analyse total phosphorus in water samples. A blank sample and analyte standards (n = 7) within the range 50–1000 µg L^{-1} were used for this analytical procedure. Samples and standards reacted with nitric acid (1 ml) were run with a rhodium internal standard. The limit of detection of the method was equal to 1.96 µg L^{-1}. All standards for the laboratory analysis were prepared by serial dilution of analytes in deionised distilled water.

The determination of metaldehyde concentration in water samples was conducted by Anglian Water's laboratory services within 7 days of sample collection using liquid chromatography with mass spectrometric detection in line with the Drinking Water Testing Specification method No CL/TO/046 (UKAS, 2019).

5.3.5 Calculations and statistical data analyses

5.3.5.1 Modelled streamflow

The Northern and Western Salary Brooks are ungauged watercourses; therefore, daily streamflow estimation at these sites was required. Daily streamflow was estimated using the Area-Ratio based method, as described by Shu and Ouarda (2012):

$$Qy = \frac{Ay}{Ax} Qx \qquad \text{equation (1)}$$

where Q_y is an estimated streamflow at an ungauged site, Q_x is recorded streamflow at a gauged site, A_y and A_x are the drainage areas of the ungauged and gauged areas, respectively.

5.3.5.2 Metaldehyde fluxes in stream water

The monthly load (ML, flux) of metaldehyde was calculated using the approach described by Rabiet et al. (2010):

$ML = Q\,C_i\,t_i$ equation (2)

where Q is the average monthly streamflow during the period t_i (L s^{-1}), C_i is the average metaldehyde concentration in water samples collected within a month (µg L^{-1}), and t_i is the time period considered (seconds i.e. 60 x 60 x 24 x number of days in the month, i stands for the month).

5.3.5.3 Concentrations and fluxes of metaldehyde in rainwater

The monthly concentrations (C_i) of metaldehyde were representative of metaldehyde concentrations in a rainwater sample collected each month (µg L^{-1}) over a unit area *i.*

The monthly atmospheric deposition fluxes of metaldehyde (wet and dry deposition) were calculated using the following equation:

$F_i = C_i\,R_i$ equation (3)

where F_i is the monthly atmospheric deposition flux of metaldehyde over over a unit area i in a given month (µg m^{-2}), C_i is metaldehyde concentration in a rainwater sample collected each month (µg L^{-1}) and R_i is the amount of monthly precipitation (mm). Atmospheric deposition flux was calculated for use in the metaldehyde mass budget in the Ardleigh Reservoir by multiplying the surface area of the reservoir and monthly atmospheric deposition flux of metaldehyde.

5.3.5.4 Mass budget

The monthly net load of metaldehyde to the Ardleigh Reservoir for the January–December 2019 period was estimated using the following equation:

$M_i = \Sigma(M_{input} - M_{output})$ equation (4)

where M_i is a net load of metaldehyde to the Ardleigh Reservoir in a given month;

M_{input} is the mass inflow from the following sources: metaldehyde flux in surface water abstracted from the River Colne, Northern Salary Brook and Western Salary Brook and atmospheric deposition. M_{output} (mass outflow) is metaldehyde flux in surface water transferred from Ardleigh Reservoir to the water supply network calculated as the product of the monthly average metaldehyde concentration in the reservoir and the monthly volume of water pumped from the reservoir.

The mass of metaldehyde retained in Ardleigh Reservoir ($M_{retained}$) was calculated as the product of metaldehyde concentration in the reservoir and the volume of water in the reservoir in each month. Monthly differences in metaldehyde mass content in the Ardleigh Reservoir ($\Delta M_{retained}$) were also established. The mass budget model was based on the concepts of an earlier nutrient budget study of the Ardleigh Reservoir (Redshaw et al., 1988).

5.3.5.5 Statistical analyses

All statistical analyses were completed in JASP 14.1 software. Descriptive statistics were used to summarise the key characteristics of the data variables considered in this study. These included mean, median, standard deviation, range, minimum and maximum values of the sample and 25th, 50th and 75th percentiles.

To compare the differences between metaldehyde concentrations at the exploratory sampling points, the Kruskal-Wallis H test (one-way ANOVA on ranks), a non-parametric test, was selected due to the non-normal distribution of the samples. A *post-hoc* Dunn's Multiple Comparison test was then applied to examine the pairwise comparisons of mean metaldehyde concentrations at the sampling sites.

Spearman and Kendall correlation tests and multivariate stepwise regression analysis were completed in order to assess the relationship between metaldehyde concentrations, water quality parameters, hydrological and climatic/terrestrial system variables. A Student's t-test was used to compare the degree of difference between the means of metaldehyde concentration in rainwater collected at the urban and rural sites.

5.4 Results

5.4.1 Hydrological conditions

Daily precipitation and modelled streamflow records over the period January 2019–February 2020 were observed (Figure 5.2, Table 5.1). Lowest mean precipitation values within the 0.3–1.2 mm range were recorded from January to May 2019 with a maximum of 9.0 mm d^{-1} in April. Mean daily precipitation values ranged between 1.5 and 2.2 mm in the period June–November 2019, with up to 18.2 mm d^{-1} in August. The highest variability (interquartile range here and further in text) in precipitation and mean/median values levels was observed between December 2019 and February 2020; mean daily precipitation values ranged between 1.2 and 3.8 mm during these three months (Figure 5.2A). Maximum daily reprecipitation recorded in the period January 2019–February 2020 was equal to 27 mm in June 2019 (Table 5.1).

When descriptive statistics of modelled streamflow in the Northern and Western Salary Brooks were analysed (Figure 5.2A, B, Table 5.1), mean streamflow varied between 0.01 and 0.02 m^3 s^{-1} (NSB) and 0.02 and 0.03 m^3 s^{-1} (WSB) during the period January–March 2019. Lowest variability and mean streamflow values were observed between April and October 2019 with mean streamflow within the range 0.005–0.01 m^3 s^{-1} (NSB) and 0.006–0.01 m^3 s^{-1} (WSB). Similar to the precipitation records, highest variability and mean values of modelled streamflow were registered in December 2020 (0.10 and 0.12 m^3 s^{-1}, NSB and WSB, respectively)). Mean streamflow in the Salary Brooks during the January-February 2020 period was also considerably higher than in January and February 2019 (up to 0.07 m^3 s^{-1} vs. 0.03 m^3 s^{-1}) (Figure 5.2 A, B). Maximum modelled streamflow during the period of the fieldwork campaign was equal to 0.41 and 0.48 m^3 s^{-1} in the Northern and Western Salary Brooks, respectively (Table 5.1).

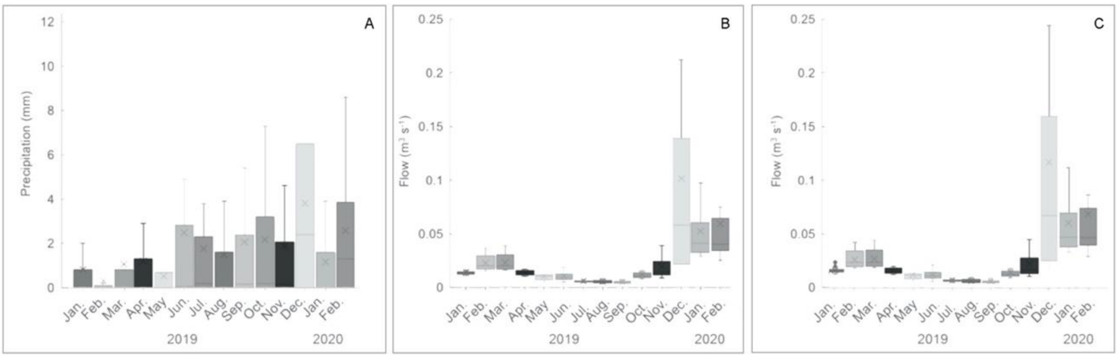


Figure 5. 2. Monthly variability in precipitation (A) and modelled streamflow in the Northern Salary Brook (B) and Western Salary Brook (C) in January 2019–February 2020, the period of the fieldwork campaign. Crosses and lines in each box indicate mean and median values, respectively; whiskers display one standard deviation of the sample range.

Table 5. 1 Descriptive statistics of daily precipitation and modelled streamflow data during the period January 2019–February 2020.

	Precipitation (mm d^{-1})	Streamflow, Northern Salary Brook (m^3 s^{-1})	Streamflow, Western Salary Brook (m^3 s^{-1})
Sample size	425	425	425
Mean	1.67	0.03	0.03
Median	0.00	0.01	0.02
Std. deviation	3.31	0.04	0.05
Range	27.0	0.41	0.47
Minimum	0.00	0.004	0.004
Maximum	27.0	0.41	0.48
25th percentile	0.00	0.01	0.01
50th percentile	0.00	0.01	0.02
75th percentile	2.00	0.03	0.03

5.4.2 Spatio-temporal variability in chemical parameters of water quality and nutrients across the Ardleigh catchment

5.4.2.1 Spatial trends

Mean and median pH values varied within the ranges 7.13–7.24 and 7.23–7.29 across monitoring points 1–5 with the highest level of variability observed at point 1 (NSB) and point 5 (WSB). Minimum and maximum pH values recorded in the watercourse network were equal to 6.31 (point 5) and 7.71 (point 1) (Figure 5.3A).

Mean electrical conductivity varied within the range 619–702 µS cm^{-1} across the monitoring points and median values ranged from 622 to 680 µS cm^{-1}. Increased mean values were observed at point 1 (NSB) and at the downstream parts of WSB (points 4 and 5). The highest variability in electrical conductivity values was recorded at points 4 and 5, where the minimum and maximum values were observed (246 and 946 µS cm^{-1}, respectively) (Figure 5.3B).

Mean dissolved oxygen values ranged between 72.5 and 80.5% within the watercourse network, and median values between 71.3–80.0%. Lower mean dissolved oxygen values were observed in the Northern Salary Brook (67.4–72.5%), compared to values recorded in the Western Salary Brook (77.5–80.5%). The lowest mean value (67.4%) and the highest level of variability in dissolved oxygen values (min.= 43.6%, max. = 88.1%) were observed at point 2 (Northern Salary Brook) (Figure 5.3C).

Mean values of water temperature were within the range 10.1–11.0 °C across the watercourse network, with median values ranging from 9.3 to 10.1 °C. Minimum and maximum values of temperature were recorded at points 5 and 2: 4.3 °C and 18.3 °C, respectively (Figure 5.3D).

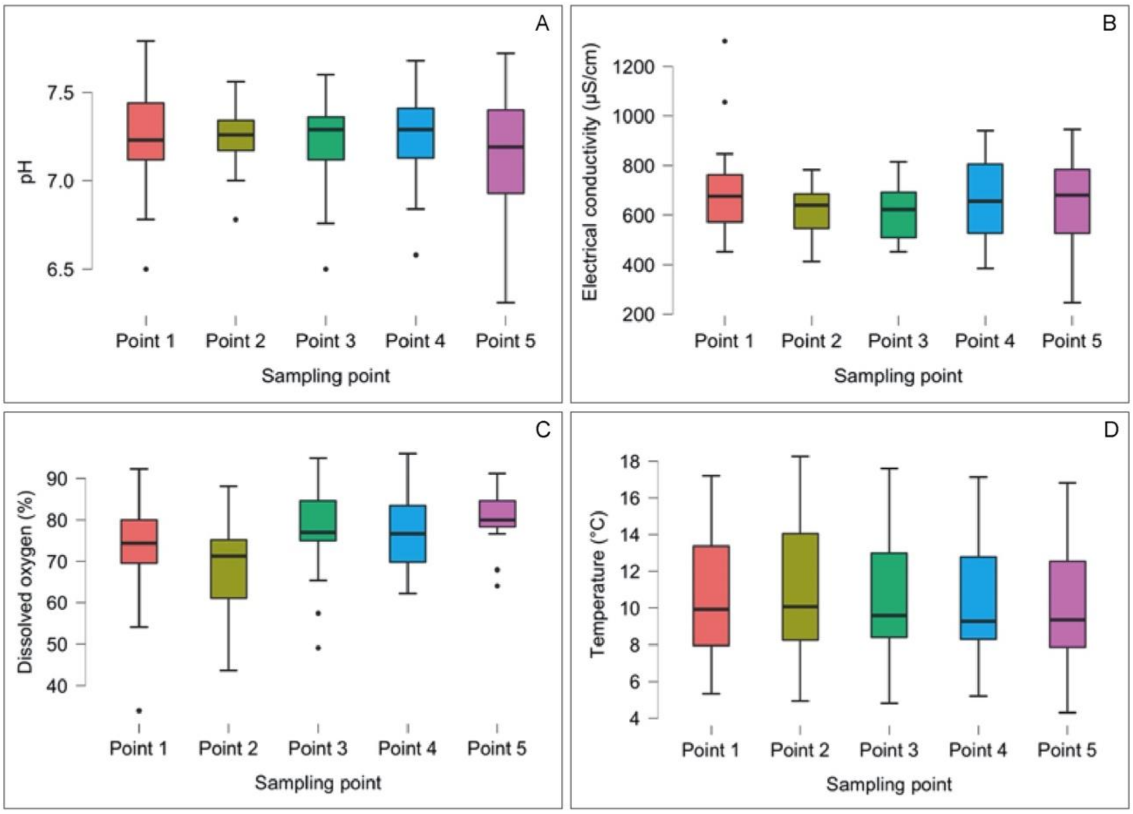


Figure 5. 3. Spatial variability in pH (A), electrical conductivity (µS cm^{-1}) (B), dissolved oxygen (%) (C) and temperature of surface water (°C) (D) in the Northern Salary Brook (points 1, 2) and Western Salary Brook (points 1–3) during the period January 2019–February 2020. Lines within each box represent median values, whiskers indicate minimum and maximum values. Circles represent outliers that are not included in the range data.

When spatial trends in nutrient concentrations in surface water were assessed across the catchment, increased mean concentrations were observed in the Northern Salary Brook (points 1, 2) compared to mean concentrations of nutrients in the Western Salary Brook (Figure 5.4). Particularly noticeable is the increase in mean values and variability of nutrient levels observed at point 2 (NSB) when phosphate, total phosphorus, nitrite and ammonia concentrations are examined across all monitoring points (Figure 5.4). Mean concentrations of these analytes in surface water collected at point 2 equalled 229, 494, 81.6 and 536 µg L^{-1}, respectively. Maximum concentrations of these nutrients were recorded in point 2 as well. To a lesser extent, this trend was observed in nitrate and total nitrogen levels at point 1 located in the Northern Salary Brook (mean concentrations of nitrate and total nitrogen equalled 6.8 mg L^{-1}) (Figure 5.4).

Concentrations of nutrients varied within the sub-catchments. In the Northern Salary Brook, phosphate, total phosphorus, nitrite and ammonia concentrations were higher at point 2 compared to concentrations of these nutrients at point 1. In the Western Salary Brook, higher mean values of total phosphorus (266 µg L^{-1}), nitrate (4.9 mg L^{-1}) and total oxidised nitrogen (4.9 mg L^{-1}) concentrations were observed at point 3 (upstream part of Western Salary Brook, Figure 5.4 B, D, F). Mean concentrations of phosphate (122 µg L^{-1}), nitrite (36.2 µg L^{-1}) and ammonia (243 µg L^{-1}), on the other hand, were higher in the medium and downstream parts of the Western Salary Brook (points 4 and 5, respectively) (5.4 A, C, E).

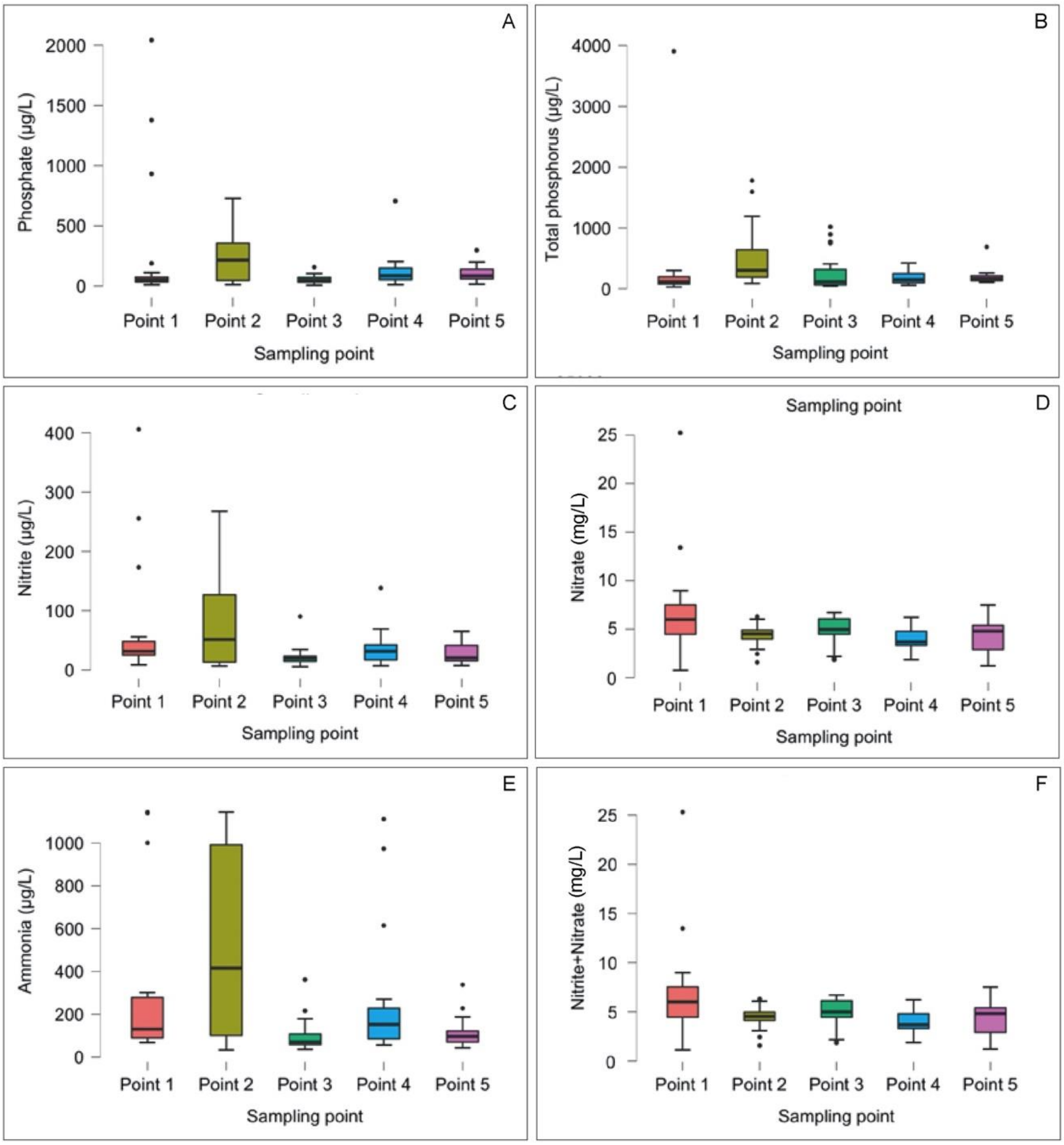


Figure 5. 4. Spatial variability in nutrient concentrations (phosphate (A), total phosphorus (B), nitrite (C), nitrate (D), ammonia (E) and total oxidised nitrogen (nitrate + nitrite) (F)) in surface waters in the Northern Salary Brook (points 1, 2) and Western Salary Brook (points 1–3) during January 2019–February 2020. Lines within each box represent median values, whiskers indicate minimum and maximum values. Circles represent outliers that are not included in the range data.

5.4.2.2 Temporal trends

Seasonal differences in values of the basic water quality parameters and nutrient concentrations were observed across the catchment (Figures 5.5 and 5.6). Highest mean (7.44), median (7.53) and maximum values (7.79) of pH were observed in the spring months (March-May). Mean pH values were lower in the summer period (7.22), reaching the lowest levels in winter months (7.11). Mean values of electrical conductivity were higher in the spring (714 µS cm^{-1}) and summer (717 µS cm^{-1}) periods compared to mean values in the autumn and winter months (592 and 638, respectively). Minimum values of pH (6.31) and electrical conductivity (409 µS cm^{-1}) were recorded during the winter period of observations (Figure 5.5).

Mean values of dissolved oxygen were lower in the autumn and summer months (71.3 and 68.0%) compared to values in the spring and winter periods (74.9, 81.5%). Lowest values of dissolved oxygen were recorded in the summer (33.9%) and maximum values in the winter (96.0%). Mean values of water temperature were lowest in the winter months (7.7 ºC), with highest values recorded in the summer period (16.0 ºC). Minimum and maximum values (4.30 and 18.3 °C) were measured in the winter and summer periods (Figure 5.5).

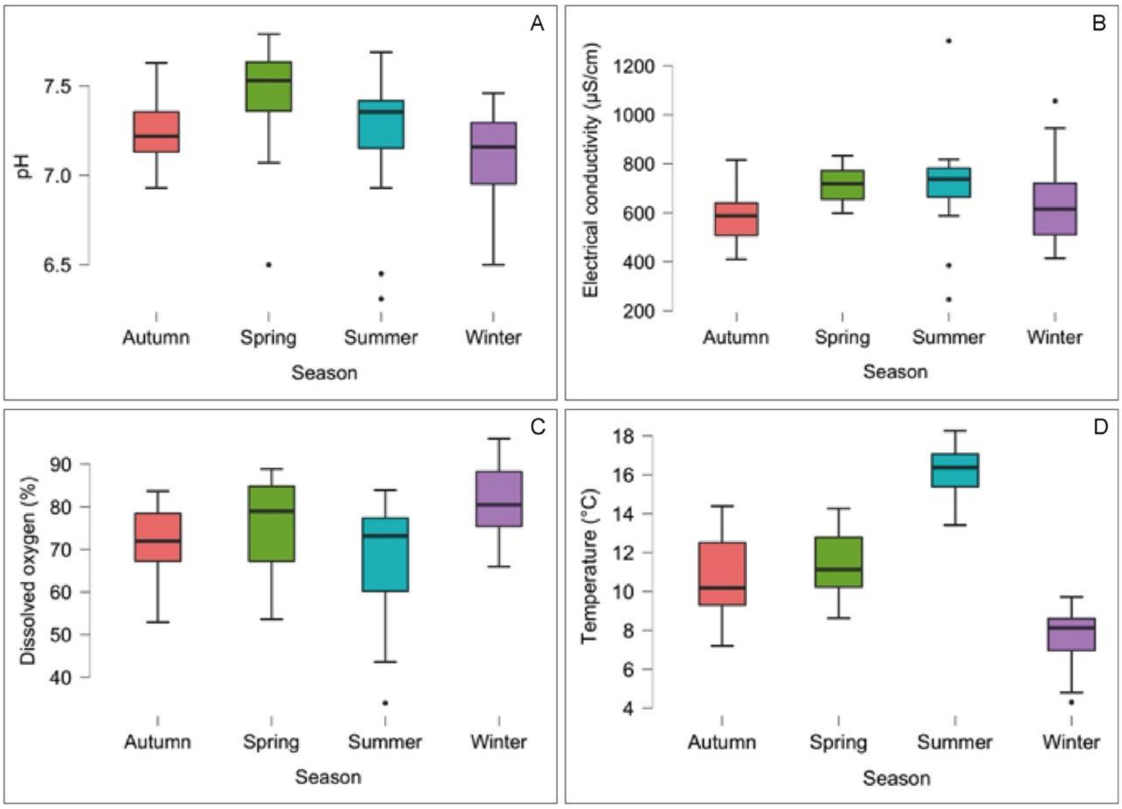


Figure 5. 5. Seasonal variability in pH (A), electrical conductivity (B), dissolved oxygen (C) and temperature of surface water (D) of surface water in the Northern and Western Salary Brooks during the period January 2019–February 2020. Lines within each box represent median values, whiskers indicate minimum and maximum values. Circles represent outliers that are not included in the range data.

When seasonal trends in nutrient concentrations were examined, increased variability (interquartile range) in phosphate, total phosphorus, nitrite and ammonia concentrations was observed during the summer period. Mean concentrations of these nutrients were at the highest level during the summer months: 347, 581, 101, 429 μg L^{-1}, respectively. Lowest variability and mean values in phosphate, total phosphorus, nitrite and ammonia concentrations were recorded during the winter months: 62.2, 162, 23.8, 166 μg L^{-1}, respectively. Minimum and maximum concentrations of these nutrients were recorded in the winter and summer periods, respectively (5.6 A, B, C, E).

Concentrations of nitrate and total nitrogen varied to a similar extent throughout the seasons; mean concentrations of nitrate and total oxidised nitrogen ranged from 3.6 and 3.7 mg L^{-1} in the summer period to 5.7 mg L^{-1} in the winter months. Minimum levels in nitrate and total nitrogen concentrations were recorded in the spring and summer periods (0.7 and 1.1 mg L^{-1}, respectively). Maximum levels (not included in the data range) were observed in the winter period (25.2 mg L^{-1} (nitrate), 25.3 mg L^{-1} (total oxidised nitrogen)) (Figure 5.6 D, F).

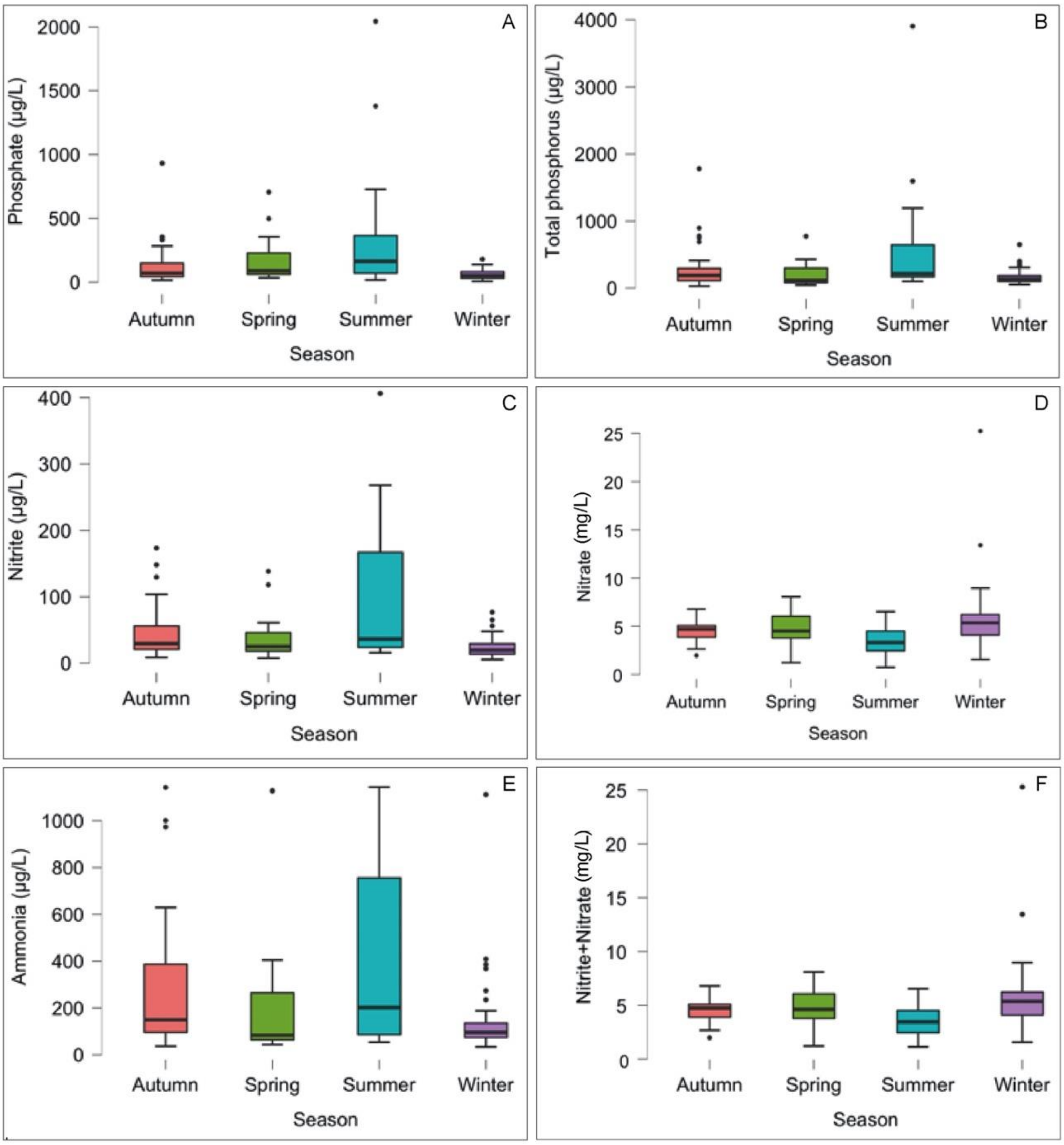


Figure 5. 6. Seasonal variability in nutrient concentrations for phosphate (A), total phosphorus (B), nitrite (C), nitrate (D), ammonia (C) and total oxidised nitrogen (nitrate + nitrite) (F) in surface water of the Northern and Western Salary Brooks during the period January 2019–February 2020. Lines within each box represent median values, whiskers indicate minimum and maximum values. Circles represent outliers that are not included in the range data.

5.4.2.3 Comparison of variability in water quality parameters of surface water and field drain runoff

Water quality parameters and concentration of nutrients in surface water and field drain runoff in the period November 2019–February 2020 were compared (Figures 5.7 and 5.8). Levels of pH and dissolved oxygen tended to be higher in surface water compared to values in field drain runoff in the upstream and downstream parts of the Western Salary Brook. The difference in values of dissolved oxygen was within 5–10%, and the difference in pH values within 0.5–1 units (Figure 5.7 A, C). Differences in electrical conductivity of surface water and field runoff were typically within 20–50 µS cm^{-1}, with higher levels in either surface water or field runoff depending on a sampling date (Figure 5.7 B). Variations in surface water and field runoff temperature were observed within the range 0.2–1°C on any given sampling date. Field drain runoff temperature values tended to be slightly higher compared to surface water temperatures (Figure 5.7 D).

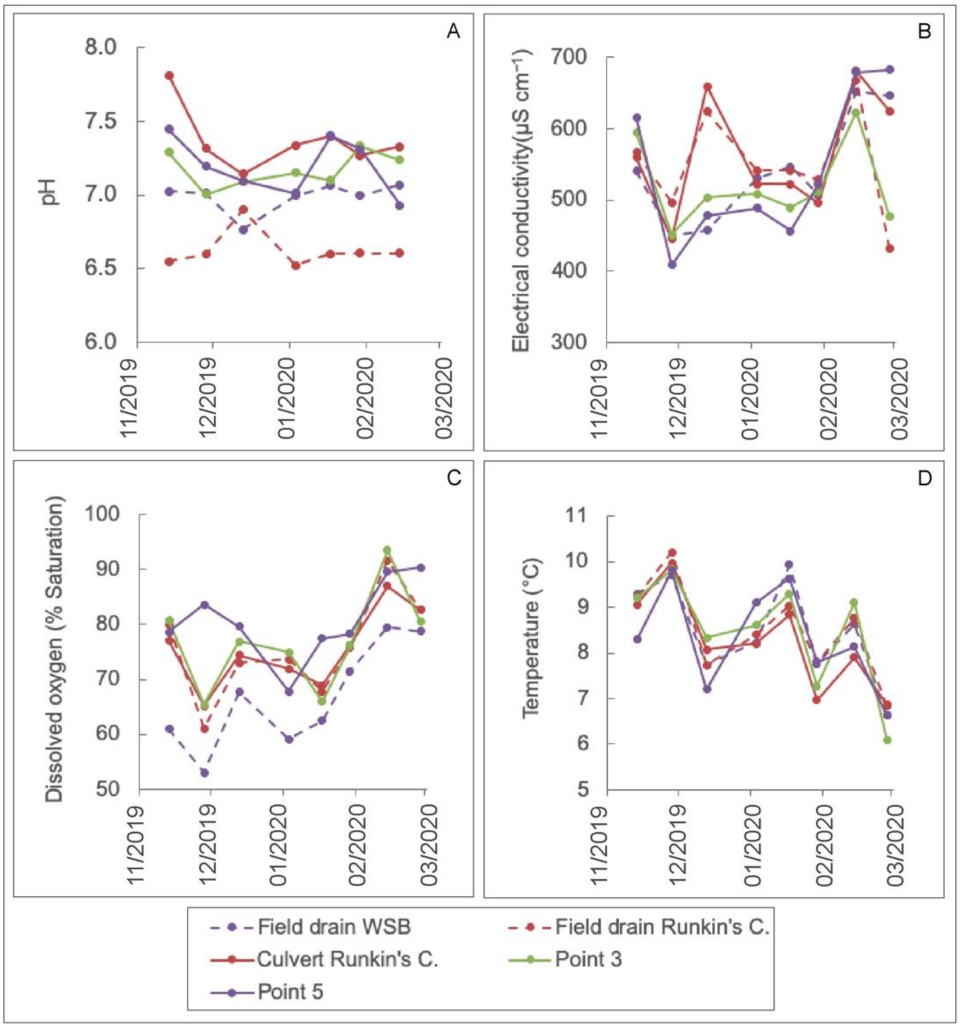


Figure 5. 7. Spatio-temporal variability in pH (A), electrical conductivity (B), dissolved oxygen (C) and temperature of surface water (D) of surface waters and field drain runoff in the Western Salary Brook sub-catchment during November 2019–February 2020.

Nutrient concentrations in surface water and field drain runoff varied spatially. Total phosphorus, nitrite and ammonia concentrations were higher in field runoff samples in comparison to concentrations in surface water upstream in the Western Salary Brook, and *vice versa* downstream (Figure 5.8 B, C, E). Nitrate and total nitrogen concentrations in surface water were elevated compared to concentrations in field runoff in the upstream part of the sub-catchment, and *vice versa* downstream (Figure 5.8 D, F). No consistent trend was observed in concentrations of phosphate in surface water and field runoff samples (Figure 5.8 A).

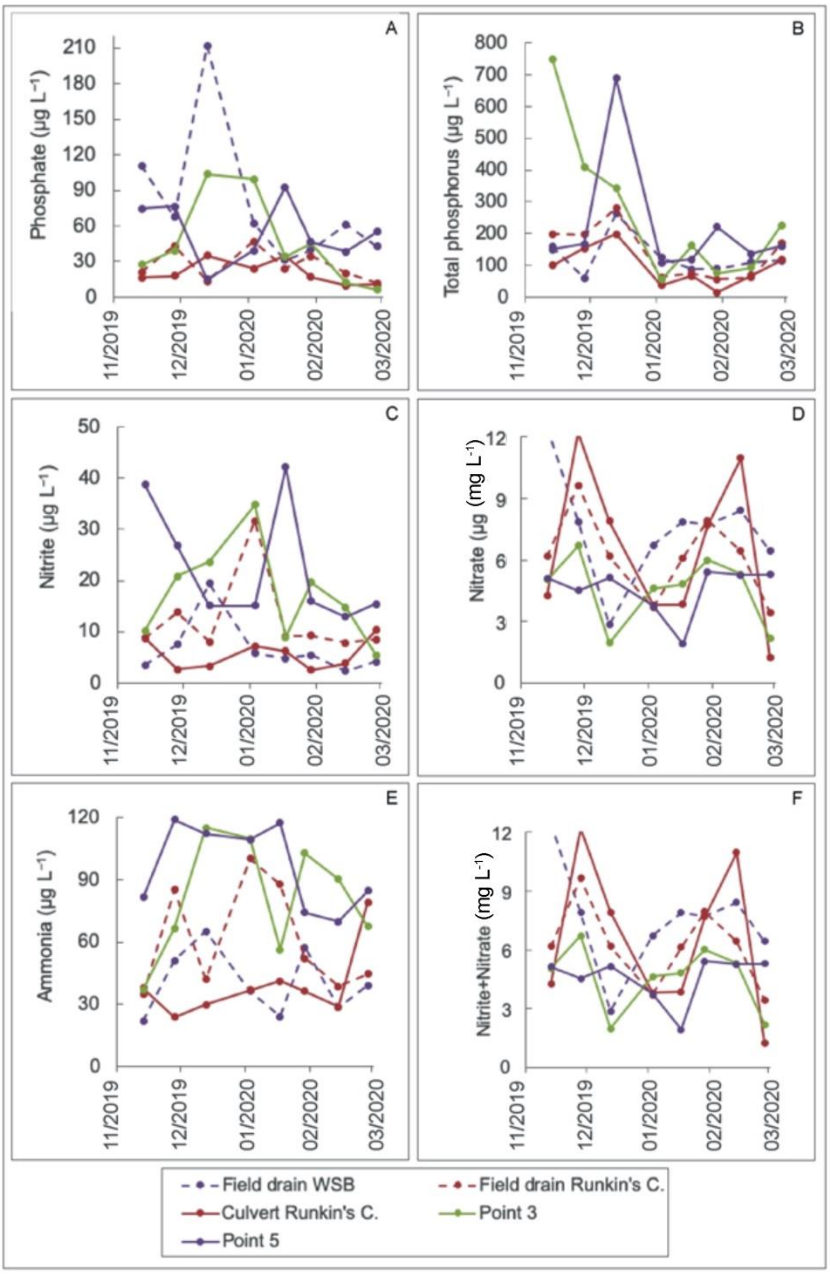


Figure 5. 8. Spatio-temporal variability in nutrient concentrations (phosphate (A), total phosphorus (B), nitrite (C), nitrate (D), ammonia (E) and total nitrogen (nitrate + nitrite) (F)) in surface waters and field drain runoff in the Western Salary Brook sub-catchment during November 2019–February 2020.

5.4.3 Relationship between metaldehyde concentrations, climatic variables and nutrients/water quality characteristics

No significant correlation between metaldehyde concentrations and water quality characteristics/nutrient concentrations was observed with the exception of the following variables: electrical conductivity, nitrate and total nitrogen concentrations. A significant ($p < 0.05$) negative relationship between metaldehyde concentration and electrical conductivity, nitrate and total nitrogen concentrations was detected in all instances. Spearman's rank correlation coefficients ranged between -0.25 and -0.27 (Table 5.2).

Table 5. 2 Results of correlation analyses showing the strength of the relationship between metaldehyde concentrations (µg L^{-1}) and water chemistry parameters: electrical conductivity (µS cm^{-1}), dissolved oxygen (%), pH, temperature (°C) and nutrients (µg L^{-1}).

Variables			p		p
		Spearman's rank correlation coefficient		Kendall's tau B correlation coefficient	
Metaldehyde (µg L^{-1})	Electrical conductivity (µS cm^{-1})	-0.27**	0.01	-0.18**	0.01
Metaldehyde (µg L^{-1})	Dissolved oxygen (%)	-0.13	0.19	-0.08	0.25
Metaldehyde (µg L^{-1})	Temperature (°C)	0.02	0.81	0.02	0.81
Metaldehyde (µg L^{-1})	pH	-0.18	0.06	-0.13	0.07
Metaldehyde (µg L^{-1})	Total phosphorus (µg L^{-1})	0.04	0.67	0.04	0.60
Metaldehyde (µg L^{-1})	Phosphate (µg L^{-1})	-0.11	0.27	-0.06	0.34
Metaldehyde (µg L^{-1})	Nitrite (µg L^{-1})	-0.06	0.52	-0.03	0.63

Metaldehyde (µg L^{-1})	Nitrate (µg L^{-1})	-0.25**	0.01	-0.17**	0.01
Metaldehyde (µg L^{-1})	Total Nitrogen (µg L^{-1})	-0.26**	0.01	-0.18**	0.01
Metaldehyde (µg L^{-1})	Ammonia (µg L^{-1})	-0.13	0.19	-0.09	0.20

* $p < .05$, ** $p < .01$

A strong negative correlation ($p < 0.001$, Spearman's rank correlation coefficients = -0.33) was observed between metaldehyde concentration (monitoring point REG2) and modelled streamflow in the Western Salary Brook. In contrast, metaldehyde concentration at point REG3 was positively correlated with streamflow data recorded in the River Colne at Lexden ($p = 0.03$, correlation coefficient = 0.22) (Table 5.3). Significant positive correlations between metaldehyde concentration at REG2 and soil moisture and soil and air temperature were recorded (p values in the range 0.01–0.001 and correlation coefficient between 0.25 and 0.33) (Table 5.3).

Table 5. 3. Results of statistical analyses showing significant correlation between metaldehyde concentration (µg L^{-1}) and climatic/terrestrial system variables: relative humidity (%), soil and air temperature (°C), soil moisture (%), streamflow (m^3 s^{-1}). * p <.05, ** p <.01, *** p <.001.

Variables		Spearman's rank correlation coefficient	p	Kendall's tau B correlation coefficient	p
Relative humidity (%)	Metaldehyde (µg L^{-1}) REG3	0.203*	0.045	0.161*	0.044
Soil temperature, 15cm depth (°C)	Metaldehyde (µg L^{-1}) REG2	0.326**	0.001	0.26**	0.001
Soil temperature, 45 cm depth (°C)	Metaldehyde (µg L^{-1}) REG2	0.325**	0.001	0.258**	0.002
Air temperature (°C)	Metaldehyde (µg L^{-1}) REG2	0.297**	0.003	0.241**	0.003
Soil moisture (%)	Metaldehyde (µg L^{-1}) REG2	-0.21*	0.038	-0.169*	0.038
Soil moisture (%)	Metaldehyde (µg L^{-1}) REG3	0.247*	0.014	0.201*	0.012
Streamflow, NSB (m^3 s^{-1})	Metaldehyde (µg L^{-1}) REG2	-0.277**	0.006	-0.247**	0.006
Streamflow, NSB (m^3 s^{-1})	Metaldehyde (µg L^{-1}) REG3	0.273**	0.007	0.243**	0.006

Streamflow, WSB ($m^3 s^{-1}$)	Metaldehyde (μg L^{-1}) REG2	-0.333***	< .001	-0.299***	< .001
Streamflow, Colne ($m^3 s^{-1}$)	Metaldehyde (μg L^{-1}) REG2	-0.274**	0.006	-0.224**	0.006
Streamflow, Colne ($m^3 s^{-1}$)	Metaldehyde (μg L^{-1}) REG3	0.216*	0.033	0.173*	0.031

5.4.4 Spatio-temporal variations in metaldehyde in surface water at the sub-catchment level

5.4.4.1 Variability in metaldehyde concentrations

Metaldehyde concentrations in the Northern Salary Brook and the Western Salary Brook sub-catchments were compared for the period January 2019–February 2020. Concentrations in the Northern Salary Brook ranged between 0.004 and 0.018 μg L^{-1} and displayed lower variability compared to metaldehyde levels in the Western Salary Brook (Figure 5.9 C).

While metaldehyde concentrations in the Western Salary Brook varied within a similar range during the period January–August 2019 (with a small rise in concentration to 0.016 μg L^{-1} in June and July 2019), metaldehyde levels during the period September–December 2019 were considerably higher at 0.04–0.05 μg L^{-1} (Figure 5.9 C). A similar trend is observed in the timing of peak metaldehyde concentrations at abstraction point REG3 (the River Colne catchment). Concentrations were less than 0.01 μg L^{-1} during the period January–May 2019, with an increase in concentrations observed in June and July 2019 (0.02-0.05 μg L^{-1}). In comparison, the highest peaks in metaldehyde concentration at point REG3 were observed in December 2019 (up to 0.2 μg L^{-1}) (Figure 5.9 D). In several instances, peak metaldehyde concentrations (Figure 5.9 D) were observed only at REG2 point, for example in October-beginning of November 2019 (Figure 5.9 C, D).

Differences in metaldehyde concentrations recorded at the outlets of the Northern and Western Salary Brooks (REG1 and REG2, respectively) and the abstraction point REG3 during January 2019–February 2020 were significantly different ($p < 0.05$). Mean concentrations of metaldehyde in points 3–5 in the Western Salary Brook (0.01 μg L^{-1}, WSB) were not significantly different. The mean value of metaldehyde concentrations at point 2 (0.005 μg L^{-1}) was significantly lower than the mean concentrations at point 1

(0.008 μg L^{-1}, NSB) and points 3–5 (Figures 5.10 B, 5.11 D, Table 5.4). Mean and median values of metaldehyde concentrations across all *in situ* monitoring points (1–5) were under 0.01 μg L^{-1} during the spring, summer and winter months of field observations, while mean and median concentrations were equal to 0.018 μg L^{-1} in Autumn 2019 (5.10 A).

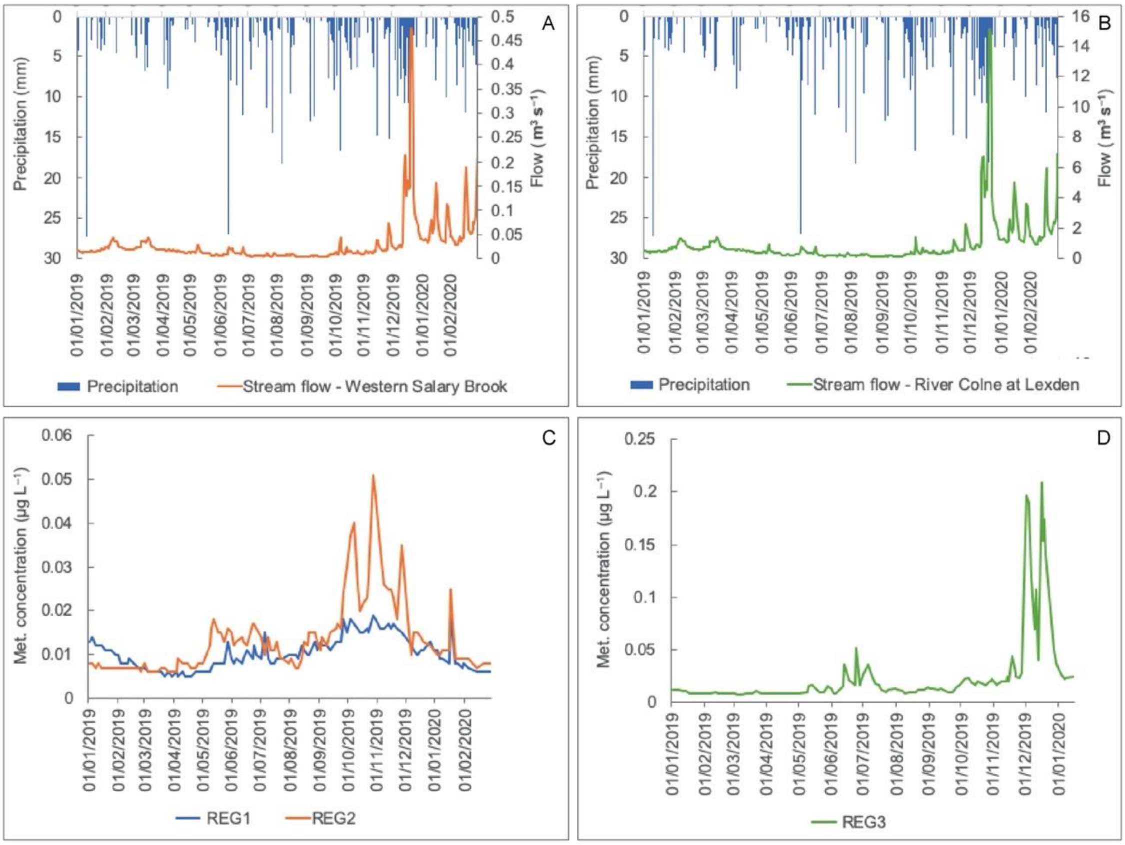


Figure 5. 9. Top panel: (A) precipitation and modelled daily streamflow (m^3 s^{-1}) in the Western Salary Brook (REG2), (B) precipitation and streamflow recorded at gauging station 37005 (River Colne at Lexden) (precipitation (mm d^{-1}) recorded in the Ardleigh catchment). Bottom panel: (C) metaldehyde concentration (μg L^{-1}) at regulatory sampling sites REG1 and REG2 in the Ardleigh catchment, and (D) at the abstraction site at the River Colne (REG3).

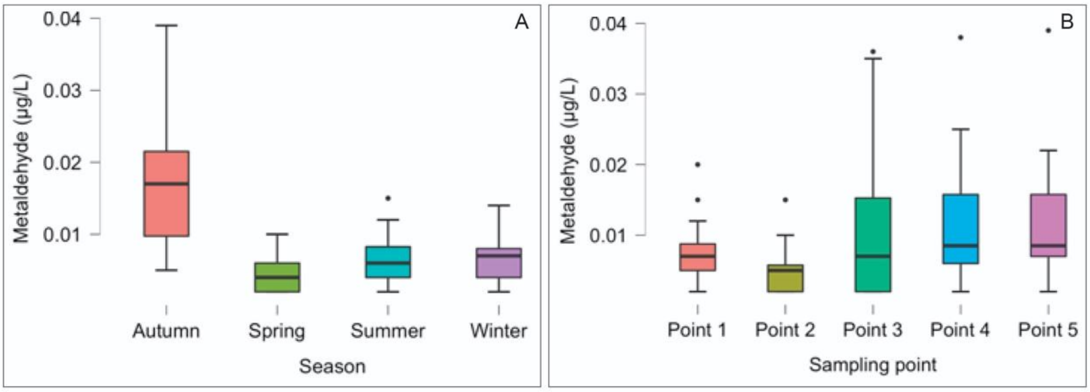


Figure 5. 10. (A) Temporal and (B) spatial variability in metaldehyde concentrations in the Ardleigh catchment during the period of January 2019–February 2020. Lines within each box represent median values, whiskers indicate minimum and maximum values. Circles represent outliers that are not included in the range data.

Table 5.4. Table 5. 4. Dunn's post hoc comparisons of mean metaldehyde concentrations at monitoring points 1-5.

Comparison	z	W_i	W_j	p	p_{bonf}	p_{holm}
Point 1 - point 2	2.16	54.21	33.59	0.016*	0.16	0.11
Point 1 - point 3	-0.10	54.21	55.18	0.46	1.00	0.85
Point 1 - point 4	-1.27	54.21	66.34	0.10	1.00	0.44
Point 1 - point 5	-1.46	54.21	68.18	0.07	0.72	0.43
point 2 - point 3	-2.26	33.59	55.18	0.012*	0.12	0.10
point 2 - point 4	-3.42	33.59	66.34	< .001***	0.003**	0.003**
point 2 - point 5	-3.62	33.59	68.18	< .001***	0.001**	0.001**
point 3 - point 4	-1.17	55.18	66.34	0.12	1.00	0.44
point 3 - point 5	-1.36	55.18	68.18	0.09	0.87	0.44
point 4 - point 5	-0.19	66.34	68.18	0.42	1.00	0.85

* p < .05, ** p < .01, *** p < .001

5.4.4.2 Spatio-temporal patterns in metaldehyde fluxes

Spatio-temporal trends in metaldehyde fluxes across the sub-catchments were similar to patterns in metaldehyde concentrations in the watercourse network (Figure 5.11). Lowest measured flux values in the range 0.11–0.26 g month^{-1} were observed in the Northern Salary Brook (points 1, 2) during January–October 2019. Fluxes within a similar range (up to 0.4 g in June 2019, point 5) were recorded in the Western Salary Brook during the period January-August 2019, with a considerable increase in values (0.57–1.26 g month^{-1}) during September-November 2019 (Figure 5.11).

Maximum increases in flux values across all monitoring points were observed during December 2019–February 2020 when fluxes ranged between 0.43 and 4.1 g month^{-1} in the Northern Salary Brook and within the range 1.0–5.33 g month^{-1} in the Western Salary Brook. Annual cumulative flux values were equal to 8.65 and 4.79 g a^{-1} (points 1, 2, respectively) in the Northern Salary Brook and within the range 11.65–12.53 g a^{-1} in the Western Salary Brook (points 3–5) (Figure 5.11).

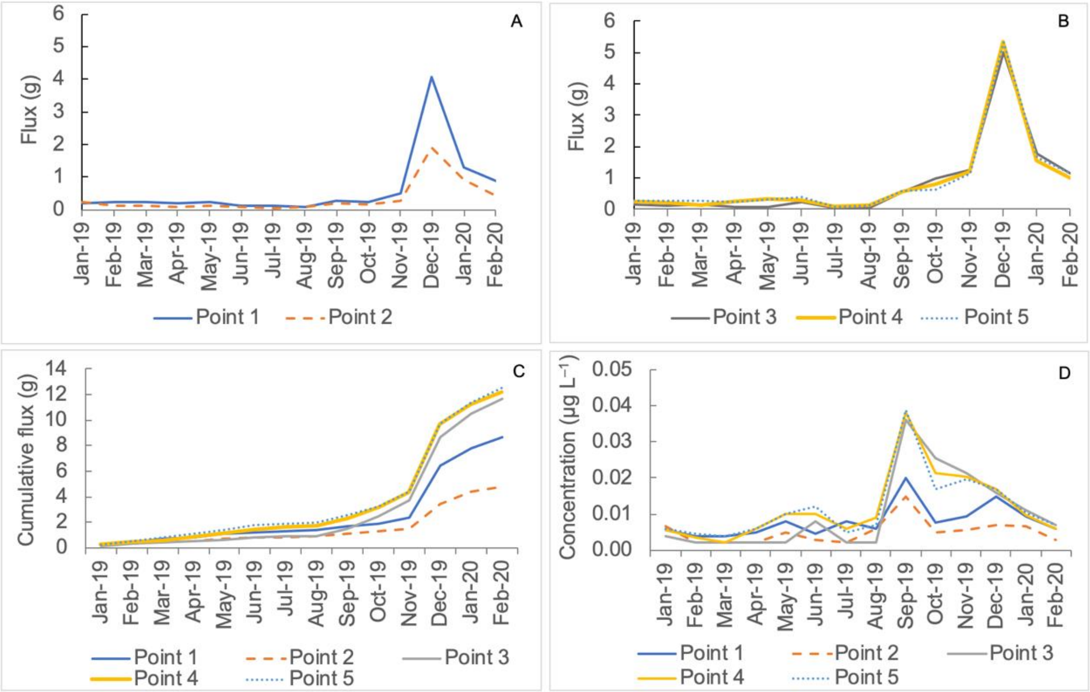


Figure 5. 11. Top panel: monthly flux of metaldehyde (g) in the Northern Salary Brook (A) and Western Salary Brook (B). Bottom panel: cumulative metaldehyde flux (C) and metaldehyde concentration (D) in the Northern Salary Brook (points 1, 2) and Western Salary Brooks (points 3–5) during the period January 2019–February 2020.

When metaldehyde flux values during the periods of typical application timings were examined, fluxes during the autumn-winter application period (August–December 2019) were equal to 77–90% of the annual flux values at the individual sampling points. Fluxes during the spring-summer application period (February–June 2019) accounted for 8–16% of the annual flux values (Table 5.5).

Table 5. 5. Seasonal flux (g) at individual monitoring points expressed as the percentage (%) of the total annual flux.

Metaldehyde application season	Monitoring points				
	Point 1	Point 2	Point 3	Point 4	Point 5
Spring-summer application (February–June 2019)	15%	15%	8%	13%	16%
Autumn-winter application (August–December 2019)	80%	77%	90%	84%	81%
No application (January, July 2019)	5%	8%	2%	4%	4%

5.4.5 Deposition of metaldehyde from atmospheric input and field drain runoff

Metaldehyde concentrations in rainwater samples collected monthly within the study area ranged between 0.004–0.05 µg L^{-1} during February 2019-February 2020 (Figure 5.12). Lowest concentrations below 0.01 µg L^{-1} were observed in the periods February–March 2019 and January–February 2020, increasing to 0.03 µg L^{-1} in May and June 2019. Highest levels were observed during the period August–November 2019 when concentrations varied within the range 0.03–0.05 µg L^{-1} with a peak value of 0.05 µg L^{-1} in October (Figure 5.12).

Metaldehyde concentrations in rainwater in the periods April-June, September and November 2019 were 0.01 µg L^{-1} higher than maximum concentrations observed during these same months in the Western Salary Brook (Figures 5.11 D, 5.12). The largest difference in maximum atmospheric deposition values versus maximum levels recorded in surface water was observed in August and October 2019 when metaldehyde concentrations were 0.03 and 0.02 µg L^{-1} higher in rainwater. Average monthly concentrations in rainwater and surface water were less than 0.01 µg L^{-1} in March 2019, during the winter months in 2019 and in January–February 2020 (Figures 5.10, 5.11 D, 5.12).

Mean values of metaldehyde concentration in rainwater collected in the area of the Ardleigh Reservoir tended to be lower than the mean concentration in rainwater measured at the Colchester site, although the difference between the means ($n = 12$) was not statistically significant ($p = 0.46$). The quality control results indicated that the dry deposition of metaldehyde (the metaldehyde concentrations detected in ultra-purified water samples at the gauge sites) were 0.004 and <0.008 µg L^{-1} in October and November 2020, respectively.

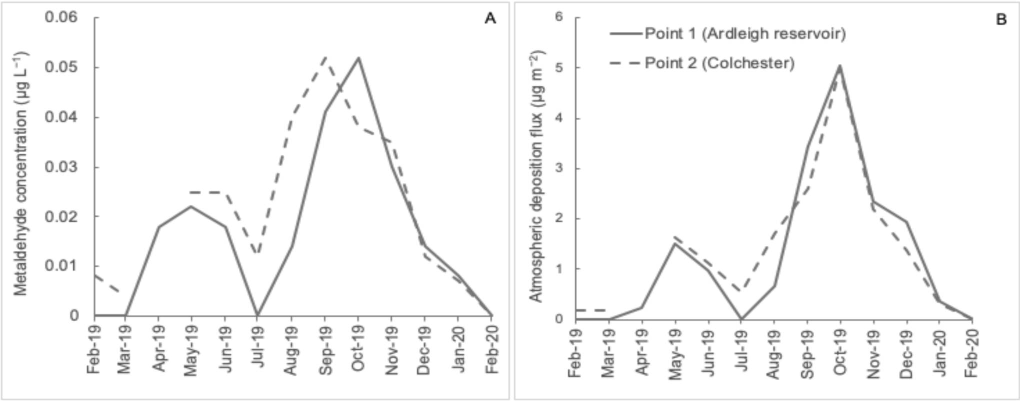


Figure 5. 12. (A) Monthly metaldehyde concentration (µg L^{-1}) in precipitation and (B) atmospheric deposition flux (µg m^{-2}) recorded during January 2019–February 2020 in the Ardleigh catchment.

Concentrations in field runoff samples collected upstream (field drain Runkin's C) and downstream (field drain WSB next to point 5) in the Western Salary Brook were generally lower compared to metaldehyde levels in surface water samples collected at the adjacent sampling points (Figure 5.13). The difference between metaldehyde levels in field drain runoff and surface water tended to be more prominent downstream (up to 0.01 µg L^{-1} difference) at the end of November 2019. Concentrations in surface water, field drain runoff and rainwater followed similar trends: peak values were observed at the end of November and in December 2019, with a gradual decline in concentrations during the period January-March 2020 (concentrations remained below 0.015 µg L^{-1}) (Figure 5.13).

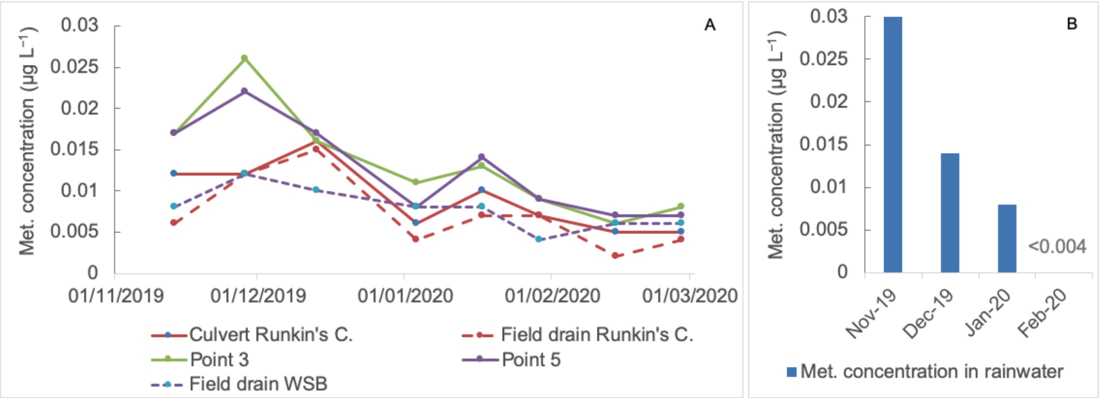


Figure 5. 13. (A) Metaldehyde concentration ($\mu g\ L^{-1}$) in surface water and field drain runoff in the Western Salary Brook sub-catchment in the period November 2019–February 2020. (B) Metaldehyde concentration in rainwater collected at the rain gauge located near Ardleigh Reservoir during the period November 2019–February 2020.

5.4.6 Mass budget of metaldehyde in Ardleigh Reservoir

Metaldehyde fluxes from individual sources displayed a similar temporal pattern with rising levels in May–June and September–December 2019 (Figures 5.14, 5.15). Spatially, the magnitude of sources varied considerably. The smallest contribution of metaldehyde to the Ardleigh Reservoir was observed within the watercourse network of the Ardleigh catchment (REG1, REG2 points), with flux values varying within the range 0.15–3.12 g month^{-1} (REG1) and 0.18–4.11 g month^{-1} (REG2). Lowest flux values were observed in the Northern and Western Salary Brooks in July 2019 (0.35 g month^{-1}, 4% of the cumulative flux), and maximum values were registered in December 2019 (7.25 g month^{-1}, 40% of the cumulative flux) (Figures 5.14, 5.15). Fluxes in the watercourse network of the Ardleigh catchment were equal to 17 and 9% when expressed as a percentage of the total flux/load into the Ardleigh Reservoir during the autumn-winter (August–December 2019) and spring-summer (February–June 2019) application periods (Figure 5.15), respectively.

Monthly atmospheric deposition ranged from 0.11 g (April 2019, 2% of cumulative flux) to 1.99 g (October 2019, 10% of cumulative flux). Metaldehyde atmospheric deposition was equal to 8 and 3% when expressed as a percentage of total influx to the Ardleigh Reservoir during the autumn-winter and the spring-summer application periods (Figure 5.15), respectively. No atmospheric input of metaldehyde to the Ardleigh Reservoir and catchment occurred during the periods February–March 2019 and July 2019 (Figures 5.14, 5.15).

The highest fluxes were measured in surface water abstracted from the River Colne (REG3). Values varied from 3.99 g in February 2019 to 15.5 g in October 2019. Minimum and maximum percent contributions to the total monthly input to the Ardleigh Reservoir of metaldehyde occurred in December and July 2019 (56 and 97%, respectively). The metaldehyde flux in surface water from the River Colne was equal to 75 and 88% when expressed as a percentage of the total influx to the Ardleigh Reservoir during the autumn-winter and the spring-summer application periods (Figure 5.15), respectively.

The mass of metaldehyde in the Ardleigh Reservoir ranged between 27.6 g (September 2019) and 47.4 g (December 2019) in the period January–December 2019. Seasonal peaks were observed in January, July and December 2019 (Figure 5.14, Table 5.6). Peaks in the monthly values of mass of metaldehyde in the Ardleigh Reservoir followed the pattern of increase in metaldehyde flux from the River Colne but with a 1-month lag (Figure 5.14).

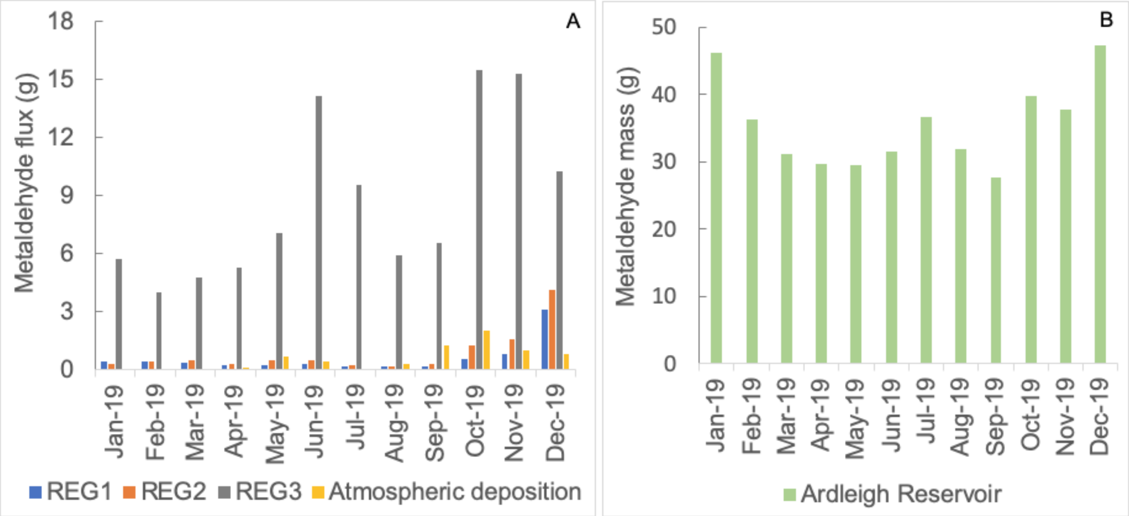


Figure 5. 14. (A) Monthly metaldehyde flux (g month^{-1}) recorded within the Ardleigh catchment stream network, abstraction point REG3 at the River Colne outlet, and atmospheric deposition of metaldehyde to Ardleigh Reservoir. (B) Monthly mass content (g month^{-1}) of metaldehyde retained within Ardleigh Reservoir.

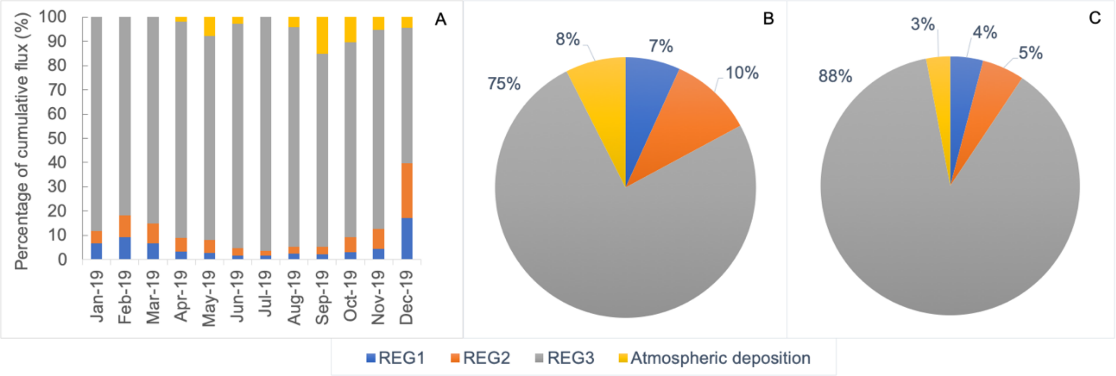


Figure 5. 15. (A) Individual loads of metaldehyde expressed as a percentage of monthly total/cumulative metaldehyde load to Ardleigh Reservoir for the period January 2019–February 2020. (B) Metaldehyde flux from the individual sources expressed as a percentage of the total flux during the autumn-winter application period (August–December 2019) and (C) the spring-summer application period (February–June 2019).

Monthly values of the mass of metaldehyde in the Ardleigh Reservoir decreased from January until May 2019 and in the following months of August, September and November 2019. The largest increases in the mass of metaldehyde occurred in October and December 2019 (12.2 and 9.64 g, respectively; Table 5.6). Values of the net load of metaldehyde to the Ardleigh Reservoir were negative in the periods January–May and July–September 2019, indicating higher outflux of metaldehyde compared to influx. Monthly net load values ranged from -8.43 to 8.18 g during the period January-December 2019 (Table 5.6).

Table 5. 6. Variations in monthly mass budget parameters of metaldehyde mass/loads (g) within the Ardleigh Reservoir in 2019.

Month	$M_{retained}$	$\Delta M_{retained}$	M_i (Net load)	($\Delta M_{retained}$–M_i)
January	46.20	-8.27	-8.43	0.16
February	36.34	-9.86	-6.09	-3.77
March	31.22	-5.12	-3.71	-1.41
April	29.65	-1.57	-2.06	0.49
May	29.51	-0.14	-0.05	-0.09
June	31.56	2.04	7.18	-5.13
July	36.63	5.07	-1.28	6.35
August	31.79	-4.83	-3.69	-1.14
September	27.64	-4.16	-1.35	-2.81
October	39.78	12.15	6.36	5.79
November	37.72	-2.06	8.18	-10.24
December	47.36	9.64	3.45	6.19

M_i (Net load) = mass inflow – mass outflow

$M_{retained}$: mass of metaldehyde retained in the Ardleigh Reservoir

$\Delta M_{retained}$: monthly difference in the change in mass content in the Ardleigh Reservoir

5.5 Discussion

5.5.1 Spatial and temporal patterns in water quality parameters and nutrient concentrations

Water quality parameters displayed seasonal trends with an inverse relationship between dissolved oxygen and temperature. Highest levels of dissolved oxygen were observed in the winter months: cold and fast-moving water has a higher capacity to store oxygen (USGS, 2021). Moreover, dissolved oxygen and pH data displayed similar trends during all seasons except in winter months, which suggests a causal relationship. An increase in hydrogen ions (decreasing pH) and oxygen reaction with water then causes a subsequent decrease in dissolved oxygen levels (Zang et al., 2011).

Nitrate is the dominant N form within the catchment, higher levels were observed at points 1 and 3 (Northern and Western Salary Brook sub-catchments, respectively). Both points (1 and 3) are situated in arable land, and elevated levels of nitrate-N (mean values = 6.77 and 4.88 mg L^{-1} at points 1 and 3, respectively) are likely associated with agricultural diffuse pollution (Kay et al., 2009; WHO, 2011; Holden et al., 2017). Lower mean values at point 4 (3.97 mg L^{-1}) compared to point 3 upstream are likely to be explained by dilution/mixing with water from the tributary that flows from the urban north Colchester area (Figure 5.1).

Ammonia-N and nitrite-N levels are highest at point 2 (Northern Salary Brook) followed by concentrations detected at point 4. Elevated total P and phosphate-P were also observed at point 2. Due to its close proximity to a livery yard, the origin of phosphorus is likely to be associated with a point source of nutrients from manure/animal waste. Grassland is predominant in the area of the Northern Salary Brook sub-catchment where sampling point 2 is located. In the study by Dupas et al. (2017), increased phosphorus solubilisation was observed in grassland areas compared to arable land, while nitrate-N levels were lower due to a better N utilisation compared to cropland due to a longer growth period (Dupas et al., 2017). Bieroza et al. (2014) reported increased total reactive phosphorus (TRP) concentrations in acid and neutral (pH 5.5-6.5) grassland compared to built-up areas. Increased nitrite-N and ammonia levels at point 4 compared to concentrations detected in the upstream and downstream parts of Western Salary Brook are likely to be linked to an urban source since point 4 is adjacent to the tributary flowing from the Colchester area.

When N and P temporal variability was considered, phosphorus displayed heightened levels in the summer months, similarly to nitrite-N and ammonia. Total oxidised nitrogen and nitrate-N reached their maximum levels in winter months. Peak levels of nitrate-N during the winter period could be due to increased hydrological connectivity within the catchment and more frequent runoff associated with wet weather conditions, causing increased soil erosion and N from the previous harvest being washed-off and mobilised with soil particles. Similar observations were reported by Royer et al. (2004), when the majority of nitrate-N was exported during autumn and winter months associated with the shorter residence time of stream water and tile drainage was active, allowing flushing of the soil profile of mobile nitrate-N. Similarly, higher TRP concentrations in surface water during summer and higher nitrate-N in winter months were reported by Bieroza et al. (2014). A study on nutrients in the Ardleigh Reservoir also reported lowest P concentrations and greatest loading of nitrate-N during the winter months (Redshaw et al., 1988).

A significant positive correlation between metaldehyde concentrations at REG2 and soil moisture, and soil and air temperature (Table 5.3) is indicative of the environmental conditions that impact on metaldehyde levels observed in stream water. Slug populations grow during wet and mild weather conditions, prompting metaldehyde application. Increased hydrological connectivity and saturated soils mobilise metaldehyde in soil via runoff, resulting in a rise of metaldehyde concentrations and fluxes in surface waters.

5.5.2 Metaldehyde transfer within the catchment: source-mobilisation-pathway-delivery perspective

Overall, trends observed in pathway-delivery mechanisms of metaldehyde transport within the catchment were similar to those observed within the catchment in previous years (2008–2018, Chapter 4). Metaldehyde transport patterns displayed seasonality, peaks in the pesticide levels from all pathways to a various extent were observed during the March–June and September–December 2019 application periods. Although concentrations detected in the Northern and Western Salary Brooks remained under the DWD limit of 0.1 μg L^{-1}, the autumn/winter application period was associated with a noticeably higher increase in metaldehyde concentrations and fluxes compared to the rise observed in the spring-summer months. Between 80 and 90% of the annual metaldehyde flux was generated in the August–December 2019 (Table 5.5). These periods coincided with typical application times in the spring/summer (February–June) and autumn/winter period (August–December) to protect winter cereal and oil seed rape crops, the predominant crops within the Ardleigh catchment. Trends in metaldehyde levels are highly compatible with those reported in previous studies (e.g. Kay and Grayson, 2014; Lu et al., 2017; Castle et al., 2018).

In addition to temporal trends in metaldehyde levels across the catchment, spatial distribution suggests that agricultural sources are predominant. A noticeable contrast in metaldehyde levels in the Northern and Western Salary Brook sub-catchments was observed (Figures 5.9, 5.11; Table 5.4). Significantly lower ($p < 0.05$) concentrations were recorded in the Northern Salary Brook compared to the Western Salary Brook that could be due to multiple factors, including relative size of the catchments and land use. The smaller size of the Northern Salary Brook sub-catchment combined with a larger grassland/non-arable area compared to the Western Salary Brook sub-catchment create conditions that lead to reduced metaldehyde use.

Soil type is an additional factor that may contribute to differences in metaldehyde levels observed it the sub-catchments. The Tendring soil association is predominant in the upper part of the Ardleigh catchment, with Wix soils situated at the lower part of the catchment. Tendring soils are well drained with little surface runoff during winter periods, with these soils generally not suitable for direct drilling of autumn-sown cereal crops due to a large fine sand-silt content of the topsoils that leads to restricted rooting and associated loss of yield (Cranfield University, 2021).

On the other hand, where Wix soils are dominant with reduced permeability, waterlogging occasionally occurs that leads to soil erosion and gully formation. Winter cereals are the main crops grown on Wix soils (Cranfield University, 2021). These soils are also affected by high groundwater levels, which increases the potential for waterlogging and subsequent runoff, thus facilitating metaldehyde transfer to surface water. The above factors, combined, create favourable conditions for increased metaldehyde loss to surface waters in the lower part of the Ardleigh catchment, compared to the upper part (Northern Salary Brook sub-catchment) (Figure 5.16).

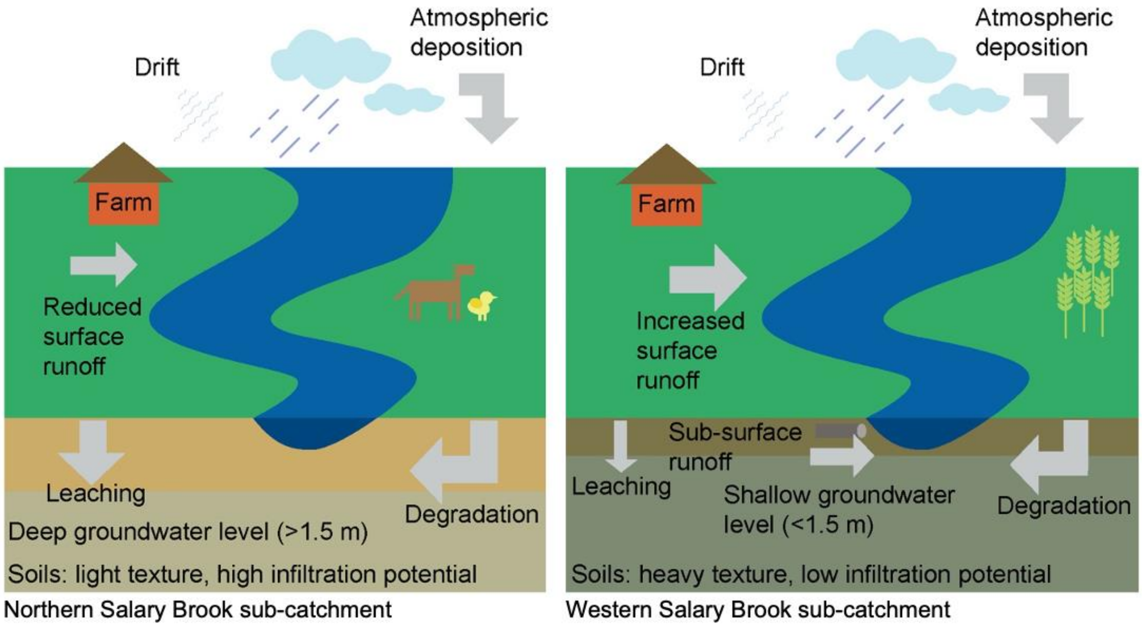


Figure 5. 16. Schematic representation of metaldehyde transfer in the Ardleigh catchment: the Northern Salary Brook and Western Salary Brook sub-catchments. The arrow size represents the scale of processes within the source-pathway-mobilisation-delivery continuum.

When metaldehyde concentrations in the upstream area of the Western Salary Brook (point 3) were compared with point 4 that represents a potential urban source of metaldehyde, no statistically significant difference was observed. Furthermore, a sharp rise in metaldehyde levels observed in the Western Salary Brook during the period October–December 2019 was indicative of an agricultural source for metaldehyde. Metaldehyde applications in non-agricultural settings (e.g. private gardens and allotments) are less likely to be in place when the highest peaks of metaldehyde are observed in the autumn/early winter. Urban/non-agricultural land use constituted < 15% of the catchment, which indicates that urban/domestic sources of metaldehyde are a minor contributor to metaldehyde loss to surface waters compared to agricultural sources.

Peaks in metaldehyde levels in runoff during periods when tile drainage was active is consistent with patterns of metaldehyde concentrations in surface water at adjacent sampling locations. This observation suggests high mobility in the soil profile due to the physiochemical properties of metaldehyde, for example its high solubility (188–190 mg L^{-1} at 20 °C) and low adsorption properties (K_{oc} of 35 L kg^{-1}) (PAN, 2020; PPDB, 2020). Such a pattern also indicates that it is likely that metaldehyde observed in drain runoff samples originates in recent applications rather than as a result of legacy applications due to the high biodegradation potential of metaldehyde (Thomas et al. 2013; Balashova et al., 2020). Water soluble pesticides with weak sorption capacity, such as metaldehyde, tend to stay at the surface in soil organic matter and are likely to be released into soil water solution and enter surface water as runoff (Blessing, 1998). The significant correlation ($p = 0.01$) between nitrate-N (a mobile species) and metaldehyde, further support the argument for high mobility of the compound, given its physico-chemical properties.

An increase in levels following wet weather conditions in June 2019 also suggests that metaldehyde is mobilised relatively rapidly in the environment. Maximum annual precipitation (27 mm d^{-1}) was observed on 10 June 2019, and a rise in concentration was observed at all regulatory points. For example, metaldehyde concentrations of 0.006 and 0.008 μg L^{-1} at REG1 and REG2 points on 5 June increased to 0.02 μg L^{-1} on 12 June within the Ardleigh catchment. A similar trend was observed in the abstraction point in the River Colne (REG3), where concentrations increased from 0.26 to 0.61 μg L^{-1}. A modelled travel time of metaldehyde transport in runoff was reported to be 5-80 h for a catchment size of 75.4 km^2 (Asfaw et al, 2018), indicating fast rates of metaldehyde loss to surface waters via runoff.

A high mobility of metaldehyde is supported by trends in atmospheric deposition of metaldehyde that follows a similar seasonal pattern to that observed in metaldehyde levels in surface water of the Ardleigh catchment and the River Colne. Peaks in concentrations detected in rainwater were observed in the March–June and August–November months, before decreasing in December. In certain months (e.g. March, August 2019), metaldehyde levels detected in rainwater were up to 0.03 $\mu g\ L^{-1}$, higher than concentrations detected in the River Colne (REG3). This observation indicates that metaldehyde is susceptible to wind-borne drift during the early stages of the application seasons, up to several months before a noticeable increase in concentrations is observed in surface water. This time lag could be due to several factors: i) amounts applied are lower due to less 'slug pressure' in the early stages of the application season, and ii) reduced hydrological connectivity in the early stages of the autumn/winter application season.

Metaldehyde is a soil-applied pesticide, mainly applied in a dry form of pellets that form dust during the application procedure (Farmers Guide, 2016). The fine particles are subject to drift and have the potential to be transported over long distances. Although no published peer-reviewed studies on atmospheric transport of metaldehyde are available to date, research on atmospheric transport and deposition of other agrochemicals demonstrate that a wide range of pesticides are subject to being transported at a regional/long-range scale. Elevated levels in rainwater are typically associated with seasonal application times (Unsworth et al., 1999; De Rossi et al., 2003; Asman et al., 2005; Kreuger et al., 2006; Vogel et al., 2008; Huang et al., 2010).

5.5.3 Mass budget and seasonal dynamics of metaldehyde in the Ardleigh Reservoir

Metaldehyde was present in the reservoir during all observation months in 2019 (Figure 5.14, Table 5.6). Overall, the mass balance model showed that the largest input of metaldehyde to the Ardleigh Reservoir originated in the River Colne: typically, 75–90% of the total input flux, depending on metaldehyde application season (Figure5.15)). The mass outflow was larger than the total inflow of metaldehyde during the year except in June and the October-December 2019 periods that coincide with the application seasons of the pesticide. Increases in mass were comparable with variations in input flux of metaldehyde to the reservoir from various sources, particularly from the River Colne (REG3). Due to the consistent influx of metaldehyde from the River Colne, the slow degradation rates of metaldehyde in water and the high aqueous solubility of the pesticide, metaldehyde mass in the reservoir remained relatively stable (min = 27.7 g month^{-1} and > 30 g month^{-1} in the majority of months (Figure 5.14, Table 5.6)).

While metaldehyde flux from the Colne rose steadily during the period February–June 2019, an increase in the mass of metaldehyde in the Ardleigh Reservoir was observed in the period May–July 2019. Following peaks were observed in October and December 2019, when metaldehyde loads from individual sources (Northern and Western Salary Brooks, the River Colne and the atmospheric deposition) were at their highest levels (Figure 5.14). A delay of up to two months in peaks of metaldehyde mass in the reservoir could be due to mixing mechanisms and the residence time required to observe a rise in metaldehyde mass.

Negative net load values observed during the periods January–May and July–September are likely to be the result of the higher volumes of water abstracted from the reservoir compared to the volumes pumped into the reservoir from the River Colne. While volumes of water abstracted from the reservoir were also higher than water volumes pumped into the reservoir from the River Colne in November and December 2019, the monthly net loads were at their highest values due to the maximum mass inflow observed throughout the year and the cumulative effect of metaldehyde mass build-up. To comply with the DWD standards and regulate metaldehyde concentrations in water abstracted from the Ardleigh Reservoir for drinking water supply, an abstraction management policy is in place. This approach minimises volumes abstracted from the Colne to Ardleigh Reservoir during periods when high concentrations of metaldehyde are detected in surface water at the East Mills abstraction point (REG3). Metaldehyde transport modelling conducted by Nineham et al. (2015) indicated that no application of metaldehyde in water abstraction catchments with current metaldehyde use would have limited effect. Nineham et al. (2015) found that in order to successfully reduce metaldehyde concentration below 0.1 μg L^{-1} in the Ardleigh reservoir, the maximum application rate in the Colne catchment, that partly supplies the reservoir, should be reduced to 60 g ha^{-1}. In addition, no metaldehyde application was recommended in the areas with impeded drainage.

5.6 Conclusions

Temporal variability in nutrient concentrations included increases in P levels in summer and elevated N concentrations in winter months. The spatial distribution of nutrients was influenced by land use. Elevated levels of P and ammonia-N at point 2 in the Northern Salary Brook could be due to animal derived waste. Increased concentrations of nitrate-N, observed at points 1 and 3 in both the Northern and Western Salary Brooks, could be linked to agricultural diffuse pollution sources; these monitoring points were situated in areas with predominantly arable land use. A significant positive correlation between metaldehyde concentrations, soil moisture, soil and air temperature was observed. This relationship is likely linked forward to environmental conditions (mild and wet weather) that favour slug population growth and thus the need for metaldehyde applications.

Spatial trends in metaldehyde concentrations and fluxes at the sub-catchment level were likely to be driven by a combination of factors: land use, soil type and topography of the sub-catchments. Levels of pesticide were significantly lower in the Northern Salary Brook sub-catchment that has a larger proportion of grassland and more permeable soils in comparison with the Western Salary Brook sub-catchment in the lower part of Ardleigh catchment. Temporal patterns in metaldehyde levels were very similar to those observed and discussed in Chapter 4: spikes in metaldehyde concentrations and increased fluxes at all monitoring points occurred between September and December, with the origin of the pesticide likely to be from agricultural use.

Metaldehyde concentrations in field drain runoff and variations in atmospheric deposition indicate a high environmental mobility of the pesticide. Concentrations in runoff peaked in December 2019 (up to 0.015 $\mu g\ L^{-1}$) with a gradual decrease in the period January–February 2020. Metaldehyde detected in rainwater displayed seasonal variability similar to seasonal variations in surface runoff. An increase in the levels of atmospheric deposition was observed 1–2 months before the rise in concentrations observed in surface waters. Consequently, this creates implications for interpretation of the sources of metaldehyde.

Temporal variations in metaldehyde mass in the Ardleigh Reservoir showed a consistent presence of the pesticide (mass varied from 27.7 to 47.4 g month^{-1}), with an increase in mass during the typical application times. Due to limited degradation potential and high solubility of metaldehyde in water, its presence in the reservoir is likely to persist for several years following the withdrawal of metaldehyde for outdoor use (March 2022). However, reduced levels of metaldehyde are likely to be seen in stream/river water following the ban i.e. when the input source is terminated. This would, in turn, result in a noticeable decrease in the influx of the pesticide to the Ardleigh Reservoir, particularly from the River Colne, which represents the major and the most prominent source of metaldehyde influx to the reservoir. With decreasing concentrations of metaldehyde in feed waters that replenish the reservoir, a decrease in the metaldehyde load, via dilution, would be expected in subsequent years.

Chapter 6 Conclusions

6.1 Main research developments

The overarching aim of this research was to advance the existing understanding of metaldehyde fate and transport in the environment at a catchment scale. The goal was reached by achieving the set of individual objectives/contributions to the field of knowledge as follows:

1. A literature review of metaldehyde transport, persistence and fate in the environment was produced. Metaldehyde transport and fate were discussed in the context of the source-mobilisation-pathway-delivery paradigm, and factors affecting metaldehyde transport and fate were reviewed.
2. Metaldehyde mineralisation rates in dissimilar soils with contrasting application regimes were quantified. The effects of soil properties, such as SOM, pH and soil texture on metaldehyde biodegradation were assessed (Chapter 3; Balashova et al, 2020).
3. Long-term and seasonal trends in metaldehyde concentrations and fluxes in surface water networks of the River Colne and Ardleigh Reservoir catchments were examined at a temporal scale over a decade. The impacts of metaldehyde application regime and hydrological conditions on metaldehyde levels in surface watercourses were evaluated (Chapter 4; Balashova et al, 2021).
4. Metaldehyde transport and source-mobilisation-pathway-delivery mechanisms driving metaldehyde transfer at a sub-catchment scale in the Ardleigh catchment were examined. This objective included analysis of metaldehyde atmospheric deposition fluxes over a one-year period, as well as the comparison of metaldehyde concentrations in surface water and field drain runoff (Chapter 5).
5. A mass budget of metaldehyde for the Ardleigh Reservoir was quantified, and the dynamics of monthly changes in mass and the scale of input sources were explored (Chapter 5).

6.1.1 Metaldehyde biodegradation potential in dissimilar soils

^{14}C-metaldehyde mineralisation experiments were conducted to explore the competence of microbial communities to break down metaldehyde in soils with contrasting characteristics collected from various settings (agricultural fields, allotments and gardens in residential settings). High biodegradation (% mineralisation) potential was ubiquitously observed across all soil types, both top and sub-soils. This in in agreement with the physico-chemical properties and chemical structure of metaldehyde with its simple chemical structure that is easy to break down, making carbon available to bacteria. An increased biodegradation capacity was observed in soils with a lighter texture and Soil Organic Matter above 12%.

The findings of this study on microbial degradation of metaldehyde suggest that this chemical compound is likely to have low soil persistence, and its long-lived persistence in the environment is not expected. The results contribute further knowledge that can be applied as a tool for catchment strategies in risk management evaluation of legacy metaldehyde residues in soil.

6.1.2 Long term and seasonal spatio-temporal trends of metaldehyde concentrations and fluxes in stream water

This part of the research included the analysis of long-term and seasonal spatio-temporal variations in metaldehyde levels in stream water, where the impact of hydrological conditions and application regime on metaldehyde concentrations and fluxes was assessed. The assessment highlighted the following:

i) Seasonal application and trends in metaldehyde levels. Metaldehyde concentration spikes above the DWD limit and increased variability of metaldehyde concentrations were consistently observed during the main application season of metaldehyde in the UK (August-December). In contrast, metaldehyde concentrations in watercourses during months when metaldehyde was not normally applied to agricultural land in the study area (January, July) and during the spring-summer application time (February-June) were typically an order of magnitude lower than the regulatory limit of 0.1 $\mu g\ L^{-1}$.

ii) Impact of hydrological conditions. Seasonally, DWD exceedances of metaldehyde concentrations were mainly associated with wet weather conditions and occurred during the August-December application period. Concentration peaks were observed up to 7 days following events with >10 mm precipitation. Surface and subsurface runoff-driven transport of metaldehyde serves as a major pathway in explaining the presence of metaldehyde in surface water. At the annual scale, a noticeable contrast in metaldehyde concentrations and fluxes was observed in wet versus dry years (e.g. 2016 and 2018). Despite the same annual metaldehyde use (kg a^{-1} active ingredient) in 2016 and 2018; metaldehyde losses (g ha^{-1}), fluxes (kg a^{-1}) and concentrations (μg L^{-1}) were noticeably lower in 2018.

As part of this research, an extensive dataset of metaldehyde flux values was generated. Combined with hydrological data, this dataset provides a continuous 10-year period of observations that can be applied in transport models to further advance understanding of metaldehyde transfer in the aquatic environment. The research highlights that periods of application *versus* no application are a significant factor controlling metaldehyde occurrence in surface water. Beyond application, precipitation was a significant causal driver of metaldehyde presence in surface water. In general, both causal drivers of application and precipitation were needed to illicit increases in metaldehyde concentrations in water. While, on the face of it, only using metaldehyde in drier months could be perceived as a pragmatic solution, this is impractical as the mollusc pressures on crops are synonymous with wetter periods of the year.

6.1.3 Metaldehyde transport processes at a sub-catchment scale

The third part of this research focused on metaldehyde transport in the Ardleigh catchment, which is one of the trial catchments in the Slug It Out campaign.

This study explored temporal and spatial trends in metaldehyde concentrations and fluxes in stream water, atmospheric deposition and concentrations in field runoff in the 5th year of the campaign (January 2019-February 2020). These trends were discussed within the source-mobilisation-pathway-delivery paradigm, and a conceptual model of metaldehyde transfer within the sub-catchments was produced.

This study is the first to quantify a metaldehyde mass budget for a surface water catchment. A simple mass budget model was produced to evaluate and discuss changes in the metaldehyde mass budget for the Ardleigh Reservoir. The key findings indicated the following:

i) Agricultural source of the chemical. Although concentrations detected in the Northern and Western Salary Brooks remained under the DWD limit of 0.01 μg L^{-1}, the autumn/winter application period was associated with a noticeably higher increase in metaldehyde concentrations and fluxes compared to the rise observed in the spring-summer months. Between 80 and 90% of the annual metaldehyde flux generated in the stream network of the catchment occurred in the period August–December 2019.

ii) Difference at sub-catchment level. Significantly lower ($p < 0.05$) concentrations were recorded in the Northern Salary Brook compared to the Western Salary Brook due to differences in land use and soil type (that in concept would favour runoff and metaldehyde transport to surface water) within the sub-catchments.

iii) Scale of individual input/load sources. The mass balance model showed that the largest input of metaldehyde to the Ardleigh Reservoir originates in the River Colne transfer, representing typically 75–90% of the total input flux depending on the metaldehyde application season.

iv) Temporal variations in metaldehyde mass. Temporal variations in metaldehyde mass in the Ardleigh Reservoir showed a consistent presence of the molluscicide (mass varied from 27.7 to 47.4 g month^{-1}). Relatively stable levels are likely caused by the consistent influx of metaldehyde from the River Colne, the slow degradation rate of metaldehyde in water, and the high aqueous solubility of metaldehyde.

Although the atmospheric deposition in certain months accounted for a higher input than surface influx from the Salary Brooks (May, August–October 2019), surface and field drain runoff are likely to be the predominant mode of transfer to surface waters. The results of this study further highlighted the high mobility of metaldehyde: elevated levels of metaldehyde were observed during autumn and early winter months: an observation which is consistent with previous studies (e.g. Kay and Grayson, 2014, Castle et al., 2018; Castle et al., 2019).

The overall findings regarding spatial and temporal trends in metaldehyde concentrations discussed in this research provide knowledge contribution towards the wider understanding of polar pesticides with physico-chemical characteristics similar to metaldehyde. Monitoring polar pesticides is important, since polar chemicals (compounds with polar molecules due to an electronegativity difference between the bonded atoms) are mobile in an aquatic environment, and analytical methods for detection of these compounds in water are lacking (Kolkman et al., 2021). Consequently, findings of this research could be further extrapolated and incorporated into monitoring, catchment management and risk assessment practices with relation to such pesticides.

6.2 Policy implications

It often takes a prolonged period to see the impact and benefit of land-use management strategies and catchment-based approaches (Holden et al., 2017). In this research, long-term spatio-temporal trends proved a gradual decline in metaldehyde levels from 2017 onwards, in line with increasing demand for ferric phosphate (Table 4.10; Pesticide Usage Survey, 2021). Combined with the seasonal nature of metaldehyde peaks occurring in surface waters, it is expected that the problem of DWD exceedances of metaldehyde concentrations is likely to be substantially reduced in the UK after the withdrawal of this pesticide for outdoor use in March 2022.

The research findings showed that surface and subsurface runoff serves as a main transport mechanism of metaldehyde delivery to surface waters. Agri-environmental schemes aimed to reduce diffuse pollution from agriculture via reducing runoff within similar catchments will have wider positive implications for the ecological and water quality status of surface waters (e.g. Water Framework Directive) and flood risk management (Flood Directive). Incorporation of nature-based solutions in the agricultural sector and integrated catchment management combined with a better alignment of environmental and agricultural policies would, therefore, lead to improved environmental outcomes. Policies that consider the trade-offs between economic, social and environmental outcomes are more effective in general (Piñeiro et al., 2020).

While the recent policy change on metaldehyde use in the UK should positively benefit water quality aspects, the primary motivation for the March 2022 outdoor use withdrawal is the risk to wildlife due to metaldehyde toxicity. Although metaldehyde poisoning is rarely reported because the diagnosis is often difficult (Botelho et al., 2020), cases of metaldehyde poisoning in pets, terrestrial animals and birds in the UK will likely decrease. It is further noted that ferric phosphate is not without its drawbacks. Most notably the need for this product to be co-formulated with iron-chelators, such as (ETDA). These iron-chelators, are not considered as “active ingredients” and are therefore not subject to pesticide regulatory requirements (under e.g. the WFD). They have, however, been reported to be toxic to soil biota (far more toxic than metaldehyde) and could threaten soil ecosystems as a result (Edwards et al., 2009; Duo et al., 2018).

6.3 Research limitations and recommendations for further research

Although it was established that bacterial capacity to degrade metaldehyde in dissimilar soils is high (Balashova et al, 2020), analysis of metaldehyde concentration in soil samples was outside of the scope of this research. To date, the research regarding metaldehyde fate in soil profiles is limited to several short-term studies (up to one month) (Bieri, 2003; Zhang, 2011). Further research into metaldehyde concentration trends in dissimilar soils over a longer time period, e.g. one year, is needed. Such studies in controlled field settings would be beneficial to understanding aging mechanisms of metaldehyde and its leaching through soil profiles.

An extended sampling point network in areas with known application regimes (controlled environment) combined with automated passive sampling could provide information about hot spots/risks zones (critical source areas) at a catchment scale. With passive sampling conducted during high intensity hydrological conditions, such research would help advance existing knowledge of metaldehyde transfer mechanisms. The addition to existing metaldehyde monitoring datasets generated via passive and spot sampling techniques (e.g. Castle et al., 2019) could be further applied to metaldehyde transport modelling. Research in this area currently remains limited (Lu et al., 2017, Asfaw et al, 2018, Purnell, 2020). Purnell et al. (2020) established that the amount and timing of pesticide application were one of the most important parameters for the prediction of metaldehyde peaks using the SWAT model. While often challenging to obtain, metaldehyde use surveys from individual farmers within the study area could be an extremely valuable input for improved accuracy of metaldehyde load simulation.

Continuous regulatory monitoring of metaldehyde would enable researchers and stakeholders to assess changes in metaldehyde levels following the metaldehyde ban and legacy metaldehyde loss to surface waters in the UK. This will allow an evaluation of the legacy effects and metaldehyde transport dynamics in the aquatic environment when an ongoing/seasonal application is no longer in place. Ongoing sampling after the metaldehyde ban would also provide new insight on metaldehyde degradation rates in the Ardleigh reservoir. Additionally, continuous monitoring of atmospheric deposition of metaldehyde after the ban in the UK would allow assessment of regional-scale pollutant transport cross national boundaries.

The scale of the slug problem and slug control measures in agriculture are not universal across EU countries and are linked to factors such as climate and cropping systems. Slug ‘pressure’ and higher demand on slug control methods are expected in regions with a mild temperate climate, such as The Netherlands. While outdoor use of metaldehyde is banned in The Netherlands, as well as prohibited in Denmark, Sweden and Finland (UK Parliament, 2019), metaldehyde use is permitted in 20 EU States, including France and Germany, as well as counties outside the EU. The research findings should further inform environmental, and pesticide use policies in EU countries and other countries outside the EU, where metaldehyde application is permitted.

The climatic similarity in northern France and Germany, combined with similar cropping systems (the countries are one of the largest producers of cereals among the EU Member States), create potential conditions where seasonal metaldehyde DWD exceedances are likely to occur. Atmospheric transport/drift of metaldehyde from these countries in particular (due to relatively close geographical proximity) and other regions where it is registered for use could affect concentrations in UK waters following metaldehyde withdrawal in the UK. Hence, an extended sampling network across regions in the long term, including in remote areas, would be required for better understanding of complex atmospheric transport mechanisms.

A simple mass budget model at a long-term temporal scale (10+ years) using both historic and post-ban metaldehyde concentrations data would offer more in-depth understanding of metaldehyde transport, scale of metaldehyde sources and its impact on metaldehyde mass in the Ardleigh Reservoir. The implementation of such a model at a larger scale for multiple catchments with contrasting land use would provide more robust evidence of changes in metaldehyde levels over a longer period that covers changes in policy and the evolution of stewardship initiatives.

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Appendix A: Supplementary material for Chapter 3

Table A 1 Soil characteristics and metaldehyde mineralisation data.

Sample	Texture	Texture category	Setting	Metaldehyde application history	Mataldehyde application *in situ* (lab)	Soil Organic Matter	pH	Mineralisation (%)
FT(n)1-	Sand	Light	Field	FALSE	FALSE	3.50	6.68	31.04
FS(n)2-	Sand	Light	Field	FALSE	FALSE	1.82	7.55	30.03
FS(n)4-	Sand	Light	Field	FALSE	FALSE	2.38	7.21	30.50
AS(n)1-	Sand	Light	Allotment	FALSE	FALSE	1.36	7.05	60.01
AS(p)2-	Sand	Light	Allotment	TRUE	FALSE	1.17	7.18	48.26
AT(n)1-	Loamy Sand	Light	Allotment	FALSE	FALSE	7.91	7.58	36.19
AT(p)2-	Loamy Sand	Light	Allotment	TRUE	FALSE	5.24	7.44	34.35
FT(n)2-	Loamy Sand	Light	Field	FALSE	FALSE	3.08	7.55	21.15
GT(n)2-	Loamy Sand	Light	Garden	FALSE	FALSE	7.18	7.54	31.61
GT(n)3-	Loamy Sand	Light	Garden	FALSE	FALSE	25.29	6.92	34.05
GT(n)4-	Loamy Sand	Light	Garden	FALSE	FALSE	16.22	7.49	38.88
GT(n)5-	Loamy Sand	Light	Garden	FALSE	FALSE	11.83	8.02	40.84
GT(n)6-	Loamy Sand	Light	Garden	FALSE	FALSE	11.43	8.01	52.75
FT(n)3-	Sandy Loam	Light	Field	FALSE	FALSE	2.53	6.57	28.67
FT(n)4-	Sandy Loam	Light	Field	FALSE	FALSE	3.85	6.35	28.77
FT(n)5-	Sandy Loam	Light	Field	FALSE	FALSE	4.52	7.19	21.41
FT(p)6-	Sandy Loam	Light	Field	TRUE	FALSE	2.80	8.21	18.22
GT(n)1-	Sandy Loam	Light	Garden	FALSE	FALSE	52.14	7.10	46.43

FT(n)8-	Loam	Medium	Field	FALSE	FALSE	4.02	6.15	26.82
FT(p)9-	Loam	Medium	Field	TRUE	FALSE	3.40	7.11	23.64
FT(p)10-	Loam	Medium	Field	TRUE	FALSE	2.67	7.73	19.54
FT(p)11-	Sandy Loam Clay	Medium	Field	TRUE	FALSE	3.96	6.44	26.38
GT(n)7-	Sandy Clay Loam	Medium	Garden	FALSE	FALSE	10.19	7.65	28.94
GT(n)8-	Sandy Clay Loam	Medium	Garden	FALSE	FALSE	12.44	7.52	33.98
GT(n)9-	Sandy Clay Loam	Medium	Garden	FALSE	FALSE	5.48	8.15	34.21
GT(n)10-	Sandy Clay	Medium	Garden	FALSE	FALSE	8.58	7.70	33.48
FT(p)7-	Silty Loam	Medium	Field	TRUE	FALSE	3.89	7.24	17.65
FT(p)12-	Silty Clay Loam	Medium	Field	TRUE	FALSE	4.02	7.29	19.27
FT(n)1+	Sand	Light	Field	FALSE	TRUE	3.50	6.68	29.62
FS(n)2+	Sand	Light	Field	FALSE	TRUE	1.82	7.55	38.93
FS(n)4+	Sand	Light	Field	FALSE	TRUE	2.38	7.21	30.61
AS(n)1+	Sand	Light	Allotment	FALSE	TRUE	1.36	7.05	66.45
AS(p)2+	Sand	Light	Allotment	TRUE	TRUE	1.17	7.18	58.20
AT(n)1+	Loamy Sand	Light	Allotment	FALSE	TRUE	7.91	7.58	38.21
AT(p)2+	Loamy Sand	Light	Allotment	TRUE	TRUE	5.24	7.44	35.69
FT(n)2+	Loamy Sand	Light	Field	FALSE	TRUE	3.08	7.55	23.90
GT(n)2+	Loamy Sand	Light	Garden	FALSE	TRUE	7.18	7.54	39.87
GT(n)3+	Loamy Sand	Light	Garden	FALSE	TRUE	25.29	6.92	48.44
GT(n)4+	Loamy Sand	Light	Garden	FALSE	TRUE	16.22	7.49	45.59
GT(n)5+	Loamy Sand	Light	Garden	FALSE	TRUE	11.83	8.02	50.87
GT(n)6+	Loamy Sand	Light	Garden	FALSE	TRUE	11.43	8.01	52.97
FT(n)3+	Sandy Loam	Light	Field	FALSE	TRUE	2.53	6.57	30.31
FT(n)4+	Sandy Loam	Light	Field	FALSE	TRUE	3.85	6.35	27.03
FT(n)5+	Sandy Loam	Light	Field	FALSE	TRUE	4.52	7.19	23.74
FT(p)6+	Sandy Loam	Light	Field	TRUE	TRUE	2.80	8.21	21.65
GT(n)1+	Sandy Loam	Light	Garden	FALSE	TRUE	52.14	7.10	48.24
FT(n)8+	Loam	Medium	Field	FALSE	TRUE	4.02	6.15	16.52
FT(p)9+	Loam	Medium	Field	TRUE	TRUE	3.40	7.11	16.72
FT(p)10+	Loam	Medium	Field	TRUE	TRUE	2.67	7.73	21.51
FT(p)11+	Sandy Loam Clay	Medium	Field	TRUE	TRUE	3.96	6.44	17.73

GT(n)7+	Sandy Clay Loam	Medium	Garden	FALSE	TRUE	10.19	7.65	44.21
GT(n)8+	Sandy Clay Loam	Medium	Garden	FALSE	TRUE	12.44	7.52	46.61
GT(n)9+	Sandy Clay Loam	Medium	Garden	FALSE	TRUE	5.48	8.15	47.05
GT(n)10+	Sandy Clay	Medium	Garden	FALSE	TRUE	8.58	7.70	50.42
FT(p)7+	Silty Loam	Medium	Field	TRUE	TRUE	3.89	7.24	21.40
FT(p)12+	Silty Clay Loam	Medium	Field	TRUE	TRUE	4.02	7.29	17.66

Appendix B: Supplementary material for Chapter 4

Table B 1 Coordinates of sample site locations.

Site	Coordinates (Decimal Degrees)	
REG1 - Northern Salary Brook	51.92962	0.96693
REG2 - Western Salary Brook	51.92289	0.93568
REG3 - River Colne at Eastmill	51.89208	0.91557
C1 - River Colne Church Road/Nuns Walk Great Yeldham	52.01649	0.56167
C2 - River Colne Tributary Highfields Close Great Yeldham	52.01452	0.56480
C3 - Toppesfield Brook A604 Road	52.00995	0.56619
C4 - River Colne Langley Mill	51.93651	0.66845
C5 - Bourne Brook Nightingale Hall Farm	51.92236	0.66872
C6 - River Colne Earls Colne	51.92774	0.71318

Table B 2 Regulatory metaldehyde concentration data for sites REG1-REG3.

Sampling date	Metaldehyde concentration (μg L^{-1}) at REG1	Sampling date	Metaldehyde concentration (μg L^{-1}) at REG2	Sampling date	Metaldehyde concentration (μg L^{-1}) at REG3
09/06/2008	0.014	09/06/2008	0.025	17/06/2008	0.043
17/06/2008	0.017	17/06/2008	0.039	24/06/2008	0.03
24/06/2008	0.012	24/06/2008	0.032	02/07/2008	0.034
02/07/2008	0.023	02/07/2008	0.031	02/09/2008	0.044
02/09/2008	0.021	02/09/2008	0.031	16/09/2008	2.63
16/09/2008	0.05	16/09/2008	0.187	23/09/2008	0.893
23/09/2008	0.086	23/09/2008	0.134	01/10/2008	0.253
01/10/2008	0.075	01/10/2008	0.179	07/10/2008	0.156
07/10/2008	0.079	07/10/2008	0.304	14/10/2008	0.207
14/10/2008	0.093	14/10/2008	0.31	21/10/2008	1.21
21/10/2008	0.075	21/10/2008	0.183	22/10/2008	1.18
22/10/2008	0.07	22/10/2008	0.19	28/10/2008	0.639
28/10/2008	0.105	28/10/2008	0.242	04/11/2008	0.275
29/10/2008	0.096	29/10/2008	0.235	11/11/2008	1.71
04/11/2008	0.111	04/11/2008	0.164	18/11/2008	0.832
11/11/2008	0.114	11/11/2008	0.118	19/11/2008	0.693
18/11/2008	0.107	18/11/2008	0.175	25/11/2008	0.44
25/11/2008	0.123	18/11/2008	0.151	02/12/2008	1.75
02/12/2008	0.101	25/11/2008	0.149	09/12/2008	0.601

09/12/2008	0.083	02/12/2008	0.061	16/12/2008	0.744
16/12/2008	0.062	09/12/2008	0.067	23/12/2008	0.187
23/12/2008	0.049	16/12/2008	0.042	30/12/2008	0.108
30/12/2008	0.036	23/12/2008	0.043	07/01/2009	0.116
07/01/2009	0.048	30/12/2008	0.045	13/01/2009	0.095
13/01/2009	0.042	07/01/2009	0.036	20/01/2009	0.262
20/01/2009	0.026	13/01/2009	0.049	27/01/2009	0.11
27/01/2009	0.024	20/01/2009	0.033	03/02/2009	0.063
03/02/2009	0.02	27/01/2009	0.02	10/02/2009	0.04
10/02/2009	0.017	03/02/2009	0.026	17/02/2009	0.039
17/02/2009	0.016	10/02/2009	0.017	24/02/2009	0.047
24/02/2009	0.035	17/02/2009	0.016	03/03/2009	0.029
03/03/2009	0.015	24/02/2009	0.04	10/03/2009	0.037
10/03/2009	0.007	03/03/2009	0.016	17/03/2009	0.027
17/03/2009	0.005	10/03/2009	0.023	24/03/2009	0.027
24/03/2009	0.012	17/03/2009	0.013	31/03/2009	0.024
31/03/2009	0.015	24/03/2009	0.021	06/04/2009	0.037
06/04/2009	0.025	31/03/2009	0.021	14/04/2009	0.029
14/04/2009	0.015	06/04/2009	0.034	21/04/2009	0.005
21/04/2009	0.005	14/04/2009	0.024	28/04/2009	0.027
28/04/2009	0.016	21/04/2009	0.006	05/05/2009	0.025
05/05/2009	0.016	28/04/2009	0.026	12/05/2009	0.022
12/05/2009	0.014	05/05/2009	0.027	19/05/2009	0.023
19/05/2009	0.015	12/05/2009	0.022	26/05/2009	0.005
26/05/2009	0.005	19/05/2009	0.028	02/06/2009	0.014
02/06/2009	0.006	26/05/2009	0.005	09/06/2009	0.027
09/06/2009	0.021	02/06/2009	0.005	15/06/2009	0.085
15/06/2009	0.021	09/06/2009	0.037	23/06/2009	0.021
23/06/2009	0.044	15/06/2009	0.035	30/06/2009	0.031
30/06/2009	0.023	23/06/2009	0.037	07/07/2009	0.024
07/07/2009	0.025	30/06/2009	0.029	14/07/2009	0.031
14/07/2009	0.023	07/07/2009	0.034	21/07/2009	0.037
21/07/2009	0.022	14/07/2009	0.028	28/07/2009	0.023
28/07/2009	0.021	21/07/2009	0.028	04/08/2009	0.019
04/08/2009	0.025	28/07/2009	0.029	11/08/2009	0.019
11/08/2009	0.02	04/08/2009	0.034	18/08/2009	0.018
18/08/2009	0.019	11/08/2009	0.025	25/08/2009	0.019
25/08/2009	0.019	18/08/2009	0.027	01/09/2009	0.028
01/09/2009	0.026	25/08/2009	0.026	08/09/2009	0.025
08/09/2009	0.025	01/09/2009	0.021	15/09/2009	0.03
15/09/2009	0.024	08/09/2009	0.029	22/09/2009	0.035
22/09/2009	0.035	15/09/2009	0.027	29/09/2009	0.045
29/09/2009	0.036	22/09/2009	0.088	06/10/2009	0.031
06/10/2009	0.039	29/09/2009	0.074	13/10/2009	0.036
13/10/2009	0.051	06/10/2009	0.075	20/10/2009	0.048
20/10/2009	0.054	13/10/2009	0.092	27/10/2009	0.046
27/10/2009	0.067	20/10/2009	0.087	03/11/2009	0.064
03/11/2009	0.069	27/10/2009	0.097	10/11/2009	0.043
10/11/2009	0.061	03/11/2009	0.113	17/11/2009	0.047
17/11/2009	0.044	10/11/2009	0.097	24/11/2009	0.046
24/11/2009	0.058	17/11/2009	0.041	01/12/2009	0.058
01/12/2009	0.048	24/11/2009	0.052	08/12/2009	0.036

08/12/2009	0.026	01/12/2009	0.031	15/12/2009	0.022
15/12/2009	0.022	08/12/2009	0.021	22/12/2009	0.021
22/12/2009	0.02	15/12/2009	0.018	29/12/2009	0.023
29/12/2009	0.019	22/12/2009	0.017	05/01/2010	0.023
05/01/2010	0.019	29/12/2009	0.016	12/01/2010	0.017
12/01/2010	0.016	05/01/2010	0.015	19/01/2010	0.02
19/01/2010	0.014	12/01/2010	0.013	26/01/2010	0.019
26/01/2010	0.014	19/01/2010	0.013	02/02/2010	0.018
02/02/2010	0.015	26/01/2010	0.014	09/02/2010	0.015
09/02/2010	0.012	02/02/2010	0.012	16/02/2010	0.014
16/02/2010	0.011	09/02/2010	0.011	23/02/2010	0.017
23/02/2010	0.011	16/02/2010	0.011	02/03/2010	0.012
02/03/2010	0.01	23/02/2010	0.009	09/03/2010	0.015
09/03/2010	0.011	02/03/2010	0.01	16/03/2010	0.013
16/03/2010	0.01	09/03/2010	0.009	23/03/2010	0.012
23/03/2010	0.01	16/03/2010	0.009	30/03/2010	0.011
30/03/2010	0.005	23/03/2010	0.009	06/04/2010	0.011
06/04/2010	0.009	30/03/2010	0.01	13/04/2010	0.011
13/04/2010	0.008	06/04/2010	0.009	20/04/2010	0.01
20/04/2010	0.008	13/04/2010	0.009	27/04/2010	0.011
27/04/2010	0.01	20/04/2010	0.009	04/05/2010	0.013
04/05/2010	0.009	27/04/2010	0.009	11/05/2010	0.013
11/05/2010	0.007	04/05/2010	0.03	18/05/2010	0.013
18/05/2010	0.007	11/05/2010	0.024	25/05/2010	0.011
25/05/2010	0.007	18/05/2010	0.016	01/06/2010	0.013
01/06/2010	0.008	25/05/2010	0.012	08/06/2010	0.016
08/06/2010	0.008	01/06/2010	0.015	15/06/2010	0.019
15/06/2010	0.008	08/06/2010	0.015	22/06/2010	0.015
22/06/2010	0.007	15/06/2010	0.015	29/06/2010	0.014
29/06/2010	0.008	22/06/2010	0.014	06/07/2010	0.014
06/07/2010	0.01	29/06/2010	0.014	13/07/2010	0.015
13/07/2010	0.009	06/07/2010	0.013	20/07/2010	0.014
20/07/2010	0.009	13/07/2010	0.013	27/07/2010	0.01
27/07/2010	0.013	20/07/2010	0.013	03/08/2010	0.012
03/08/2010	0.007	27/07/2010	0.014	11/08/2010	0.015
11/08/2010	0.021	03/08/2010	0.014	17/08/2010	0.011
17/08/2010	0.013	11/08/2010	0.014	25/08/2010	0.014
25/08/2010	0.012	17/08/2010	0.019	31/08/2010	0.035
31/08/2010	0.014	25/08/2010	0.017	07/09/2010	0.039
07/09/2010	0.017	31/08/2010	0.024	14/09/2010	0.02
14/09/2010	0.021	07/09/2010	0.027	21/09/2010	0.025
21/09/2010	0.023	14/09/2010	0.034	28/09/2010	0.036
28/09/2010	0.028	21/09/2010	0.044	05/10/2010	0.074
05/10/2010	0.036	28/09/2010	0.06	12/10/2010	0.058
12/10/2010	0.035	05/10/2010	0.068	19/10/2010	0.04
19/10/2010	0.036	12/10/2010	0.042	26/10/2010	0.038
26/10/2010	0.037	19/10/2010	0.039	02/11/2010	0.04
02/11/2010	0.04	26/10/2010	0.042	10/11/2010	0.068
10/11/2010	0.04	02/11/2010	0.058	16/11/2010	0.244
16/11/2010	0.036	10/11/2010	0.048	23/11/2010	0.188
23/11/2010	0.031	16/11/2010	0.032	30/11/2010	0.116
30/11/2010	0.028	23/11/2010	0.023	07/12/2010	0.059

07/12/2010	0.026	30/11/2010	0.019	14/12/2010	0.098
14/12/2010	0.022	07/12/2010	0.027	21/12/2010	0.013
21/12/2010	0.018	14/12/2010	0.016	29/12/2010	0.046
29/12/2010	0.014	21/12/2010	0.072	04/01/2011	0.014
04/01/2011	0.014	29/12/2010	0.012	11/01/2011	0.027
11/01/2011	0.01	04/01/2011	0.014	18/01/2011	0.014
18/01/2011	0.01	11/01/2011	0.024	25/01/2011	0.024
25/01/2011	0.012	18/01/2011	0.008	01/02/2011	0.017
01/02/2011	0.008	25/01/2011	0.01	08/02/2011	0.01
08/02/2011	0.007	01/02/2011	0.008	15/02/2011	0.015
15/02/2011	0.008	08/02/2011	0.005	22/02/2011	0.014
22/02/2011	0.009	15/02/2011	0.008	01/03/2011	0.016
01/03/2011	0.009	22/02/2011	0.01	08/03/2011	0.011
08/03/2011	0.008	01/03/2011	0.01	15/03/2011	0.013
15/03/2011	0.01	08/03/2011	0.007	22/03/2011	0.013
22/03/2011	0.011	15/03/2011	0.011	29/03/2011	0.013
29/03/2011	0.009	22/03/2011	0.011	05/04/2011	0.015
05/04/2011	0.01	29/03/2011	0.011	12/04/2011	0.185
12/04/2011	0.009	05/04/2011	0.012	19/04/2011	0.014
19/04/2011	0.01	12/04/2011	0.012	26/04/2011	0.016
26/04/2011	0.01	19/04/2011	0.011	03/05/2011	0.013
03/05/2011	0.006	26/04/2011	0.012	10/05/2011	0.013
10/05/2011	0.008	03/05/2011	0.013	17/05/2011	0.012
17/05/2011	0.006	10/05/2011	0.014	24/05/2011	0.005
24/05/2011	0.005	17/05/2011	0.01	31/05/2011	0.007
31/05/2011	0.005	24/05/2011	0.006	07/06/2011	0.016
07/06/2011	0.005	31/05/2011	0.014	14/06/2011	0.008
14/06/2011	0.005	07/06/2011	0.013	21/06/2011	0.01
21/06/2011	0.005	14/06/2011	0.009	28/06/2011	0.011
28/06/2011	0.01	21/06/2011	0.012	05/07/2011	0.012
05/07/2011	0.009	28/06/2011	0.018	12/07/2011	0.006
12/07/2011	0.006	05/07/2011	0.016	19/07/2011	0.009
19/07/2011	0.006	12/07/2011	0.017	26/07/2011	0.02
26/07/2011	0.01	19/07/2011	0.012	02/08/2011	0.006
02/08/2011	0.005	26/07/2011	0.011	09/08/2011	0.009
09/08/2011	0.008	02/08/2011	0.005	16/08/2011	0.007
16/08/2011	0.005	09/08/2011	0.011	23/08/2011	0.005
23/08/2011	0.005	16/08/2011	0.008	30/08/2011	0.018
30/08/2011	0.007	23/08/2011	0.007	06/09/2011	0.036
06/09/2011	0.021	30/08/2011	0.019	13/09/2011	0.035
13/09/2011	0.025	06/09/2011	0.031	20/09/2011	0.03
20/09/2011	0.025	13/09/2011	0.044	27/09/2011	0.019
27/09/2011	0.024	20/09/2011	0.045	04/10/2011	0.025
04/10/2011	0.026	27/09/2011	0.04	11/10/2011	0.057
11/10/2011	0.033	04/10/2011	0.037	18/10/2011	0.036
18/10/2011	0.03	11/10/2011	0.094	25/10/2011	0.028
25/10/2011	0.035	18/10/2011	0.078	01/11/2011	0.024
01/11/2011	0.039	25/10/2011	0.074	08/11/2011	0.038
08/11/2011	0.044	01/11/2011	0.069	15/11/2011	0.034
15/11/2011	0.037	08/11/2011	0.07	22/11/2011	0.017
22/11/2011	0.035	15/11/2011	0.065	29/11/2011	0.022
29/11/2011	0.051	22/11/2011	0.048	06/12/2011	0.019

06/12/2011	0.047	29/11/2011	0.045	13/12/2011	0.024
13/12/2011	0.043	06/12/2011	0.052	20/12/2011	0.031
20/12/2011	0.046	13/12/2011	0.037	03/01/2012	0.027
03/01/2012	0.03	20/12/2011	0.03	11/01/2012	0.031
11/01/2012	0.031	03/01/2012	0.014	17/01/2012	0.018
17/01/2012	0.029	11/01/2012	0.017	24/01/2012	0.026
24/01/2012	0.026	17/01/2012	0.014	31/01/2012	0.014
31/01/2012	0.02	24/01/2012	0.016	07/02/2012	0.009
07/02/2012	0.019	31/01/2012	0.011	14/02/2012	0.01
14/02/2012	0.021	07/02/2012	0.007	21/02/2012	0.011
21/02/2012	0.014	14/02/2012	0.01	28/02/2012	0.012
28/02/2012	0.017	21/02/2012	0.009	07/03/2012	0.008
07/03/2012	0.012	28/02/2012	0.012	13/03/2012	0.01
13/03/2012	0.011	07/03/2012	0.008	21/03/2012	0.007
21/03/2012	0.011	13/03/2012	0.008	27/03/2012	0.007
27/03/2012	0.012	21/03/2012	0.008	03/04/2012	0.006
03/04/2012	0.009	27/03/2012	0.007	10/04/2012	0.01
10/04/2012	0.009	03/04/2012	0.007	17/04/2012	0.009
17/04/2012	0.011	10/04/2012	0.003	24/04/2012	0.009
24/04/2012	0.012	17/04/2012	0.011	01/05/2012	0.093
01/05/2012	0.01	24/04/2012	0.014	08/05/2012	0.018
08/05/2012	0.009	01/05/2012	0.011	15/05/2012	0.039
15/05/2012	0.008	08/05/2012	0.009	22/05/2012	0.021
22/05/2012	0.01	15/05/2012	0.01	29/05/2012	0.018
29/05/2012	0.01	22/05/2012	0.01	05/06/2012	0.019
05/06/2012	0.009	29/05/2012	0.01	12/06/2012	0.04
12/06/2012	0.011	05/06/2012	0.014	19/06/2012	0.051
19/06/2012	0.011	12/06/2012	0.021	26/06/2012	0.063
26/06/2012	0.011	19/06/2012	0.014	03/07/2012	0.077
03/07/2012	0.016	26/06/2012	0.017	10/07/2012	0.094
10/07/2012	0.016	03/07/2012	0.016	17/07/2012	0.079
17/07/2012	0.02	10/07/2012	0.031	24/07/2012	0.043
24/07/2012	0.014	17/07/2012	0.269	31/07/2012	0.025
31/07/2012	0.015	24/07/2012	0.077	07/08/2012	0.028
07/08/2012	0.015	31/07/2012	0.035	14/08/2012	0.032
14/08/2012	0.014	07/08/2012	0.029	21/08/2012	0.02
21/08/2012	0.015	14/08/2012	0.023	28/08/2012	0.029
28/08/2012	0.02	21/08/2012	0.025	04/09/2012	0.035
04/09/2012	0.034	28/08/2012	0.036	11/09/2012	0.025
11/09/2012	0.022	04/09/2012	0.045	18/09/2012	0.04
18/09/2012	0.027	11/09/2012	0.029	25/09/2012	0.043
25/09/2012	0.04	18/09/2012	0.051	03/10/2012	0.238
03/10/2012	0.087	25/09/2012	0.311	09/10/2012	4.05
09/10/2012	0.095	03/10/2012	0.755	16/10/2012	1.1
16/10/2012	0.057	09/10/2012	2	23/10/2012	4.62
23/10/2012	0.057	16/10/2012	0.63	30/10/2012	0.921
30/10/2012	0.057	23/10/2012	0.997	06/11/2012	6.78
06/11/2012	0.061	30/10/2012	0.198	13/11/2012	0.803
13/11/2012	0.052	06/11/2012	0.256	20/11/2012	0.365
20/11/2012	0.041	13/11/2012	0.123	23/11/2012	0.575
27/11/2012	0.109	20/11/2012	0.082	27/11/2012	1.1
04/12/2012	0.074	27/11/2012	0.206	29/11/2012	1.06

11/12/2012	0.052	04/12/2012	0.13	04/12/2012	0.395
19/12/2012	0.049	11/12/2012	0.093	06/12/2012	0.468
27/12/2012	0.045	19/12/2012	0.074	11/12/2012	0.308
02/01/2013	0.039	27/12/2012	0.055	14/12/2012	0.201
08/01/2013	0.035	02/01/2013	0.049	18/12/2012	0.144
15/01/2013	0.03	08/01/2013	0.036	19/12/2012	0.21
30/01/2013	0.026	15/01/2013	0.034	21/12/2012	0.182
07/02/2013	0.026	22/01/2013	0.026	27/12/2012	0.278
15/02/2013	0.027	30/01/2013	0.038	02/01/2013	0.131
19/02/2013	0.027	07/02/2013	0.028	08/01/2013	0.081
26/02/2013	0.023	15/02/2013	0.05	11/01/2013	0.077
04/03/2013	0.021	19/02/2013	0.044	15/01/2013	0.066
14/03/2013	0.019	26/02/2013	0.028	22/01/2013	0.053
22/03/2013	0.02	04/03/2013	0.027	23/01/2013	0.049
25/03/2013	0.021	14/03/2013	0.031	29/01/2013	0.136
02/04/2013	0.017	22/03/2013	0.024	30/01/2013	0.089
10/04/2013	0.016	25/03/2013	0.022	04/02/2013	0.061
15/04/2013	0.016	02/04/2013	0.024	07/02/2013	0.046
23/04/2013	0.02	10/04/2013	0.019	12/02/2013	0.091
01/05/2013	0.016	17/04/2013	0.023	15/02/2013	0.11
10/05/2013	0.017	23/04/2013	0.024	19/02/2013	0.078
17/05/2013	0.03	01/05/2013	0.081	20/02/2013	0.067
20/05/2013	0.016	10/05/2013	0.045	26/02/2013	0.042
30/05/2013	0.028	17/05/2013	0.033	28/02/2013	0.04
06/06/2013	0.027	20/05/2013	0.029	04/03/2013	0.034
12/06/2013	0.027	30/05/2013	0.026	07/03/2013	0.033
21/06/2013	0.033	06/06/2013	0.025	12/03/2013	0.21
24/06/2013	0.028	12/06/2013	0.025	14/03/2013	0.221
02/07/2013	0.026	21/06/2013	0.021	18/03/2013	0.208
10/07/2013	0.035	24/06/2013	0.034	22/03/2013	0.167
18/07/2013	0.021	02/07/2013	0.033	25/03/2013	0.108
26/07/2013	0.019	10/07/2013	0.027	26/03/2013	0.137
29/07/2013	0.018	18/07/2013	0.017	02/04/2013	0.088
06/08/2013	0.018	26/07/2013	0.017	03/04/2013	0.077
16/08/2013	0.019	29/07/2013	0.018	10/04/2013	0.051
22/08/2013	0.018	06/08/2013	0.015	12/04/2013	0.04
30/08/2013	0.022	16/08/2013	0.09	15/04/2013	0.046
02/09/2013	0.021	22/08/2013	0.03	17/04/2013	0.112
10/09/2013	0.024	30/08/2013	0.034	23/04/2013	0.041
19/09/2013	0.175	02/09/2013	0.032	25/04/2013	0.038
26/09/2013	0.058	10/09/2013	0.031	30/04/2013	0.042
04/10/2013	0.058	18/09/2013	0.049	01/05/2013	0.039
07/10/2013	0.063	26/09/2013	0.164	08/05/2013	0.031
16/10/2013	0.078	04/10/2013	0.118	10/05/2013	0.029
24/10/2013	0.077	07/10/2013	0.134	13/05/2013	0.027
29/10/2013	0.083	16/10/2013	0.093	17/05/2013	0.028
08/11/2013	0.055	24/10/2013	0.092	20/05/2013	0.027
11/11/2013	0.049	30/10/2013	0.059	21/05/2013	0.028
19/11/2013	0.042	08/11/2013	0.035	29/05/2013	0.035
29/11/2013	0.033	11/11/2013	0.028	29/05/2013	0.032
05/12/2013	0.03	19/11/2013	0.022	06/06/2013	0.029
16/12/2013	0.03	29/11/2013	0.018	07/06/2013	0.025

06/01/2014	0.018	05/12/2013	0.015	10/06/2013	0.027
14/01/2014	0.016	16/12/2013	0.02	12/06/2013	0.023
30/01/2014	0.015	06/01/2014	0.013	17/06/2013	0.022
10/02/2014	0.012	14/01/2014	0.013	21/06/2013	0.021
18/02/2014	0.011	30/01/2014	0.01	24/06/2013	0.031
26/02/2014	0.011	10/02/2014	0.01	26/06/2013	0.027
06/03/2014	0.011	18/02/2014	0.008	02/07/2013	0.028
14/03/2014	0.01	26/02/2014	0.012	04/07/2013	0.036
17/03/2014	0.01	06/03/2014	0.009	10/07/2013	0.02
25/03/2014	0.009	14/03/2014	0.011	11/07/2013	0.019
02/04/2014	0.008	17/03/2014	0.012	18/07/2013	0.023
10/04/2014	0.01	25/03/2014	0.015	19/07/2013	0.024
17/04/2014	0.008	02/04/2014	0.011	23/07/2013	0.019
25/04/2014	0.011	10/04/2014	0.012	26/07/2013	0.015
29/04/2014	0.008	17/04/2014	0.015	29/07/2013	0.013
06/05/2014	0.009	25/04/2014	0.014	30/07/2013	0.015
15/05/2014	0.01	29/04/2014	0.013	06/08/2013	0.012
23/05/2014	0.011	06/05/2014	0.014	12/08/2013	0.013
30/05/2014	0.022	15/05/2014	0.019	16/08/2013	0.013
03/06/2014	0.018	23/05/2014	0.016	19/08/2013	0.019
11/06/2014	0.018	30/05/2014	0.015	22/08/2013	0.016
19/06/2014	0.021	03/06/2014	0.016	27/08/2013	0.06
27/06/2014	0.022	11/06/2014	0.022	30/08/2013	0.048
30/06/2014	0.02	19/06/2014	0.021	02/09/2013	0.028
08/07/2014	0.022	27/06/2014	0.018	04/09/2013	0.024
16/07/2014	0.02	30/06/2014	0.019	10/09/2013	0.022
24/07/2014	0.02	08/07/2014	0.019	12/09/2013	0.019
01/08/2014	0.019	16/07/2014	0.016	18/09/2013	0.111
04/08/2014	0.017	24/07/2014	0.017	19/09/2013	0.134
12/08/2014	0.02	01/08/2014	0.016	23/09/2013	0.09
20/08/2014	0.022	04/08/2014	0.016	26/09/2013	0.063
26/08/2014	0.023	12/08/2014	0.016	03/10/2013	0.059
03/09/2014	0.025	20/08/2014	0.024	04/10/2013	0.049
19/09/2014	0.03	26/08/2014	0.023	07/10/2013	0.056
22/09/2014	0.031	03/09/2014	0.027	09/10/2013	0.054
08/10/2014	0.042	19/09/2014	0.034	15/10/2013	0.334
16/10/2014	0.084	22/09/2014	0.057	16/10/2013	0.445
24/10/2014	0.086	08/10/2014	0.09	24/10/2013	0.151
27/10/2014	0.082	16/10/2014	0.176	25/10/2013	0.215
04/11/2014	0.092	24/10/2014	0.104	28/10/2013	0.082
12/11/2014	0.087	27/10/2014	0.073	29/10/2013	0.1
20/11/2014	0.081	04/11/2014	0.087	03/11/2013	0.113
25/11/2014	0.071	12/11/2014	0.063	04/11/2013	0.089
01/12/2014	0.047	20/11/2014	0.06	08/11/2013	0.093
09/12/2014	0.037	25/11/2014	0.061	10/11/2013	0.107
10/12/2014	0.039	01/12/2014	0.044	11/11/2013	0.107
17/12/2014	0.031	09/12/2014	0.03	12/11/2013	0.116
19/12/2014	0.03	10/12/2014	0.028	14/11/2013	0.072
23/12/2014	0.025	17/12/2014	0.028	19/11/2013	0.045
30/12/2014	0.023	19/12/2014	0.031	20/11/2013	0.041
02/01/2015	0.022	23/12/2014	0.023	24/11/2013	0.036
06/01/2015	0.024	30/12/2014	0.02	28/11/2013	0.03

09/01/2015	0.026	02/01/2015	0.019	29/11/2013	0.032
13/01/2015	0.017	06/01/2015	0.022	01/12/2013	0.032
15/01/2015	0.022	09/01/2015	0.026	02/12/2013	0.034
21/01/2015	0.02	13/01/2015	0.02	05/12/2013	0.021
23/01/2015	0.02	15/01/2015	0.022	08/12/2013	0.019
27/01/2015	0.023	21/01/2015	0.019	09/12/2013	0.02
30/01/2015	0.021	23/01/2015	0.017	15/12/2013	0.019
05/02/2015	0.022	27/01/2015	0.024	16/12/2013	0.024
11/02/2015	0.016	30/01/2015	0.025	17/12/2013	0.016
17/02/2015	0.015	05/02/2015	0.022	22/12/2013	0.059
24/02/2015	0.014	11/02/2015	0.015	06/01/2014	0.021
03/03/2015	0.013	17/02/2015	0.015	07/01/2014	0.029
12/03/2015	0.013	24/02/2015	0.015	14/01/2014	0.018
20/03/2015	0.011	03/03/2015	0.013	15/01/2014	0.015
28/03/2015	0.009	12/03/2015	0.015	22/01/2014	0.014
31/03/2015	0.011	20/03/2015	0.013	23/01/2014	0.013
09/04/2015	0.011	28/03/2015	0.011	30/01/2014	0.014
15/04/2015	0.01	31/03/2015	0.014	10/02/2014	0.009
23/04/2015	0.01	09/04/2015	0.012	18/02/2014	0.01
27/04/2015	0.01	15/04/2015	0.011	26/02/2014	0.012
08/05/2015	0.008	23/04/2015	0.012	06/03/2014	0.026
14/05/2015	0.013	27/04/2015	0.014	14/03/2014	0.011
20/05/2015	0.011	08/05/2015	0.016	17/03/2014	0.013
28/05/2015	0.012	14/05/2015	0.019	25/03/2014	0.01
04/06/2015	0.014	20/05/2015	0.017	10/04/2014	0.01
08/06/2015	0.016	28/05/2015	0.019	17/04/2014	0.011
16/06/2015	0.022	04/06/2015	0.02	25/04/2014	0.008
23/06/2015	0.02	08/06/2015	0.027	29/04/2014	0.009
01/07/2015	0.02	16/06/2015	0.019	06/05/2014	0.01
06/07/2015	0.017	23/06/2015	0.022	15/05/2014	0.021
13/07/2015	0.014	01/07/2015	0.022	23/05/2014	0.014
22/07/2015	0.014	06/07/2015	0.019	30/05/2014	0.028
29/07/2015	0.01	13/07/2015	0.016	03/06/2014	0.053
03/08/2015	0.012	22/07/2015	0.016	05/06/2014	0.055
06/08/2015	0.013	29/07/2015	0.009	11/06/2014	0.023
10/08/2015	0.011	03/08/2015	0.011	19/06/2014	0.018
15/08/2015	0.013	06/08/2015	0.011	27/06/2014	0.016
17/08/2015	0.013	10/08/2015	0.009	30/06/2014	0.02
19/08/2015	0.015	15/08/2015	0.011	08/07/2014	0.016
25/08/2015	0.016	17/08/2015	0.011	16/07/2014	0.021
27/08/2015	0.018	19/08/2015	0.016	24/07/2014	0.02
01/09/2015	0.024	25/08/2015	0.02	01/08/2014	0.017
03/09/2015	0.027	27/08/2015	0.023	04/08/2014	0.028
07/09/2015	0.041	01/09/2015	0.036	12/08/2014	0.017
09/09/2015	0.027	03/09/2015	0.051	20/08/2014	0.017
15/09/2015	0.031	07/09/2015	0.069	26/08/2014	0.02
18/09/2015	0.032	09/09/2015	0.049	02/09/2014	0.651
21/09/2015	0.036	15/09/2015	0.061	03/09/2014	0.751
24/09/2015	0.037	18/09/2015	0.065	08/09/2014	0.235
29/09/2015	0.037	21/09/2015	0.108	16/09/2014	0.062
03/10/2015	0.037	24/09/2015	0.082	19/09/2014	0.046
06/10/2015	0.039	25/09/2015	0.033	22/09/2014	0.041

08/10/2015	0.04	25/09/2015	0.042	24/09/2014	0.042
13/10/2015	0.042	25/09/2015	0.024	01/10/2014	0.103
15/10/2015	0.048	25/09/2015	0.048	02/10/2014	0.126
20/10/2015	0.045	25/09/2015	0.015	08/10/2014	0.121
22/10/2015	0.049	29/09/2015	0.055	10/10/2014	0.304
26/10/2015	0.041	03/10/2015	0.043	13/10/2014	0.285
28/10/2015	0.069	06/10/2015	0.043	16/10/2014	2.02
02/11/2015	0.087	08/10/2015	0.045	21/10/2014	0.512
04/11/2015	0.089	13/10/2015	0.048	24/10/2014	0.272
10/11/2015	0.142	15/10/2015	0.054	27/10/2014	0.211
13/11/2015	0.082	20/10/2015	0.055	30/10/2014	0.175
17/11/2015	0.073	22/10/2015	0.07	04/11/2014	0.118
19/11/2015	0.065	26/10/2015	0.07	07/11/2014	0.135
25/11/2015	0.068	28/10/2015	0.076	10/11/2014	0.153
27/11/2015	0.06	02/11/2015	0.161	11/11/2014	0.428
30/11/2015	0.071	04/11/2015	0.155	12/11/2014	0.51
03/12/2015	0.077	10/11/2015	0.228	13/11/2014	0.418
09/12/2015	0.044	13/11/2015	0.154	17/11/2014	0.355
11/12/2015	0.045	17/11/2015	0.068	17/11/2014	0.353
14/12/2015	0.037	19/11/2015	0.06	18/11/2014	0.316
17/12/2015	0.035	25/11/2015	0.064	20/11/2014	0.276
21/12/2015	0.037	27/11/2015	0.038	24/11/2014	0.188
23/12/2015	0.029	30/11/2015	0.045	25/11/2014	0.253
29/12/2015	0.029	03/12/2015	0.047	26/11/2014	0.21
31/12/2015	0.027	09/12/2015	0.03	01/12/2014	0.076
05/01/2016	0.027	11/12/2015	0.031	03/12/2014	0.074
07/01/2016	0.023	14/12/2015	0.03	04/12/2014	0.045
12/01/2016	0.02	17/12/2015	0.03	09/12/2014	0.053
14/01/2016	0.021	21/12/2015	0.034	10/12/2014	0.048
18/01/2016	0.023	23/12/2015	0.026	12/12/2014	0.044
20/01/2016	0.019	29/12/2015	0.024	15/12/2014	0.04
25/01/2016	0.018	31/12/2015	0.024	17/12/2014	0.039
27/01/2016	0.019	05/01/2016	0.024	19/12/2014	0.066
04/02/2016	0.015	07/01/2016	0.023	23/12/2014	0.032
10/02/2016	0.009	12/01/2016	0.021	30/12/2014	0.03
15/02/2016	0.015	14/01/2016	0.022	02/01/2015	0.023
24/02/2016	0.018	18/01/2016	0.024	06/01/2015	0.025
01/03/2016	0.016	20/01/2016	0.019	09/01/2015	0.039
09/03/2016	0.012	25/01/2016	0.018	13/01/2015	0.019
14/03/2016	0.011	27/01/2016	0.018	15/01/2015	0.024
22/03/2016	0.013	04/02/2016	0.016	21/01/2015	0.018
24/03/2016	0.01	10/02/2016	0.009	23/01/2015	0.021
31/03/2016	0.014	15/02/2016	0.018	27/01/2015	0.027
07/04/2016	0.013	24/02/2016	0.02	30/01/2015	0.027
17/04/2016	0.017	01/03/2016	0.017	05/02/2015	0.023
18/04/2016	0.016	09/03/2016	0.013	11/02/2015	0.017
27/04/2016	0.014	14/03/2016	0.011	17/02/2015	0.017
05/05/2016	0.015	22/03/2016	0.012	24/02/2015	0.024
12/05/2016	0.017	24/03/2016	0.01	03/03/2015	0.016
16/05/2016	0.017	31/03/2016	0.014	12/03/2015	0.016
27/05/2016	0.014	07/04/2016	0.017	20/03/2015	0.016
31/05/2016	0.014	17/04/2016	0.024	28/03/2015	0.013

09/06/2016	0.018	18/04/2016	0.023	31/03/2015	0.014
17/06/2016	0.018	27/04/2016	0.018	10/04/2015	0.014
22/06/2016	0.082	05/05/2016	0.019	15/04/2015	0.012
27/06/2016	0.056	12/05/2016	0.019	23/04/2015	0.012
04/07/2016	0.039	16/05/2016	0.017	27/04/2015	0.012
13/07/2016	0.031	27/05/2016	0.029	08/05/2015	0.018
13/07/2016	0.032	31/05/2016	0.017	14/05/2015	0.014
15/07/2016	0.03	09/06/2016	0.016	20/05/2015	0.016
21/07/2016	0.027	17/06/2016	0.03	28/05/2015	0.013
29/07/2016	0.026	22/06/2016	0.037	04/06/2015	0.019
01/08/2016	0.027	27/06/2016	0.023	08/06/2015	0.018
03/08/2016	0.029	04/07/2016	0.019	16/06/2015	0.011
09/08/2016	0.028	13/07/2016	0.026	23/06/2015	0.016
11/08/2016	0.026	13/07/2016	0.029	01/07/2015	0.02
15/08/2016	0.026	15/07/2016	0.027	06/07/2015	0.029
18/08/2016	0.021	21/07/2016	0.024	13/07/2015	0.019
22/08/2016	0.024	29/07/2016	0.021	22/07/2015	0.016
25/08/2016	0.03	01/08/2016	0.023	29/07/2015	0.01
31/08/2016	0.028	03/08/2016	0.028	03/08/2015	0.012
02/09/2016	0.028	09/08/2016	0.026	06/08/2015	0.011
06/09/2016	0.029	11/08/2016	0.019	10/08/2015	0.008
08/09/2016	0.027	15/08/2016	0.022	15/08/2015	0.01
13/09/2016	0.029	18/08/2016	0.017	17/08/2015	0.01
15/09/2016	0.026	22/08/2016	0.019	19/08/2015	0.016
20/09/2016	0.099	25/08/2016	0.019	25/08/2015	0.013
22/09/2016	0.043	31/08/2016	0.039	27/08/2015	0.019
26/09/2016	0.047	02/09/2016	0.041	01/09/2015	0.048
28/09/2016	0.047	06/09/2016	0.042	03/09/2015	0.066
04/10/2016	0.049	08/09/2016	0.04	07/09/2015	0.104
07/10/2016	0.049	13/09/2016	0.04	09/09/2015	0.065
10/10/2016	0.044	15/09/2016	0.034	15/09/2015	0.1
12/10/2016	0.052	20/09/2016	0.068	18/09/2015	0.145
17/10/2016	0.054	22/09/2016	0.067	21/09/2015	0.116
19/10/2016	0.053	26/09/2016	0.059	23/09/2015	0.063
25/10/2016	0.057	28/09/2016	0.057	24/09/2015	0.063
27/10/2016	0.057	04/10/2016	0.05	29/09/2015	0.09
01/11/2016	0.06	07/10/2016	0.051	03/10/2015	0.059
03/11/2016	0.058	10/10/2016	0.047	06/10/2015	0.054
07/11/2016	0.059	12/10/2016	0.083	08/10/2015	0.038
09/11/2016	0.051	17/10/2016	0.069	13/10/2015	0.04
16/11/2016	0.105	19/10/2016	0.087	15/10/2015	0.049
18/11/2016	0.066	25/10/2016	0.108	21/10/2015	0.048
21/11/2016	0.067	27/10/2016	0.092	22/10/2015	0.036
24/11/2016	0.075	01/11/2016	0.084	26/10/2015	0.034
01/12/2016	0.074	03/11/2016	0.066	28/10/2015	0.04
03/12/2016	0.066	07/11/2016	0.078	02/11/2015	0.241
07/12/2016	0.058	09/11/2016	0.083	04/11/2015	0.055
11/12/2016	0.061	16/11/2016	0.124	10/11/2015	0.349
13/12/2016	0.064	18/11/2016	0.185	13/11/2015	0.131
15/12/2016	0.063	21/11/2016	0.087	17/11/2015	0.066
20/12/2016	0.058	24/11/2016	0.084	19/11/2015	0.243
23/12/2016	0.054	01/12/2016	0.048	25/11/2015	0.05

29/12/2016	0.053	03/12/2016	0.043	27/11/2015	0.203
30/12/2016	0.057	07/12/2016	0.031	30/11/2015	0.095
03/01/2017	0.051	11/12/2016	0.05	03/12/2015	0.055
05/01/2017	0.049	13/12/2016	0.061	09/12/2015	0.084
10/01/2017	0.05	15/12/2016	0.058	11/12/2015	0.042
12/01/2017	0.049	20/12/2016	0.043	14/12/2015	0.027
17/01/2017	0.04	23/12/2016	0.035	17/12/2015	0.052
20/01/2017	0.042	29/12/2016	0.043	21/12/2015	0.087
24/01/2017	0.042	30/12/2016	0.044	23/12/2015	0.038
31/01/2017	0.031	03/01/2017	0.041	29/12/2015	0.032
09/02/2017	0.027	05/01/2017	0.034	31/12/2015	0.029
16/02/2017	0.022	10/01/2017	0.033	05/01/2016	0.026
23/02/2017	0.02	12/01/2017	0.031	07/01/2016	0.022
28/02/2017	0.015	17/01/2017	0.024	12/01/2016	0.019
06/03/2017	0.014	20/01/2017	0.022	14/01/2016	0.03
16/03/2017	0.015	24/01/2017	0.018	18/01/2016	0.019
24/03/2017	0.014	31/01/2017	0.026	20/01/2016	0.018
31/03/2017	0.014	09/02/2017	0.02	25/01/2016	0.018
07/04/2017	0.014	16/02/2017	0.017	04/02/2016	0.015
13/04/2017	0.013	23/02/2017	0.017	10/02/2016	0.015
18/04/2017	0.013	28/02/2017	0.013	15/02/2016	0.019
20/04/2017	0.019	06/03/2017	0.013	24/02/2016	0.019
28/04/2017	0.02	16/03/2017	0.014	01/03/2016	0.017
05/05/2017	0.026	24/03/2017	0.015	09/03/2016	0.014
10/05/2017	0.032	31/03/2017	0.016	14/03/2016	0.015
11/05/2017	0.028	07/04/2017	0.013	22/03/2016	0.013
22/05/2017	0.013	13/04/2017	0.024	24/03/2016	0.01
01/06/2017	0.013	18/04/2017	0.018	31/03/2016	0.017
09/06/2017	0.013	20/04/2017	0.017	07/04/2016	0.016
12/06/2017	0.014	28/04/2017	0.022	17/04/2016	0.072
23/06/2017	0.012	05/05/2017	0.025	18/04/2016	0.051
27/06/2017	0.013	10/05/2017	0.02	27/04/2016	0.02
04/07/2017	0.012	11/05/2017	0.02	03/05/2016	0.02
14/07/2017	0.013	22/05/2017	0.022	05/05/2016	0.018
17/07/2017	0.015	01/06/2017	0.017	12/05/2016	0.017
25/07/2017	0.014	09/06/2017	0.033	16/05/2016	0.018
31/07/2017	0.015	12/06/2017	0.032	27/05/2016	0.016
02/08/2017	0.014	23/06/2017	0.023	31/05/2016	0.029
08/08/2017	0.014	27/06/2017	0.023	09/06/2016	0.044
11/08/2017	0.011	04/07/2017	0.013	17/06/2016	0.031
16/08/2017	0.013	14/07/2017	0.011	22/06/2016	0.101
18/08/2017	0.015	17/07/2017	0.012	27/06/2016	0.082
21/08/2017	0.012	25/07/2017	0.014	04/07/2016	0.056
22/08/2017	0.01	31/07/2017	0.015	13/07/2016	0.045
30/08/2017	0.013	02/08/2017	0.016	13/07/2016	0.044
01/09/2017	0.013	08/08/2017	0.017	15/07/2016	0.045
04/09/2017	0.018	11/08/2017	0.011	21/07/2016	0.039
07/09/2017	0.018	16/08/2017	0.01	29/07/2016	0.02
09/09/2017	0.022	18/08/2017	0.012	01/08/2016	0.022
14/09/2017	0.021	21/08/2017	0.014	03/08/2016	0.026
19/09/2017	0.028	22/08/2017	0.014	09/08/2016	0.021
21/09/2017	0.029	30/08/2017	0.017	11/08/2016	0.017

27/09/2017	0.031	01/09/2017	0.024	15/08/2016	0.018
29/09/2017	0.032	04/09/2017	0.026	18/08/2016	0.013
03/10/2017	0.032	07/09/2017	0.035	22/08/2016	0.017
05/10/2017	0.033	09/09/2017	0.039	25/08/2016	0.015
11/10/2017	0.036	14/09/2017	0.049	31/08/2016	0.039
13/10/2017	0.033	19/09/2017	0.082	02/09/2016	0.025
17/10/2017	0.035	21/09/2017	0.076	06/09/2016	0.024
20/10/2017	0.055	27/09/2017	0.065	08/09/2016	0.028
23/10/2017	0.039	29/09/2017	0.061	13/09/2016	0.02
25/10/2017	0.036	03/10/2017	0.066	15/09/2016	0.022
01/11/2017	0.037	05/10/2017	0.06	20/09/2016	0.063
03/11/2017	0.037	11/10/2017	0.056	22/09/2016	0.239
07/11/2017	0.039	13/10/2017	0.053	26/09/2016	2.28
09/11/2017	0.044	17/10/2017	0.048	28/09/2016	1.38
13/11/2017	0.046	20/10/2017	0.063	04/10/2016	0.445
15/11/2017	0.044	23/10/2017	0.071	07/10/2016	0.292
22/11/2017	0.04	25/10/2017	0.062	10/10/2016	0.153
24/11/2017	0.041	01/11/2017	0.053	12/10/2016	0.141
28/11/2017	0.043	03/11/2017	0.047	14/10/2016	0.126
30/11/2017	0.042	07/11/2017	0.086	17/10/2016	0.052
06/12/2017	0.038	09/11/2017	0.089	18/10/2016	0.059
08/12/2017	0.041	13/11/2017	0.078	19/10/2016	0.059
12/12/2017	0.037	15/11/2017	0.068	19/10/2016	0.056
14/12/2017	0.032	22/11/2017	0.047	20/10/2016	0.057
19/12/2017	0.03	24/11/2017	0.046	25/10/2016	0.044
21/12/2017	0.027	28/11/2017	0.05	26/10/2016	0.051
28/12/2017	0.024	30/11/2017	0.049	27/10/2016	0.051
29/12/2017	0.022	06/12/2017	0.036	27/10/2016	0.049
03/01/2018	0.018	08/12/2017	0.035	28/10/2016	0.048
05/01/2018	0.018	12/12/2017	0.018	01/11/2016	0.031
08/01/2018	0.016	14/12/2017	0.019	02/11/2016	0.046
11/01/2018	0.016	19/12/2017	0.018	03/11/2016	0.031
15/01/2018	0.011	21/12/2017	0.015	03/11/2016	0.035
18/01/2018	0.011	28/12/2017	0.018	04/11/2016	0.039
24/01/2018	0.009	29/12/2017	0.015	07/11/2016	0.038
26/01/2018	0.009	03/01/2018	0.015	07/11/2016	0.035
29/01/2018	0.009	05/01/2018	0.016	08/11/2016	0.039
01/02/2018	0.009	08/01/2018	0.014	09/11/2016	0.057
06/02/2018	0.01	11/01/2018	0.013	11/11/2016	0.051
09/02/2018	0.008	15/01/2018	0.01	14/11/2016	0.046
12/02/2018	0.01	18/01/2018	0.01	15/11/2016	0.044
20/02/2018	0.01	24/01/2018	0.01	16/11/2016	0.06
26/02/2018	0.009	26/01/2018	0.01	18/11/2016	0.08
07/03/2018	0.007	29/01/2018	0.009	18/11/2016	0.076
15/03/2018	0.009	01/02/2018	0.008	21/11/2016	0.085
23/03/2018	0.008	06/02/2018	0.011	22/11/2016	0.207
27/03/2018	0.006	09/02/2018	0.009	23/11/2016	1.96
05/04/2018	0.008	12/02/2018	0.01	24/11/2016	2.28
11/04/2018	0.007	20/02/2018	0.009	24/11/2016	2.25
23/04/2018	0.007	26/02/2018	0.01	28/11/2016	0.951
26/04/2018	0.006	07/03/2018	0.008	01/12/2016	0.513
01/05/2018	0.006	15/03/2018	0.008	01/12/2016	0.499

10/05/2018	0.007	23/03/2018	0.008	02/12/2016	0.487
18/05/2018	0.007	27/03/2018	0.006	05/12/2016	0.245
24/05/2018	0.008	05/04/2018	0.008	07/12/2016	0.196
29/05/2018	0.007	11/04/2018	0.007	07/12/2016	0.167
31/05/2018	0.007	20/04/2018	0.008	08/12/2016	0.19
08/06/2018	0.008	23/04/2018	0.008	09/12/2016	0.12
14/06/2018	0.011	01/05/2018	0.008	12/12/2016	0.119
15/06/2018	0.012	10/05/2018	0.009	13/12/2016	0.109
18/06/2018	0.008	18/05/2018	0.011	15/12/2016	0.089
21/06/2018	0.01	24/05/2018	0.01	15/12/2016	0.09
27/06/2018	0.009	29/05/2018	0.011	16/12/2016	0.091
29/06/2018	0.009	31/05/2018	0.01	19/12/2016	0.096
02/07/2018	0.008	08/06/2018	0.017	20/12/2016	0.101
10/07/2018	0.008	14/06/2018	0.018	21/12/2016	0.096
12/07/2018	0.009	15/06/2018	0.019	23/12/2016	0.074
17/07/2018	0.005	18/06/2018	0.016	23/12/2016	0.075
20/07/2018	0.01	21/06/2018	0.017	28/12/2016	0.062
23/07/2018	0.011	27/06/2018	0.014	29/12/2016	0.057
25/07/2018	0.024	29/06/2018	0.014	30/12/2016	0.056
31/07/2018	0.011	05/07/2018	0.013	03/01/2017	0.051
02/08/2018	0.012	10/07/2018	0.011	03/01/2017	0.053
07/08/2018	0.011	12/07/2018	0.011	05/01/2017	0.169
09/08/2018	0.01	17/07/2018	0.008	05/01/2017	0.15
14/08/2018	0.01	20/07/2018	0.012	06/01/2017	0.154
16/08/2018	0.011	23/07/2018	0.012	09/01/2017	0.084
21/08/2018	0.01	25/07/2018	0.01	10/01/2017	0.065
22/08/2018	0.01	31/07/2018	0.006	10/01/2017	0.067
29/08/2018	0.013	02/08/2018	0.007	12/01/2017	0.057
31/08/2018	0.014	07/08/2018	0.008	12/01/2017	0.053
04/09/2018	0.015	09/08/2018	0.011	13/01/2017	0.04
06/09/2018	0.017	14/08/2018	0.014	16/01/2017	0.109
11/09/2018	0.02	16/08/2018	0.014	17/01/2017	0.076
13/09/2018	0.021	21/08/2018	0.014	17/01/2017	0.074
17/09/2018	0.019	22/08/2018	0.014	18/01/2017	0.068
20/09/2018	0.019	29/08/2018	0.028	20/01/2017	0.064
25/09/2018	0.024	31/08/2018	0.028	24/01/2017	0.05
27/09/2018	0.019	04/09/2018	0.026	27/01/2017	0.039
03/10/2018	0.023	06/09/2018	0.026	31/01/2017	0.038
05/10/2018	0.021	11/09/2018	0.031	03/02/2017	0.077
08/10/2018	0.024	13/09/2018	0.032	09/02/2017	0.054
11/10/2018	0.024	17/09/2018	0.052	14/02/2017	0.041
15/10/2018	0.025	20/09/2018	0.043	16/02/2017	0.115
17/10/2018	0.029	25/09/2018	0.064	23/02/2017	0.03
23/10/2018	0.031	27/09/2018	0.048	28/02/2017	0.022
25/10/2018	0.032	03/10/2018	0.033	06/03/2017	0.019
30/10/2018	0.038	05/10/2018	0.031	16/03/2017	0.02
01/11/2018	0.031	08/10/2018	0.029	24/03/2017	0.016
06/11/2018	0.041	11/10/2018	0.031	31/03/2017	0.017
08/11/2018	0.039	15/10/2018	0.079	07/04/2017	0.015
14/11/2018	0.033	17/10/2018	0.078	13/04/2017	0.014
16/11/2018	0.032	23/10/2018	0.064	20/04/2017	0.013
19/11/2018	0.032	25/10/2018	0.073	28/04/2017	0.018

22/11/2018	0.03	30/10/2018	0.054	05/05/2017	0.013
26/11/2018	0.031	01/11/2018	0.044	10/05/2017	0.014
29/11/2018	0.029	06/11/2018	0.043	11/05/2017	0.013
03/12/2018	0.027	08/11/2018	0.033	22/05/2017	0.045
05/12/2018	0.027	14/11/2018	0.023	01/06/2017	0.02
11/12/2018	0.023	16/11/2018	0.021	09/06/2017	0.038
13/12/2018	0.022	19/11/2018	0.022	12/06/2017	0.029
19/12/2018	0.02	22/11/2018	0.03	23/06/2017	0.036
21/12/2018	0.019	26/11/2018	0.025	27/06/2017	0.023
24/12/2018	0.015	29/11/2018	0.019	04/07/2017	0.01
27/12/2018	0.014	03/12/2018	0.015	14/07/2017	0.039
02/01/2019	0.013	05/12/2018	0.014	17/07/2017	0.015
04/01/2019	0.014	11/12/2018	0.011	25/07/2017	0.016
08/01/2019	0.012	13/12/2018	0.01	31/07/2017	0.013
11/01/2019	0.012	19/12/2018	0.01	02/08/2017	0.017
14/01/2019	0.012	21/12/2018	0.008	08/08/2017	0.017
18/01/2019	0.011	24/12/2018	0.009	11/08/2017	0.175
22/01/2019	0.011	27/12/2018	0.009	16/08/2017	0.031
25/01/2019	0.011	02/01/2019	0.008	18/08/2017	0.026
30/01/2019	0.01	04/01/2019	0.008	18/08/2017	0.025
01/02/2019	0.01	08/01/2019	0.007	21/08/2017	0.021
04/02/2019	0.008	11/01/2019	0.008	22/08/2017	0.02
07/02/2019	0.008	14/01/2019	0.007	30/08/2017	0.021
11/02/2019	0.008	18/01/2019	0.007	01/09/2017	0.028
13/02/2019	0.009	22/01/2019	0.007	04/09/2017	0.038
18/02/2019	0.008	25/01/2019	0.007	07/09/2017	0.023
22/02/2019	0.007	30/01/2019	0.007	08/09/2017	0.019
25/02/2019	0.007	01/02/2019	0.007	12/09/2017	0.03
01/03/2019	0.007	04/02/2019	0.007	13/09/2017	0.038
04/03/2019	0.006	07/02/2019	0.007	14/09/2017	0.042
08/03/2019	0.006	11/02/2019	0.007	15/09/2017	0.039
13/03/2019	0.006	13/02/2019	0.007	18/09/2017	0.06
15/03/2019	0.006	18/02/2019	0.007	19/09/2017	0.077
18/03/2019	0.006	22/02/2019	0.007	20/09/2017	0.042
22/03/2019	0.005	25/02/2019	0.006	21/09/2017	0.045
26/03/2019	0.006	01/03/2019	0.008	22/09/2017	0.042
29/03/2019	0.005	04/03/2019	0.006	25/09/2017	0.04
03/04/2019	0.006	08/03/2019	0.006	26/09/2017	0.036
05/04/2019	0.005	13/03/2019	0.006	27/09/2017	0.038
10/04/2019	0.006	15/03/2019	0.006	28/09/2017	0.034
12/04/2019	0.005	18/03/2019	0.007	29/09/2017	0.028
15/04/2019	0.005	22/03/2019	0.007	02/10/2017	0.028
18/04/2019	0.005	26/03/2019	0.006	03/10/2017	0.026
23/04/2019	0.006	29/03/2019	0.006	04/10/2017	0.022
26/04/2019	0.006	03/04/2019	0.006	05/10/2017	0.024
29/04/2019	0.006	05/04/2019	0.009	06/10/2017	0.026
01/05/2019	0.006	10/04/2019	0.008	09/10/2017	0.036
09/05/2019	0.006	12/04/2019	0.008	10/10/2017	0.043
10/05/2019	0.007	15/04/2019	0.008	11/10/2017	0.033
13/05/2019	0.008	18/04/2019	0.007	12/10/2017	0.03
17/05/2019	0.008	23/04/2019	0.007	13/10/2017	0.027
20/05/2019	0.008	26/04/2019	0.008	16/10/2017	0.022

24/05/2019	0.008	29/04/2019	0.008	17/10/2017	0.022
28/05/2019	0.013	01/05/2019	0.008	18/10/2017	0.023
31/05/2019	0.009	09/05/2019	0.012	19/10/2017	0.028
03/06/2019	0.008	10/05/2019	0.016	20/10/2017	0.033
05/06/2019	0.009	13/05/2019	0.018	23/10/2017	0.03
12/06/2019	0.008	17/05/2019	0.015	24/10/2017	0.029
13/06/2019	0.009	20/05/2019	0.015	25/10/2017	0.025
17/06/2019	0.011	24/05/2019	0.013	26/10/2017	0.023
20/06/2019	0.009	28/05/2019	0.016	27/10/2017	0.025
24/06/2019	0.012	31/05/2019	0.015	30/10/2017	0.034
27/06/2019	0.01	03/06/2019	0.012	31/10/2017	0.03
01/07/2019	0.009	05/06/2019	0.013	01/11/2017	0.026
05/07/2019	0.015	12/06/2019	0.014	02/11/2017	0.026
09/07/2019	0.009	13/06/2019	0.013	03/11/2017	0.025
12/07/2019	0.008	17/06/2019	0.012	06/11/2017	0.046
15/07/2019	0.008	20/06/2019	0.017	07/11/2017	0.035
18/07/2019	0.009	24/06/2019	0.017	08/11/2017	0.031
22/07/2019	0.009	27/06/2019	0.016	09/11/2017	0.028
24/07/2019	0.009	01/07/2019	0.014	10/11/2017	0.025
31/07/2019	0.01	05/07/2019	0.01	13/11/2017	0.03
02/08/2019	0.01	09/07/2019	0.014	14/11/2017	0.028
07/08/2019	0.01	12/07/2019	0.011	15/11/2017	0.024
09/08/2019	0.009	15/07/2019	0.011	16/11/2017	0.028
13/08/2019	0.012	18/07/2019	0.013	17/11/2017	0.026
16/08/2019	0.011	22/07/2019	0.009	20/11/2017	0.024
19/08/2019	0.01	24/07/2019	0.009	21/11/2017	0.022
21/08/2019	0.01	31/07/2019	0.008	22/11/2017	0.02
27/08/2019	0.013	02/08/2019	0.009	23/11/2017	0.021
30/08/2019	0.011	07/08/2019	0.007	24/11/2017	0.021
02/09/2019	0.013	09/08/2019	0.007	27/11/2017	0.021
04/09/2019	0.012	13/08/2019	0.009	28/11/2017	0.024
09/09/2019	0.012	16/08/2019	0.013	29/11/2017	0.025
12/09/2019	0.011	19/08/2019	0.012	30/11/2017	0.022
18/09/2019	0.013	21/08/2019	0.015	01/12/2017	0.022
20/09/2019	0.013	27/08/2019	0.015	04/12/2017	0.02
23/09/2019	0.013	30/08/2019	0.013	05/12/2017	0.019
26/09/2019	0.018	02/09/2019	0.011	06/12/2017	0.018
30/09/2019	0.015	04/09/2019	0.014	07/12/2017	0.017
04/10/2019	0.018	09/09/2019	0.012	08/12/2017	0.018
07/10/2019	0.017	12/09/2019	0.015	11/12/2017	0.015
11/10/2019	0.016	18/09/2019	0.016	12/12/2017	0.017
14/10/2019	0.015	20/09/2019	0.017	13/12/2017	0.019
17/10/2019	0.015	23/09/2019	0.016	14/12/2017	0.023
21/10/2019	0.016	26/09/2019	0.024	15/12/2017	0.024
23/10/2019	0.015	30/09/2019	0.03	18/12/2017	0.088
28/10/2019	0.019	04/10/2019	0.037	19/12/2017	0.075
30/10/2019	0.018	07/10/2019	0.04	20/12/2017	0.062
04/11/2019	0.016	11/10/2019	0.026	21/12/2017	0.05
08/11/2019	0.016	14/10/2019	0.02	22/12/2017	0.047
13/11/2019	0.017	17/10/2019	0.022	28/12/2017	0.03
15/11/2019	0.016	21/10/2019	0.023	29/12/2017	0.051
18/11/2019	0.017	23/10/2019	0.027	02/01/2018	0.035

22/11/2019	0.016	28/10/2019	0.051	03/01/2018	0.03
27/11/2019	0.015	30/10/2019	0.046	04/01/2018	0.026
29/11/2029	0.015	04/11/2019	0.034	05/01/2018	0.03
04/12/2019	0.013	08/11/2019	0.026	08/01/2018	0.024
06/12/2019	0.012	13/11/2019	0.025	09/01/2018	0.023
09/12/2019	0.011	15/11/2019	0.025	10/01/2018	0.022
13/12/2019	0.01	18/11/2019	0.023	11/01/2018	0.02
16/12/2019	0.011	22/11/2019	0.018	12/01/2018	0.018
19/12/2019	0.011	27/11/2019	0.035	15/01/2018	0.015
23/12/2019	0.015	29/11/2029	0.024	16/01/2018	0.015
27/12/2019	0.013	04/12/2019	0.015	17/01/2018	0.013
30/12/2019	0.011	06/12/2019	0.01	18/01/2018	0.016
03/01/2020	0.011	09/12/2019	0.015	19/01/2018	0.015
06/01/2020	0.009	13/12/2019	0.015	22/01/2018	0.014
08/01/2020	0.009	16/12/2019	0.014	23/01/2018	0.017
15/01/2020	0.008	19/12/2019	0.013	24/01/2018	0.015
17/01/2020	0.019	23/12/2019	0.016	25/01/2018	0.014
22/01/2020	0.008	27/12/2019	0.012	26/01/2018	0.014
24/01/2020	0.008	30/12/2019	0.011	29/01/2018	0.013
29/01/2020	0.007	03/01/2020	0.01	30/01/2018	0.012
31/01/2020	0.008	06/01/2020	0.01	01/02/2018	0.011
05/02/2020	0.007	08/01/2020	0.011	06/02/2018	0.014
14/02/2020	0.006	15/01/2020	0.011	09/02/2018	0.01
21/02/2020	0.006	17/01/2020	0.025	12/02/2018	0.012
28/02/2020	0.006	22/01/2020	0.009	20/02/2018	0.012
08/03/2020	0.006	24/01/2020	0.009	26/02/2018	0.01
12/03/2020	0.006	29/01/2020	0.009	07/03/2018	0.01
18/03/2020	0.005	31/01/2020	0.009	15/03/2018	0.009
25/03/2020	0.006	05/02/2020	0.009	23/03/2018	0.008
03/04/2020	0.005	14/02/2020	0.007	27/03/2018	0.007
06/04/2020	0.005	21/02/2020	0.008	05/04/2018	0.007
14/04/2020	0.004	28/02/2020	0.008	11/04/2018	0.007
24/04/2020	0.004	08/03/2020	0.007	20/04/2018	0.007
29/04/2020	0.006	12/03/2020	0.007	23/04/2018	0.007
07/05/2020	0.004	18/03/2020	0.005	01/05/2018	0.1
11/05/2020	0.004	25/03/2020	0.006	10/05/2018	0.014
21/05/2020	0.005	03/04/2020	0.005	18/05/2018	0.011
29/05/2020	0.004	06/04/2020	0.006	24/05/2018	0.009
01/06/2020	0.004	14/04/2020	0.005	29/05/2018	0.008
09/06/2020	0.004	24/04/2020	0.005	31/05/2018	0.013
16/06/2020	0.004	29/04/2020	0.006	08/06/2018	0.055
23/06/2020	0.005	07/05/2020	0.005	14/06/2018	0.026
29/06/2020	0.004	11/05/2020	0.006	18/06/2018	0.021
06/07/2020	0.004	21/05/2020	0.007	21/06/2018	0.016
13/07/2020	0.006	29/05/2020	0.007	27/06/2018	0.022
21/07/2020	0.006	01/06/2020	0.007	29/06/2018	0.018
27/07/2020	0.005	09/06/2020	0.007	02/07/2018	0.037
03/08/2020	0.006	16/06/2020	0.006	10/07/2018	0.107
10/08/2020	0.006	23/06/2020	0.007	12/07/2018	0.082
17/08/2020	0.006	29/06/2020	0.006	17/07/2018	0.102
24/08/2020	0.007	06/07/2020	0.008	20/07/2018	0.053
04/09/2020	0.009	13/07/2020	0.012	23/07/2018	0.043

11/09/2020	0.008
17/09/2020	0.008
25/09/2020	0.009
30/09/2020	0.009
05/10/2020	0.016
15/10/2020	0.016
21/10/2020	0.016
28/10/2020	0.014
02/11/2020	0.016

21/07/2020	0.011
27/07/2020	0.01
03/08/2020	0.01
10/08/2020	0.009
17/08/2020	0.007
24/08/2020	0.009
04/09/2020	0.017
11/09/2020	0.022
17/09/2020	0.019
25/09/2020	0.013
30/09/2020	0.013
05/10/2020	0.036
15/10/2020	0.022
21/10/2020	0.02
28/10/2020	0.014
02/11/2020	0.023

25/07/2018	0.021
31/07/2018	0.013
02/08/2018	0.013
07/08/2018	0.014
09/08/2018	0.011
14/08/2018	0.013
16/08/2018	0.01
21/08/2018	0.207
22/08/2018	0.069
28/08/2018	0.018
29/08/2018	0.02
31/08/2018	0.025
03/09/2018	0.019
04/09/2018	0.019
05/09/2018	0.019
06/09/2018	0.021
07/09/2018	0.018
10/09/2018	0.03
11/09/2018	0.023
12/09/2018	0.022
13/09/2018	0.022
14/09/2018	0.023
17/09/2018	0.022
18/09/2018	0.02
19/09/2018	0.019
20/09/2018	0.018
21/09/2018	0.016
24/09/2018	0.035
25/09/2018	0.038
26/09/2018	0.03
27/09/2018	0.045
28/09/2018	0.021
01/10/2018	0.017
02/10/2018	0.017
03/10/2018	0.022
04/10/2018	0.022
05/10/2018	0.022
08/10/2018	0.017
09/10/2018	0.017
10/10/2018	0.015
11/10/2018	0.013
12/10/2018	0.013
15/10/2018	0.029
16/10/2018	0.047
17/10/2018	0.035
18/10/2018	0.024
22/10/2018	0.029
23/10/2018	0.032
24/10/2018	0.034
25/10/2018	0.028
26/10/2018	0.023
29/10/2018	0.022

30/10/2018	0.023
31/10/2018	0.022
01/11/2018	0.027
02/11/2018	0.019
05/11/2018	0.018
06/11/2018	0.029
07/11/2018	0.023
08/11/2018	0.061
09/11/2018	0.061
12/11/2018	0.042
13/11/2018	0.031
14/11/2018	0.026
15/11/2018	0.022
16/11/2018	0.024
19/11/2018	0.022
20/11/2018	0.023
21/11/2018	0.022
22/11/2018	0.021
23/11/2018	0.02
26/11/2018	0.016
27/11/2018	0.015
28/11/2018	0.016
29/11/2018	0.015
30/11/2018	0.018
03/12/2018	0.022
04/12/2018	0.023
05/12/2018	0.021
06/12/2018	0.017
07/12/2018	0.02
10/12/2018	0.017
11/12/2018	0.017
12/12/2018	0.017
13/12/2018	0.019
14/12/2018	0.018
17/12/2018	0.017
18/12/2018	0.015
19/12/2018	0.016
20/12/2018	0.012
21/12/2018	0.013
24/12/2018	0.014
27/12/2018	0.015
28/12/2018	0.017
31/12/2018	0.014
02/01/2019	0.012
03/01/2019	0.013
04/01/2019	0.012
07/01/2019	0.012
08/01/2019	0.012
09/01/2019	0.013
10/01/2019	0.012
11/01/2019	0.011
14/01/2019	0.011

15/01/2019	0.013
16/01/2019	0.009
17/01/2019	0.009
18/01/2019	0.009
21/01/2019	0.009
22/01/2019	0.009
23/01/2019	0.008
24/01/2019	0.009
25/01/2019	0.008
28/01/2019	0.008
29/01/2019	0.009
30/01/2019	0.008
31/01/2019	0.009
01/02/2019	0.009
04/02/2019	0.009
07/02/2019	0.008
11/02/2019	0.01
13/02/2019	0.008
18/02/2019	0.009
22/02/2019	0.008
25/02/2019	0.008
01/03/2019	0.008
04/03/2019	0.007
08/03/2019	0.007
13/03/2019	0.008
15/03/2019	0.008
18/03/2019	0.008
21/03/2019	0.011
26/03/2019	0.008
29/03/2019	0.008
03/04/2019	0.008
05/04/2019	0.008
10/04/2019	0.008
12/04/2019	0.008
15/04/2019	0.008
18/04/2019	0.008
23/04/2019	0.008
26/04/2019	0.009
29/04/2019	0.009
01/05/2019	0.008
09/05/2019	0.01
10/05/2019	0.015
13/05/2019	0.016
17/05/2019	0.013
20/05/2019	0.01
24/05/2019	0.01
28/05/2019	0.015
31/05/2019	0.013
03/06/2019	0.008
05/06/2019	0.009
12/06/2019	0.015
13/06/2019	0.036

17/06/2019	0.021
20/06/2019	0.016
24/06/2019	0.051
27/06/2019	0.016
01/07/2019	0.027
05/07/2019	0.036
09/07/2019	0.025
12/07/2019	0.018
15/07/2019	0.016
18/07/2019	0.012
22/07/2019	0.01
24/07/2019	0.012
29/07/2019	0.011
30/07/2019	0.011
31/07/2019	0.013
01/08/2019	0.013
02/08/2019	0.012
05/08/2019	0.01
06/08/2019	0.01
07/08/2019	0.011
08/08/2019	0.01
09/08/2019	0.009
12/08/2019	0.009
13/08/2019	0.01
14/08/2019	0.011
15/08/2019	0.01
16/08/2019	0.01
19/08/2019	0.01
20/08/2019	0.011
21/08/2019	0.012
22/08/2019	0.013
23/08/2019	0.016
27/08/2019	0.012
28/08/2019	0.012
29/08/2019	0.013
30/08/2019	0.014
02/09/2019	0.013
03/09/2019	0.012
04/09/2019	0.013
05/09/2019	0.012
06/09/2019	0.011
09/09/2019	0.012
10/09/2019	0.014
11/09/2019	0.013
12/09/2019	0.013
13/09/2019	0.012
16/09/2019	0.012
17/09/2019	0.011
18/09/2019	0.01
19/09/2019	0.01
20/09/2019	0.01
23/09/2019	0.01

25/09/2019	0.011
25/09/2019	0.011
27/09/2019	0.014
27/09/2019	0.013
01/10/2019	0.016
01/10/2019	0.014
03/10/2019	0.024
04/10/2019	0.018
05/10/2019	0.022
08/10/2019	0.023
09/10/2019	0.021
10/10/2019	0.019
11/10/2019	0.021
11/10/2019	0.019
14/10/2019	0.016
17/10/2019	0.02
21/10/2019	0.018
23/10/2019	0.017
24/10/2019	0.016
28/10/2019	0.02
29/10/2019	0.02
30/10/2019	0.022
04/11/2019	0.016
08/11/2019	0.02
13/11/2019	0.02
14/11/2019	0.024
15/11/2019	0.02
18/11/2019	0.044
21/11/2019	0.028
22/11/2019	0.024
25/11/2019	0.023
27/11/2019	0.028
29/11/2029	0.149
02/12/2019	0.196
04/12/2019	0.19
06/12/2019	0.119
09/12/2019	0.07
10/12/2019	0.107
13/12/2019	0.04
16/12/2019	0.209
17/12/2019	0.153
18/12/2019	0.174
19/12/2019	0.174
19/12/2019	0.141
22/12/2019	0.099
24/12/2019	0.107
27/12/2019	0.086
29/12/2019	0.05
30/12/2019	0.037
02/01/2020	0.031
03/01/2020	0.027
06/01/2020	0.027

06/01/2020	0.022
08/01/2020	0.026
09/01/2020	0.023
10/01/2020	0.021
13/01/2020	0.019
14/01/2020	0.036
15/01/2020	0.029
15/01/2020	0.024
17/01/2020	0.025
20/01/2020	0.073
21/01/2020	0.037
22/01/2020	0.029
22/01/2020	0.024
24/01/2020	0.022
24/01/2020	0.022
28/01/2020	0.015
29/01/2020	0.012
29/01/2020	0.013
31/01/2020	0.055
31/01/2020	0.045
05/02/2020	0.016
07/02/2020	0.016
14/02/2020	0.011
14/02/2020	0.01
21/02/2020	0.018
26/02/2020	0.011
28/02/2020	0.012
05/03/2020	0.031
08/03/2020	0.013
12/03/2020	0.012
12/03/2020	0.011
17/03/2020	0.01
18/03/2020	0.008
25/03/2020	0.008
25/03/2020	0.008
02/04/2020	0.007
03/04/2020	0.006
09/04/2020	0.008
14/04/2020	0.006
14/04/2020	0.007
17/04/2020	0.021
24/04/2020	0.007
24/04/2020	0.006
29/04/2020	0.007
04/05/2020	0.006
04/05/2020	0.007
11/05/2020	0.006
14/05/2020	0.006
15/05/2020	0.007
20/05/2020	0.006
26/05/2020	0.007
26/05/2020	0.006

29/05/2020	0.007
02/06/2020	0.006
08/06/2020	0.005
09/06/2020	0.005
11/06/2020	0.005
16/06/2020	0.005
19/06/2020	0.005
23/06/2020	0.008
29/06/2020	0.009
29/06/2020	0.005
06/07/2020	0.012
10/07/2020	0.006
10/07/2020	0.009
13/07/2020	0.01
21/07/2020	0.007
21/07/2020	0.009
27/07/2020	0.01
29/07/2020	0.007
03/08/2020	0.007
05/08/2020	0.007
06/08/2020	0.007
10/08/2020	0.008
17/08/2020	0.014
17/08/2020	0.009
24/08/2020	0.016
25/08/2020	0.019
01/09/2020	0.028
04/09/2020	0.12
04/09/2020	0.046
07/09/2020	0.03
08/09/2020	0.027
10/09/2020	0.023
11/09/2020	0.021
11/09/2020	0.019
15/09/2020	0.02
16/09/2020	0.024
17/09/2020	0.024
17/09/2020	0.021
23/09/2020	0.014
25/09/2020	0.011
28/09/2020	0.01
01/10/2020	0.011
01/10/2020	0.01
05/10/2020	0.016
05/10/2020	0.02
07/10/2020	0.02
08/10/2020	0.025
09/10/2020	0.023
09/10/2020	0.026
13/10/2020	0.022
14/10/2020	0.025
15/10/2020	0.02

16/10/2020	0.024
19/10/2020	0.044
20/10/2020	0.061
20/10/2020	0.056
22/10/2020	0.043
23/10/2020	0.031
26/10/2020	0.028
27/10/2020	0.071
28/10/2020	0.038
28/10/2020	0.129
30/10/2020	0.058
02/11/2020	0.038
03/11/2020	0.052
04/11/2020	0.062
05/11/2020	0.122
05/11/2020	0.091
06/11/2020	0.073

Table B 3 Regulatory metaldehyde concentration data for sites C1-C6.

Sampling date	Metaldehyde concentration (µg L^{-1}) at site C1	Sampling date	Metaldehyde concentration (µg L^{-1}) at site C2	Sampling date	Metaldehyde concentration (µg L^{-1}) at site C3	Sampling date	Metaldehyde concentration (µg L^{-1}) at site C4	Sampling date	Metaldehyde concentration (µg L^{-1}) at site C5	Sampling date	Metaldehyde concentration (µg L^{-1}) at site C6
29/07/2015	0.016	29/07/2015	0.025	07/01/2016	0.017	15/04/2015	0.013	15/04/2015	0.017	15/04/2015	0.012
06/08/2015	0.02	06/08/2015	0.008	12/01/2016	0.021	23/04/2015	0.011	23/04/2015	0.014	23/04/2015	0.011
15/08/2015	0.018	15/08/2015	0.009	20/01/2016	0.023	27/04/2015	0.012	27/04/2015	0.017	27/04/2015	0.013
17/08/2015	0.016	17/08/2015	0.036	25/01/2016	0.021	08/05/2015	0.011	08/05/2015	0.019	08/05/2015	0.012
25/08/2015	0.047	25/08/2015	0.04	04/02/2016	0.023	14/05/2015	0.014	14/05/2015	0.014	14/05/2015	0.014
03/09/2015	0.054	03/09/2015	0.034	10/02/2016	0.012	20/05/2015	0.015	20/05/2015	0.017	20/05/2015	0.016
09/09/2015	0.032	09/09/2015	0.018	15/02/2016	0.024	28/05/2015	0.013	28/05/2015	0.01	28/05/2015	0.028
18/09/2015	0.169	18/09/2015	0.057	24/02/2016	0.023	04/06/2015	0.013	04/06/2015	0.01	04/06/2015	0.013
21/09/2015	0.081	21/09/2015	0.097	01/03/2016	0.028	08/06/2015	0.015	08/06/2015	0.012	08/06/2015	0.015
29/09/2015	0.055	29/09/2015	0.071	09/03/2016	0.014	16/06/2015	0.009	16/06/2015	0.009	16/06/2015	0.012
06/10/2015	0.104	06/10/2015	0.052	14/03/2016	0.014	23/06/2015	0.03	23/06/2015	0.012	23/06/2015	0.014
15/10/2015	0.164	15/10/2015	0.037	22/03/2016	0.017	01/07/2015	0.03	01/07/2015	0.011	01/07/2015	0.027
22/10/2015	0.105	22/10/2015	0.046	31/03/2016	0.014	06/07/2015	0.019	06/07/2015	0.013	06/07/2015	0.023
28/10/2015	0.146	28/10/2015	0.176	07/04/2016	0.019	22/07/2015	0.008	13/07/2015	0.006	13/07/2015	0.019
02/11/2015	0.703	02/11/2015	0.316	17/04/2016	0.018	29/07/2015	0.007	22/07/2015	0.007	22/07/2015	0.009
10/11/2015	0.198	10/11/2015	0.274	18/04/2016	0.019	06/08/2015	0.005	29/07/2015	0.01	29/07/2015	0.01
19/11/2015	0.447	19/11/2015	0.08	27/04/2016	0.017	15/08/2015	0.007	06/08/2015	0.004	06/08/2015	0.006
27/11/2015	0.073	27/11/2015	0.041	05/05/2016	0.024	17/08/2015	0.008	15/08/2015	0.007	15/08/2015	0.01
30/11/2015	0.081	30/11/2015	0.04	12/05/2016	0.026	25/08/2015	0.02	17/08/2015	0.007	17/08/2015	0.008
09/12/2015	0.075	09/12/2015	0.046	16/05/2016	0.025	03/09/2015	0.117	25/08/2015	0.041	25/08/2015	0.024
17/12/2015	0.041	17/12/2015	0.025	27/05/2016	0.025	09/09/2015	0.171	03/09/2015	0.08	03/09/2015	0.116
23/12/2015	0.065	23/12/2015	0.04	31/05/2016	0.017	18/09/2015	0.078	09/09/2015	0.025	09/09/2015	0.094

31/12/2015	0.035	31/12/2015	0.026	09/06/2016	0.052	21/09/2015	0.439	18/09/2015	0.107	18/09/2015	0.103
07/01/2016	0.021	07/01/2016	0.017	17/06/2016	0.035	29/09/2015	0.061	21/09/2015	0.07	21/09/2015	0.384
12/01/2016	0.03	12/01/2016	0.017	22/06/2016	0.027	06/10/2015	0.092	29/09/2015	0.035	29/09/2015	0.046
20/01/2016	0.026	20/01/2016	0.018	27/06/2016	0.017	15/10/2015	0.035	06/10/2015	0.032	06/10/2015	0.044
25/01/2016	0.021	25/01/2016	0.016	04/07/2016	0.019	22/10/2015	0.048	15/10/2015	0.051	15/10/2015	0.036
04/02/2016	0.029	04/02/2016	0.014	13/07/2016	0.022	28/10/2015	0.062	22/10/2015	0.052	22/10/2015	0.04
10/02/2016	0.016	10/02/2016	0.009	15/07/2016	0.021	02/11/2015	0.22	02/11/2015	0.11	28/10/2015	0.317
15/02/2016	0.029	15/02/2016	0.014	21/07/2016	0.021	10/11/2015	0.294	10/11/2015	0.253	02/11/2015	0.133
24/02/2016	0.023	24/02/2016	0.015	29/07/2016	0.021	19/11/2015	0.384	19/11/2015	0.124	10/11/2015	0.249
01/03/2016	0.036	01/03/2016	0.013	01/08/2016	0.021	27/11/2015	0.102	27/11/2015	0.131	19/11/2015	0.395
09/03/2016	0.011	09/03/2016	0.009	09/08/2016	0.019	30/11/2015	0.05	30/11/2015	0.14	27/11/2015	0.116
14/03/2016	0.018	14/03/2016	0.009	18/08/2016	0.004	09/12/2015	0.039	09/12/2015	0.08	30/11/2015	0.071
22/03/2016	0.017	22/03/2016	0.01	25/08/2016	0.008	17/12/2015	0.038	17/12/2015	0.086	09/12/2015	0.044
31/03/2016	0.016	31/03/2016	0.01	02/09/2016	0.031	23/12/2015	0.028	23/12/2015	0.032	17/12/2015	0.048
07/04/2016	0.022	07/04/2016	0.011	06/09/2016	0.017	31/12/2015	0.026	31/12/2015	0.03	23/12/2015	0.029
17/04/2016	0.019	17/04/2016	0.143	13/09/2016	0.015	07/01/2016	0.019	07/01/2016	0.022	31/12/2015	0.024
18/04/2016	0.021	18/04/2016	0.097	22/09/2016	0.497	12/01/2016	0.016	12/01/2016	0.023	07/01/2016	0.021
27/04/2016	0.037	27/04/2016	0.019	28/09/2016	0.208	20/01/2016	0.016	20/01/2016	0.007	12/01/2016	0.02
05/05/2016	0.027	05/05/2016	0.016	07/10/2016	0.112	25/01/2016	0.019	25/01/2016	0.02	20/01/2016	0.018
12/05/2016	0.044	12/05/2016	0.024	10/10/2016	0.078	04/02/2016	0.017	04/02/2016	0.016	25/01/2016	0.017
16/05/2016	0.032	16/05/2016	0.012	19/10/2016	0.087	10/02/2016	0.009	10/02/2016	0.011	04/02/2016	0.016
27/05/2016	0.027	27/05/2016	0.011	27/10/2016	0.152	15/02/2016	0.017	15/02/2016	0.017	10/02/2016	0.009
31/05/2016	0.098	31/05/2016	0.014	03/11/2016	0.124	24/02/2016	0.026	24/02/2016	0.024	15/02/2016	0.016
09/06/2016	0.027	09/06/2016	0.018	07/11/2016	0.124	01/03/2016	0.018	01/03/2016	0.017	24/02/2016	0.025
17/06/2016	0.03	17/06/2016	0.022	18/11/2016	0.213	09/03/2016	0.009	09/03/2016	0.021	01/03/2016	0.017
22/06/2016	0.026	22/06/2016	0.023	24/11/2016	1.48	14/03/2016	0.011	14/03/2016	0.025	09/03/2016	0.013
27/06/2016	0.022	27/06/2016	0.021	01/12/2016	0.421	22/03/2016	0.012	22/03/2016	0.014	14/03/2016	0.014
04/07/2016	0.025	04/07/2016	0.014	11/12/2016	0.208	31/03/2016	0.018	31/03/2016	0.02	22/03/2016	0.011

13/07/2016	0.026	13/07/2016	0.017	15/12/2016	0.174	07/04/2016	0.014	07/04/2016	0.016	31/03/2016	0.019
15/07/2016	0.021	15/07/2016	0.04	23/12/2016	0.247	17/04/2016	0.072	17/04/2016	0.028	07/04/2016	0.014
21/07/2016	0.029	21/07/2016	0.013	29/12/2016	0.576	18/04/2016	0.055	18/04/2016	0.026	17/04/2016	0.063
29/07/2016	0.029	29/07/2016	0.008	05/01/2017	0.114	27/04/2016	0.018	27/04/2016	0.032	18/04/2016	0.043
01/08/2016	0.029	01/08/2016	0.01	12/01/2017	0.09	05/05/2016	0.017	05/05/2016	0.025	27/04/2016	0.019
09/08/2016	0.052	09/08/2016	0.071	20/01/2017	0.064	12/05/2016	0.017	12/05/2016	0.024	05/05/2016	0.017
18/08/2016	0.029	18/08/2016	0.013	24/01/2017	0.064	16/05/2016	0.018	16/05/2016	0.015	12/05/2016	0.02
25/08/2016	0.032	25/08/2016	0.018	31/01/2017	0.058	27/05/2016	0.016	27/05/2016	0.023	16/05/2016	0.017
02/09/2016	0.042	02/09/2016	0.041	09/02/2017	0.03	31/05/2016	0.349	31/05/2016	0.012	27/05/2016	0.019
06/09/2016	0.049	06/09/2016	0.033	16/02/2017	0.025	09/06/2016	0.023	09/06/2016	0.015	31/05/2016	0.17
13/09/2016	0.047	13/09/2016	0.021	23/02/2017	0.023	17/06/2016	0.024	17/06/2016	0.016	09/06/2016	0.03
22/09/2016	0.18	22/09/2016	1.19	28/02/2017	0.017	22/06/2016	0.042	22/06/2016	0.053	17/06/2016	0.028
28/09/2016	0.084	28/09/2016	0.232	06/03/2017	0.019	27/06/2016	0.029	27/06/2016	0.078	22/06/2016	0.045
07/10/2016	0.134	07/10/2016	0.147	16/03/2017	0.021	04/07/2016	0.022	04/07/2016	0.041	27/06/2016	0.034
10/10/2016	0.055	10/10/2016	0.106	24/03/2017	0.021	13/07/2016	0.028	13/07/2016	0.023	04/07/2016	0.026
19/10/2016	0.063	19/10/2016	0.156	31/03/2017	0.021	15/07/2016	0.025	15/07/2016	0.027	13/07/2016	0.028
27/10/2016	0.066	27/10/2016	0.092	07/04/2017	0.023	21/07/2016	0.014	21/07/2016	0.019	15/07/2016	0.022
03/11/2016	0.064	03/11/2016	0.078	13/04/2017	0.021	29/07/2016	0.011	29/07/2016	0.013	21/07/2016	0.016
07/11/2016	0.081	07/11/2016	0.085	20/04/2017	0.022	01/08/2016	0.013	01/08/2016	0.014	29/07/2016	0.013
18/11/2016	0.549	18/11/2016	0.155	28/04/2017	0.024	09/08/2016	0.014	09/08/2016	0.015	01/08/2016	0.014
24/11/2016	1.91	24/11/2016	2.14	05/05/2017	0.024	18/08/2016	0.008	18/08/2016	0.01	09/08/2016	0.016
01/12/2016	0.286	01/12/2016	0.213	10/05/2017	0.026	25/08/2016	0.012	25/08/2016	0.008	18/08/2016	0.009
11/12/2016	0.147	11/12/2016	0.122	11/05/2017	0.025	02/09/2016	0.025	02/09/2016	0.014	25/08/2016	0.014
15/12/2016	0.116	15/12/2016	0.159	22/05/2017	0.022	06/09/2016	0.024	06/09/2016	0.015	02/09/2016	0.024
23/12/2016	0.08	23/12/2016	0.077	01/06/2017	0.025	13/09/2016	0.015	13/09/2016	0.014	06/09/2016	0.03
29/12/2016	0.07	29/12/2016	0.048	09/06/2017	0.024	22/09/2016	2.55	22/09/2016	0.032	13/09/2016	0.016
05/01/2017	0.05	05/01/2017	0.048	12/06/2017	0.022	28/09/2016	1.02	28/09/2016	0.024	22/09/2016	1.6
12/01/2017	0.07	12/01/2017	0.037	23/06/2017	0.007	07/10/2016	0.168	07/10/2016	0.024	28/09/2016	0.603

20/01/2017	0.084	20/01/2017	0.033	27/06/2017	0.004	10/10/2016	0.068	10/10/2016	0.021	07/10/2016	0.111
24/01/2017	0.077	24/01/2017	0.031	04/07/2017	0.01	19/10/2016	0.054	19/10/2016	0.032	10/10/2016	0.048
31/01/2017	0.078	31/01/2017	0.026	14/07/2017	0.01	27/10/2016	0.028	27/10/2016	0.033	19/10/2016	0.034
09/02/2017	0.06	09/02/2017	0.021	17/07/2017	0.012	03/11/2016	0.034	03/11/2016	0.03	27/10/2016	0.024
16/02/2017	0.06	16/02/2017	0.019	25/07/2017	0.017	07/11/2016	0.074	07/11/2016	0.027	03/11/2016	0.027
23/02/2017	0.034	23/02/2017	0.034	02/08/2017	0.017	18/11/2016	0.071	18/11/2016	0.063	07/11/2016	0.042
28/02/2017	0.034	28/02/2017	0.021	11/08/2017	0.17	24/11/2016	1.89	24/11/2016	0.22	18/11/2016	0.069
06/03/2017	0.039	06/03/2017	0.036	16/08/2017	0.08	01/12/2016	0.349	01/12/2016	0.093	24/11/2016	1.44
16/03/2017	0.051	16/03/2017	0.022	21/08/2017	0.05	11/12/2016	0.08	11/12/2016	0.071	01/12/2016	0.3
24/03/2017	0.024	24/03/2017	0.021	01/09/2017	0.024	15/12/2016	0.172	15/12/2016	0.098	11/12/2016	0.109
31/03/2017	0.027	31/03/2017	0.019	07/09/2017	0.02	23/12/2016	0.061	23/12/2016	0.058	15/12/2016	0.142
07/04/2017	0.028	07/04/2017	0.02	14/09/2017	0.092	29/12/2016	0.076	29/12/2016	0.051	23/12/2016	0.078
13/04/2017	0.032	13/04/2017	0.016	21/09/2017	0.19	05/01/2017	0.084	05/01/2017	0.066	29/12/2016	0.063
20/04/2017	0.032	20/04/2017	0.016	29/09/2017	0.111	12/01/2017	0.045	12/01/2017	0.073	05/01/2017	0.091
28/04/2017	0.036	28/04/2017	0.017	05/10/2017	0.181	20/01/2017	0.051	20/01/2017	0.078	12/01/2017	0.055
05/05/2017	0.034	05/05/2017	0.015	13/10/2017	0.125	24/01/2017	0.039	24/01/2017	0.06	20/01/2017	0.058
10/05/2017	0.024	10/05/2017	0.012	17/10/2017	0.097	31/01/2017	0.051	31/01/2017	0.081	24/01/2017	0.046
11/05/2017	0.027	11/05/2017	0.013	25/10/2017	0.08	09/02/2017	0.027	09/02/2017	0.157	31/01/2017	0.065
22/05/2017	0.036	22/05/2017	0.016	03/11/2017	0.106	16/02/2017	0.045	16/02/2017	0.072	09/02/2017	0.06
01/06/2017	0.027	01/06/2017	0.017	07/11/2017	0.097	23/02/2017	0.023	23/02/2017	0.049	16/02/2017	0.063
09/06/2017	0.035	09/06/2017	0.019	15/11/2017	0.077	28/02/2017	0.019	28/02/2017	0.034	23/02/2017	0.031
12/06/2017	0.027	12/06/2017	0.014	24/11/2017	0.068	06/03/2017	0.021	06/03/2017	0.033	28/02/2017	0.025
23/06/2017	0.02	23/06/2017	0.009	28/11/2017	0.071	16/03/2017	0.019	16/03/2017	0.025	06/03/2017	0.023
27/06/2017	0.027	27/06/2017	0.011	06/12/2017	0.049	24/03/2017	0.016	24/03/2017	0.021	16/03/2017	0.021
04/07/2017	0.021	04/07/2017	0.011	12/12/2017	0.054	31/03/2017	0.015	31/03/2017	0.018	24/03/2017	0.017
14/07/2017	0.021	14/07/2017	0.008	21/12/2017	0.081	07/04/2017	0.014	07/04/2017	0.014	31/03/2017	0.015
17/07/2017	0.023	17/07/2017	0.011	28/12/2017	0.07	13/04/2017	0.056	13/04/2017	0.013	07/04/2017	0.013
25/07/2017	0.02	25/07/2017	0.01	03/01/2018	0.036	20/04/2017	0.012	20/04/2017	0.012	13/04/2017	0.012

02/08/2017	0.02	02/08/2017	0.015	11/01/2018	0.024	28/04/2017	0.015	28/04/2017	0.013	20/04/2017	0.011
11/08/2017	0.018	11/08/2017	0.02	18/01/2018	0.016	05/05/2017	0.014	05/05/2017	0.012	28/04/2017	0.014
16/08/2017	0.022	16/08/2017	0.011	26/01/2018	0.014	10/05/2017	0.011	10/05/2017	0.012	05/05/2017	0.011
21/08/2017	0.025	21/08/2017	0.044	01/02/2018	0.013	11/05/2017	0.012	11/05/2017	0.011	10/05/2017	0.01
01/09/2017	0.031	01/09/2017	0.024	09/02/2018	0.013	22/05/2017	0.019	22/05/2017	0.02	11/05/2017	0.011
07/09/2017	0.032	07/09/2017	0.021	12/02/2018	0.014	01/06/2017	0.015	01/06/2017	0.012	22/05/2017	0.02
14/09/2017	0.053	14/09/2017	0.055	20/02/2018	0.013	09/06/2017	0.015	09/06/2017	0.018	01/06/2017	0.029
21/09/2017	0.11	21/09/2017	0.084	26/02/2018	0.013	12/06/2017	0.012	12/06/2017	0.013	09/06/2017	0.017
29/09/2017	0.063	29/09/2017	0.042	07/03/2018	0.009	23/06/2017	0.01	23/06/2017	0.006	12/06/2017	0.014
05/10/2017	0.038	05/10/2017	0.042	15/03/2018	0.009	27/06/2017	0.009	27/06/2017	0.004	23/06/2017	0.012
13/10/2017	0.042	13/10/2017	0.031	23/03/2018	0.01	04/07/2017	0.009	04/07/2017	0.007	27/06/2017	0.011
17/10/2017	0.039	17/10/2017	0.025	27/03/2018	0.01	14/07/2017	0.01	14/07/2017	0.013	04/07/2017	0.018
25/10/2017	0.052	25/10/2017	0.039	05/04/2018	0.008	17/07/2017	0.009	17/07/2017	0.009	14/07/2017	0.011
03/11/2017	0.046	03/11/2017	0.024	11/04/2018	0.007	25/07/2017	0.008	25/07/2017	0.013	17/07/2017	0.01
07/11/2017	0.044	07/11/2017	0.026	20/04/2018	0.009	02/08/2017	0.009	02/08/2017	0.009	25/07/2017	0.01
15/11/2017	0.043	15/11/2017	0.03	23/04/2018	0.01	11/08/2017	0.011	11/08/2017	0.023	02/08/2017	0.011
24/11/2017	0.034	24/11/2017	0.024	01/05/2018	0.009	16/08/2017	0.011	16/08/2017	0.024	11/08/2017	0.02
28/11/2017	0.03	28/11/2017	0.023	10/05/2018	0.009	21/08/2017	0.026	21/08/2017	0.012	16/08/2017	0.011
06/12/2017	0.023	06/12/2017	0.019	18/05/2018	0.012	01/09/2017	0.019	01/09/2017	0.015	21/08/2017	0.02
12/12/2017	0.026	12/12/2017	0.019	24/05/2018	0.012	07/09/2017	0.019	07/09/2017	0.011	01/09/2017	0.025
21/12/2017	0.029	21/12/2017	0.017	31/05/2018	0.063	14/09/2017	0.044	14/09/2017	0.019	07/09/2017	0.02
28/12/2017	0.04	28/12/2017	0.05	08/06/2018	0.035	21/09/2017	0.028	21/09/2017	0.025	14/09/2017	0.051
03/01/2018	0.024	03/01/2018	0.031	14/06/2018	0.029	29/09/2017	0.033	29/09/2017	0.028	21/09/2017	0.031
11/01/2018	0.026	11/01/2018	0.019	18/06/2018	0.022	05/10/2017	0.027	05/10/2017	0.019	29/09/2017	0.022
18/01/2018	0.023	18/01/2018	0.014	29/06/2018	0.005	13/10/2017	0.022	13/10/2017	0.017	05/10/2017	0.023
26/01/2018	0.02	26/01/2018	0.011	02/07/2018	0.004	17/10/2017	0.021	17/10/2017	0.015	13/10/2017	0.02
01/02/2018	0.015	01/02/2018	0.009	10/07/2018	0.004	25/10/2017	0.025	25/10/2017	0.02	17/10/2017	0.017
09/02/2018	0.015	09/02/2018	0.009	17/07/2018	0.004	03/11/2017	0.017	03/11/2017	0.019	25/10/2017	0.021

12/02/2018	0.018	12/02/2018	0.01	25/07/2018	0.004	07/11/2017	0.021	07/11/2017	0.022	03/11/2017	0.02
20/02/2018	0.016	20/02/2018	0.009	02/08/2018	0.004	15/11/2017	0.024	15/11/2017	0.024	07/11/2017	0.02
26/02/2018	0.018	26/02/2018	0.009	09/08/2018	0.004	24/11/2017	0.018	24/11/2017	0.02	15/11/2017	0.023
07/03/2018	0.012	07/03/2018	0.007	14/08/2018	0.01	28/11/2017	0.017	28/11/2017	0.022	24/11/2017	0.019
15/03/2018	0.011	15/03/2018	0.007	21/08/2018	0.043	06/12/2017	0.012	06/12/2017	0.02	28/11/2017	0.017
23/03/2018	0.011	23/03/2018	0.006	31/08/2018	0.063	12/12/2017	0.02	12/12/2017	0.026	06/12/2017	0.013
27/03/2018	0.011	27/03/2018	0.005	06/09/2018	0.052	21/12/2017	0.06	21/12/2017	0.033	12/12/2017	0.019
05/04/2018	0.01	05/04/2018	0.006	13/09/2018	0.033	28/12/2017	0.094	28/12/2017	0.051	21/12/2017	0.045
11/04/2018	0.008	11/04/2018	0.005	17/09/2018	0.031	03/01/2018	0.027	03/01/2018	0.032	28/12/2017	0.058
20/04/2018	0.011	20/04/2018	0.006	25/09/2018	0.022	11/01/2018	0.019	11/01/2018	0.024	03/01/2018	0.028
23/04/2018	0.01	23/04/2018	0.006	03/10/2018	0.02	18/01/2018	0.015	18/01/2018	0.019	11/01/2018	0.019
01/05/2018	0.116	01/05/2018	0.005	11/10/2018	0.013	26/01/2018	0.014	26/01/2018	0.015	18/01/2018	0.016
10/05/2018	0.015	10/05/2018	0.032	17/10/2018	0.123	01/02/2018	0.011	01/02/2018	0.012	26/01/2018	0.013
18/05/2018	0.016	18/05/2018	0.007	25/10/2018	0.095	09/02/2018	0.008	09/02/2018	0.01	01/02/2018	0.023
24/05/2018	0.016	24/05/2018	0.007	30/10/2018	0.045	12/02/2018	0.013	12/02/2018	0.014	09/02/2018	0.01
31/05/2018	0.016	31/05/2018	0.007	08/11/2018	0.071	20/02/2018	0.012	20/02/2018	0.011	12/02/2018	0.013
08/06/2018	0.013	08/06/2018	0.006	16/11/2018	1.57	26/02/2018	0.012	26/02/2018	0.011	20/02/2018	0.011
14/06/2018	0.015	14/06/2018	0.007	19/11/2018	1.18	07/03/2018	0.009	07/03/2018	0.011	26/02/2018	0.011
18/06/2018	0.014	18/06/2018	0.01	29/11/2018	0.246	15/03/2018	0.008	15/03/2018	0.009	07/03/2018	0.009
29/06/2018	0.011	29/06/2018	0.01	05/12/2018	0.206	23/03/2018	0.009	23/03/2018	0.008	15/03/2018	0.008
02/07/2018	0.011	02/07/2018	0.009	13/12/2018	0.105	27/03/2018	0.007	27/03/2018	0.006	23/03/2018	0.008
10/07/2018	0.01	10/07/2018	0.008	19/12/2018	0.047	05/04/2018	0.007	05/04/2018	0.008	27/03/2018	0.006
17/07/2018	0.008	17/07/2018	0.004	24/12/2018	0.027	11/04/2018	0.007	11/04/2018	0.008	05/04/2018	0.007
25/07/2018	0.011	25/07/2018	0.01	02/01/2019	0.036	20/04/2018	0.008	20/04/2018	0.006	11/04/2018	0.007
02/08/2018	0.014	02/08/2018	0.008	11/01/2019	0.028	23/04/2018	0.009	23/04/2018	0.007	20/04/2018	0.007
09/08/2018	0.01	09/08/2018	0.006	18/01/2019	0.025	01/05/2018	0.03	01/05/2018	0.007	23/04/2018	0.008
14/08/2018	0.013	14/08/2018	0.008	22/01/2019	0.022	10/05/2018	0.009	10/05/2018	0.007	01/05/2018	0.009
21/08/2018	0.014	21/08/2018	0.007	01/02/2019	0.013	18/05/2018	0.01	18/05/2018	0.006	10/05/2018	0.009

31/08/2018	0.017	31/08/2018	0.029	07/02/2019	0.011	24/05/2018	0.008	24/05/2018	0.005	18/05/2018	0.009
06/09/2018	0.02	06/09/2018	0.018	11/02/2019	0.011	31/05/2018	0.045	31/05/2018	0.007	24/05/2018	0.007
13/09/2018	0.032	13/09/2018	0.026	22/02/2019	0.014	08/06/2018	0.017	08/06/2018	0.009	31/05/2018	0.013
17/09/2018	0.023	17/09/2018	0.024			14/06/2018	0.013	14/06/2018	0.008	08/06/2018	0.019
25/09/2018	0.04	25/09/2018	0.033			18/06/2018	0.011	18/06/2018	0.004	14/06/2018	0.013
03/10/2018	0.022	03/10/2018	0.015			29/06/2018	0.007	29/06/2018	0.004	18/06/2018	0.01
11/10/2018	0.018	11/10/2018	0.017			02/07/2018	0.006	02/07/2018	0.004	29/06/2018	0.007
17/10/2018	0.038	17/10/2018	0.054			10/07/2018	0.006	10/07/2018	0.004	02/07/2018	0.007
25/10/2018	0.042	25/10/2018	0.028			17/07/2018	0.004	17/07/2018	0.004	10/07/2018	0.007
30/10/2018	0.046	30/10/2018	0.023			25/07/2018	0.004	25/07/2018	0.004	17/07/2018	0.005
08/11/2018	0.046	08/11/2018	0.035			02/08/2018	0.005	02/08/2018	0.004	25/07/2018	0.01
16/11/2018	0.038	16/11/2018	0.02			09/08/2018	0.005	09/08/2018	0.004	02/08/2018	0.007
19/11/2018	0.031	19/11/2018	0.018			14/08/2018	0.008	14/08/2018	0.013	09/08/2018	0.005
29/11/2018	0.045	29/11/2018	0.015			21/08/2018	0.006	21/08/2018	0.014	14/08/2018	0.01
05/12/2018	0.027	05/12/2018	0.012			31/08/2018	0.012	31/08/2018	0.02	21/08/2018	0.011
13/12/2018	0.021	13/12/2018	0.012			06/09/2018	0.009	06/09/2018	0.02	31/08/2018	0.016
19/12/2018	0.01	19/12/2018	0.01			13/09/2018	0.043	13/09/2018	0.032	06/09/2018	0.011
24/12/2018	0.022	24/12/2018	0.016			17/09/2018	0.016	17/09/2018	0.014	13/09/2018	0.038
02/01/2019	0.018	02/01/2019	0.008			25/09/2018	0.025	25/09/2018	0.026	17/09/2018	0.018
11/01/2019	0.014	11/01/2019	0.008			03/10/2018	0.011	03/10/2018	0.012	25/09/2018	0.043
18/01/2019	0.013	18/01/2019	0.009			11/10/2018	0.011	11/10/2018	0.012	03/10/2018	0.011
22/01/2019	0.013	22/01/2019	0.008			17/10/2018	0.03	17/10/2018	0.03	11/10/2018	0.012
01/02/2019	0.013	01/02/2019	0.009			25/10/2018	0.018	25/10/2018	0.018	17/10/2018	0.031
07/02/2019	0.011	07/02/2019	0.009			30/10/2018	0.015	30/10/2018	0.015	25/10/2018	0.017
11/02/2019	0.012	11/02/2019	0.008			08/11/2018	0.027	08/11/2018	0.02	30/10/2018	0.016
22/02/2019	0.01	22/02/2019	0.006			16/11/2018	0.017	16/11/2018	0.022	08/11/2018	0.043
25/02/2019	0.009	25/02/2019	0.006			19/11/2018	0.017	19/11/2018	0.016	16/11/2018	0.02
						29/11/2018	0.054	29/11/2018	0.017	19/11/2018	0.015

05/12/2018	0.031	05/12/2018	0.016	29/11/2018	0.028
13/12/2018	0.023	13/12/2018	0.015	05/12/2018	0.02
19/12/2018	0.019	19/12/2018	0.016	13/12/2018	0.018
24/12/2018	0.027	24/12/2018	0.016	19/12/2018	0.015
02/01/2019	0.011	02/01/2019	0.014	24/12/2018	0.014
11/01/2019	0.01	11/01/2019	0.008	02/01/2019	0.011
18/01/2019	0.009	18/01/2019	0.008	11/01/2019	0.009
22/01/2019	0.007	22/01/2019	0.008	18/01/2019	0.008
01/02/2019	0.009	01/02/2019	0.01	22/01/2019	0.007
07/02/2019	0.01	07/02/2019	0.011	01/02/2019	0.008
11/02/2019	0.009	11/02/2019	0.01	07/02/2019	0.009
22/02/2019	0.008	22/02/2019	0.007	11/02/2019	0.008
25/02/2019	0.006	25/02/2019	0.006	22/02/2019	0.007

Appendix C: Supplementary material for Chapter 5

Table C 1 Coordinates of sample site locations.

Media	Code	Coordinates (Decimal Degrees)	
Stream water	1 - Northern Salary Brook (Blue Barns Farm)	51.93321	0.94776
Stream water	2 - Northern Salary Brook (Hart’s Lane)	51.93628	0.96613
Stream water	3 - Western Salary Brook A	51.92869	0.91480
Stream water	4 - Western Salary Brook B	51.92686	0.91998
Stream water	5 - Western Salary Brook C	51.92636	0.92915
Stream water	Culvert Runkin's Corner	51.93039	0.91508
Field drain runoff	Field Drain Western Salary Brook	51.92643	0.92925
Field drain runoff	Field Drain Runkin's Corner	51.93034	0.91507
Rain water	RW Ardleigh	51.92966	0.96738
Rain water	RW Colchester	51.86341	0.87902

Table C 2 Dataset containing metaldehyde concentrations, climatic and hydrological data variables used in linear regression analysis.

Date	Precipitation (mm)	Relative humidity (%)	Soil temperature 15cm (°C)	Soil temperature 45cm (°C)	Air temperature (°C)	Wind speed (km h^{-1})	Soil moisture (%)	Streamflow at Northern Salary Brook (m^3 s^{-1})	Streamflow at Western Salary Brook (m^3 s^{-1})	Streamflow at Lexden Colne (m^3 s^{-1})	Met. conc. (µg L^{-1}) REG1	Met. conc. (µg L^{-1}) REG2	Met. conc. (µg L^{-1}) REG3
02/01/2019	4.30	95.00	2.22	3.62	1.62	14.21	20.90	0.01	0.02	0.52	0.013	0.008	0.012
04/01/2019	0.00	75.24	8.21	8.08	7.30	10.69	14.73	0.01	0.01	0.47	0.014	0.008	0.012
08/01/2019	0.00	77.41	19.58	18.79	19.14	9.24	14.45	0.01	0.01	0.46	0.012	0.007	0.012
11/01/2019	0.00	99.27	9.57	9.99	11.90	9.44	19.01	0.01	0.01	0.46	0.012	0.008	0.011
14/01/2019	0.00	87.33	6.25	7.03	5.37	10.69	19.51	0.01	0.01	0.47	0.012	0.007	0.011
18/01/2019	0.00	85.82	4.33	6.12	1.72	8.09	19.91	0.01	0.01	0.46	0.011	0.007	0.009
22/01/2019	4.00	90.41	2.98	4.27	2.72	8.35	20.15	0.01	0.02	0.54	0.011	0.007	0.009
25/01/2019	0.80	96.18	2.78	3.97	4.82	8.13	20.27	0.01	0.02	0.49	0.011	0.007	0.008
30/01/2019	2.00	92.98	3.15	4.40	0.20	7.86	20.92	0.02	0.02	0.75	0.010	0.007	0.008
01/02/2019	0.20	89.22	6.40	7.49	4.13	9.49	20.07	0.02	0.02	0.74	0.010	0.007	0.009
04/02/2019	1.00	91.40	7.75	8.00	5.32	7.27	14.26	0.02	0.03	0.82	0.008	0.007	0.009
07/02/2019	0.00	79.76	19.73	18.32	15.02	6.53	17.24	0.03	0.04	1.28	0.008	0.007	0.008
11/02/2019	4.50	88.36	10.58	10.58	11.84	12.44	19.56	0.03	0.04	1.14	0.008	0.007	0.010
13/02/2019	0.00	90.52	5.30	5.24	7.03	7.65	19.39	0.03	0.03	0.95	0.009	0.007	0.008
18/02/2019	0.30	93.79	6.10	5.80	7.52	7.27	19.06	0.02	0.02	0.71	0.008	0.007	0.009
22/02/2019	0.00	95.00	6.62	6.43	6.89	5.88	18.65	0.02	0.02	0.62	0.007	0.007	0.008
25/02/2019	0.00	76.09	5.94	6.39	6.32	3.62	18.15	0.02	0.02	0.59	0.007	0.006	0.008
01/03/2019	0.00	91.79	5.98	7.16	3.41	6.95	20.02	0.02	0.02	0.59	0.007	0.008	0.008
04/03/2019	5.10	93.06	6.86	7.66	2.79	4.56	14.72	0.02	0.02	0.78	0.006	0.006	0.007
08/03/2019	0.00	86.21	19.06	18.75	16.88	4.60	12.92	0.02	0.02	0.74	0.006	0.006	0.007
13/03/2019	0.00	71.80	6.00	6.50	7.78	24.06	19.83	0.03	0.04	1.15	0.006	0.006	0.008
15/03/2019	3.50	82.35	7.61	6.97	11.25	16.28	20.26	0.03	0.03	1.06	0.006	0.006	0.008
18/03/2019	0.00	84.83	7.05	7.31	5.80	8.32	19.91	0.04	0.04	1.30	0.006	0.007	0.008
22/03/2019	0.00	90.93	8.71	8.15	9.07	7.08	19.33	0.02	0.02	0.74	0.005	0.007	0.011
26/03/2019	0.00	78.95	7.23	7.68	5.95	7.28	17.73	0.02	0.02	0.63	0.006	0.006	0.008

29/03/2019	0.00	80.67	7.67	7.72	7.17	4.39	16.81	0.02	0.02	0.61	0.005	0.006	0.008
03/04/2019	6.10	78.98	7.15	7.15	6.69	15.00	19.66	0.02	0.02	0.60	0.006	0.006	0.008
05/04/2019	2.90	82.53	9.62	9.67	6.33	17.75	9.96	0.02	0.02	0.56	0.005	0.009	0.008
10/04/2019	0.60	88.36	12.88	13.53	13.21	11.06	18.35	0.02	0.02	0.55	0.006	0.008	0.008
12/04/2019	0.00	96.09	3.93	5.76	2.14	2.34	18.95	0.01	0.02	0.52	0.005	0.008	0.008
15/04/2019	0.00	81.60	7.00	7.28	7.13	12.50	14.57	0.01	0.02	0.51	0.005	0.008	0.008
18/04/2019	0.00	74.25	9.47	8.35	12.84	10.46	13.30	0.01	0.02	0.50	0.005	0.007	0.008
23/04/2019	0.00	70.07	10.51	9.79	12.99	8.92	10.08	0.01	0.01	0.44	0.006	0.007	0.008
26/04/2019	0.00	76.86	10.34	10.00	11.33	10.78	9.57	0.01	0.01	0.39	0.006	0.008	0.009
29/04/2019	0.10	89.97	9.34	9.50	8.54	5.78	9.43	0.01	0.01	0.41	0.006	0.008	0.009
01/05/2019	0.00	84.99	5.09	6.43	4.11	9.39	19.87	0.01	0.01	0.41	0.006	0.008	0.008
09/05/2019	0.00	64.16	15.76	16.67	13.31	10.99	10.02	0.02	0.03	0.90	0.006	0.012	0.010
10/05/2019	0.00	85.82	13.25	13.63	12.44	7.75	18.14	0.02	0.02	0.67	0.007	0.016	0.015
13/05/2019	0.00	78.44	9.68	9.66	9.15	6.90	17.85	0.01	0.01	0.43	0.008	0.018	0.016
17/05/2019	0.30	88.35	10.70	10.20	11.51	10.13	16.04	0.01	0.01	0.35	0.008	0.015	0.013
20/05/2019	0.70	87.83	11.54	10.80	13.29	8.89	15.69	0.01	0.01	0.34	0.008	0.015	0.010
24/05/2019	0.00	68.92	13.75	11.94	15.49	11.17	15.19	0.01	0.01	0.21	0.008	0.013	0.010
28/05/2019	4.30	90.78	13.70	12.95	10.96	9.71	15.13	0.01	0.01	0.26	0.013	0.016	0.015
31/05/2019	0.00	75.83	15.63	13.57	16.57	7.59	16.49	0.01	0.01	0.22	0.009	0.015	0.013
03/06/2019	2.80	90.23	7.43	7.00	9.92	15.59	19.90	0.01	0.01	0.19	0.008	0.012	0.008
05/06/2019	0.00	71.55	9.12	9.27	7.84	8.16	9.86	0.01	0.01	0.26	0.009	0.013	0.009
12/06/2019	7.90	92.10	6.38	5.83	10.58	14.16	19.79	0.02	0.02	0.61	0.008	0.014	0.015
13/06/2019	1.30	86.61	14.82	14.07	13.48	12.05	19.56	0.02	0.02	0.68	0.009	0.013	0.036
17/06/2019	0.00	74.03	16.92	15.03	16.92	8.87	18.76	0.01	0.01	0.38	0.011	0.012	0.021
23/06/2019	0.00	84.74	17.80	16.47	17.60	7.54	18.80	0.01	0.01	0.30	0.009	0.017	0.016
24/06/2019	0.20	84.46	18.80	16.67	21.28	4.63	18.72	0.01	0.01	0.30	0.012	0.017	0.051
27/06/2019	0.00	82.99	18.80	17.32	15.17	12.39	18.98	0.01	0.01	0.39	0.010	0.016	0.016
01/07/2019	0.00	88.37	6.28	6.64	8.73	10.88	19.84	0.01	0.01	0.20	0.009	0.014	0.027
05/07/2019	0.00	73.64	8.91	9.11	9.75	6.71	9.60	0.00	0.01	0.17	0.015	0.010	0.036
09/07/2019	0.30	79.88	14.62	15.72	12.29	10.98	10.42	0.01	0.01	0.20	0.009	0.014	0.025
12/07/2019	0.00	87.99	6.36	6.63	8.12	8.19	19.80	0.01	0.01	0.21	0.008	0.011	0.018
15/07/2019	0.00	79.43	18.45	17.86	14.86	5.62	13.93	0.01	0.01	0.21	0.008	0.011	0.016
18/07/2019	2.00	82.73	19.51	18.36	17.68	5.11	13.34	0.00	0.01	0.16	0.009	0.013	0.012
22/07/2019	0.00	77.14	20.26	18.28	21.66	8.30	15.05	0.01	0.01	0.25	0.009	0.009	0.010

24/07/2019	1.70	66.09	22.46	19.74	25.60	5.96	14.22	0.00	0.01	0.18	0.009	0.009	0.012
31/07/2019	0.00	73.60	19.19	18.91	18.88	9.91	15.23	0.01	0.01	0.23	0.010	0.008	0.013
02/08/2019	1.50	90.59	5.51	5.19	8.62	17.22	19.59	0.01	0.01	0.20	0.010	0.009	0.012
07/08/2019	0.00	78.89	18.27	17.76	14.24	5.13	15.43	0.00	0.01	0.17	0.010	0.007	0.011
09/08/2019	0.00	77.60	14.28	15.31	11.60	7.18	10.38	0.01	0.01	0.21	0.009	0.007	0.009
13/08/2019	0.00	75.56	17.18	17.58	14.30	6.98	12.46	0.01	0.01	0.21	0.012	0.009	0.010
16/08/2019	3.90	91.78	16.54	17.04	14.82	9.23	14.04	0.01	0.01	0.30	0.011	0.013	0.010
19/08/2019	0.00	75.75	17.20	17.22	16.05	8.12	15.59	0.01	0.01	0.24	0.010	0.012	0.010
21/08/2019	0.00	73.57	16.46	16.83	15.95	5.64	14.60	0.00	0.01	0.17	0.010	0.015	0.012
27/08/2019	0.00	77.30	18.46	17.74	21.82	5.07	10.96	0.00	0.00	0.14	0.013	0.015	0.012
30/08/2019	0.00	73.26	18.05	17.91	18.19	7.22	10.03	0.00	0.00	0.14	0.011	0.013	0.014
02/09/2019	0.10	72.91	5.63	5.53	7.89	17.45	19.62	0.00	0.00	0.14	0.013	0.011	0.013
04/09/2019	0.00	86.50	9.08	8.41	8.58	15.60	16.50	0.00	0.01	0.16	0.012	0.014	0.013
09/09/2019	5.40	96.67	13.77	15.01	10.82	3.80	10.95	0.01	0.01	0.20	0.012	0.012	0.012
12/09/2019	0.00	79.57	5.58	6.86	5.33	17.08	19.30	0.00	0.01	0.18	0.011	0.015	0.013
18/09/2019	0.00	77.81	13.45	14.81	10.96	5.45	10.10	0.00	0.00	0.15	0.013	0.016	0.010
20/09/2019	0.00	81.09	13.23	14.13	13.21	9.22	9.80	0.00	0.00	0.15	0.013	0.017	0.010
23/09/2019	0.70	83.46	14.88	14.69	16.20	9.53	9.81	0.00	0.00	0.15	0.013	0.016	0.010
26/09/2019	2.20	87.24	15.59	15.24	16.54	8.94	12.36	0.01	0.01	0.27	0.018	0.024	0.014
30/09/2019	9.20	89.55	14.69	14.96	13.80	8.87	14.64	0.01	0.01	0.32	0.015	0.030	0.016
04/10/2019	0.00	72.61	8.57	8.44	6.45	15.16	16.13	0.01	0.01	0.29	0.018	0.037	0.022
07/10/2019	0.00	72.01	19.19	17.45	20.48	4.90	15.17	0.04	0.04	1.39	0.017	0.040	0.023
11/10/2019	0.00	90.90	7.10	8.65	5.56	4.44	18.86	0.01	0.01	0.32	0.016	0.026	0.019
14/10/2019	4.20	96.94	12.83	13.32	12.59	9.48	19.11	0.02	0.02	0.72	0.015	0.020	0.016
17/10/2019	5.20	93.27	12.38	13.18	10.72	6.04	19.06	0.01	0.02	0.49	0.015	0.022	0.020
21/10/2019	2.70	95.58	11.25	12.04	11.01	13.94	19.06	0.01	0.01	0.36	0.016	0.023	0.018
23/10/2019	0.80	96.24	10.56	11.71	9.59	4.92	18.95	0.01	0.01	0.33	0.015	0.027	0.017
24/10/2019	6.30	98.51	11.63	11.86	11.73	5.01	19.30	0.01	0.01	0.39			0.016
28/10/2019	0.00	90.73	9.26	11.25	6.24	6.14	18.87	0.01	0.01	0.34	0.019	0.051	0.020
29/10/2019	0.00	84.30	9.18	10.76	7.74	8.34	18.72	0.01	0.01	0.32			0.020
30/10/2019	0.00	82.97	8.72	10.37	7.59	8.46	18.57	0.01	0.01	0.30	0.018	0.046	0.022
04/11/2019	0.00	70.10	7.90	8.22	4.91	9.36	15.68	0.01	0.01	0.45	0.016	0.034	0.016
08/11/2019	0.60	73.73	18.13	18.27	17.57	9.74	12.31	0.01	0.01	0.43	0.016	0.026	0.020
13/11/2019	0.00	88.81	6.74	8.08	5.87	7.87	19.08	0.01	0.01	0.47	0.017	0.025	0.020

14/11/2019	14.70	96.06	6.72	7.93	5.87	8.29	20.22	0.03	0.04	1.19			0.024
15/11/2019	2.30	95.17	6.67	7.88	6.14	10.58	19.54	0.03	0.04	1.20	0.016	0.025	0.020
18/11/2019	0.20	92.21	6.38	7.53	5.64	14.10	19.12	0.02	0.02	0.67	0.017	0.023	0.044
21/11/2019	0.00	91.85	5.16	6.61	5.36	12.80	18.79	0.01	0.02	0.51			0.028
22/11/2019	2.80	93.60	6.42	6.84	8.27	13.47	19.34	0.01	0.02	0.50	0.016	0.018	0.024
25/11/2019	1.60	97.47	8.04	8.00	9.41	11.92	19.37	0.01	0.02	0.52			0.023
27/11/2019	15.20	98.48	9.10	8.80	9.89	7.83	21.10	0.06	0.07	2.28	0.015	0.035	0.028
02/12/2019	0.00	87.27	4.41	5.13	5.67	5.54	19.42	0.02	0.02	0.73			0.196
04/12/2019	0.00	73.13	7.38	7.98	4.94	8.98	15.32	0.02	0.02	0.62	0.013	0.015	0.190
06/12/2019	9.90	96.19	14.93	14.14	12.28	4.60	19.44	0.02	0.02	0.68	0.012	0.010	0.119
09/12/2019	0.00	81.34	15.64	15.27	18.48	7.58	11.96	0.02	0.03	0.88	0.011	0.015	0.070
10/12/2019	7.80	98.11	13.14	13.42	11.18	4.71	19.22	0.02	0.02	0.79			0.107
13/12/2019	10.80	87.66	5.44	6.02	6.28	13.74	21.22	0.15	0.18	5.60	0.010	0.015	0.040
16/12/2019	2.70	93.69	5.04	5.68	6.83	6.40	19.78	0.11	0.13	4.07	0.011	0.014	0.209
17/12/2019	10.70	100.00	5.67	5.97	6.05	5.84	21.12	0.14	0.16	5.09			0.153
18/12/2019	0.20	96.89	4.95	5.95	5.65	10.60	20.08	0.12	0.14	4.55			0.174
19/12/2019	9.00	92.49	6.88	6.25	10.63	15.31	20.30	0.13	0.15	4.66	0.011	0.013	0.141
27/12/2019	0.00	99.17	6.21	6.24	7.34	8.00	20.15	0.07	0.08	2.43	0.013	0.012	0.050
30/12/2019	0.00	94.89	5.14	6.38	5.23	5.91	19.56	0.04	0.05	1.63	0.011	0.011	0.037
03/01/2020	0.00	76.30	4.90	5.90	5.00	14.46	21.44	0.03	0.04	1.25	0.011	0.010	0.027
06/01/2020	2.20	93.73	6.67	6.57	7.43	12.63	19.97	0.03	0.04	1.22	0.009	0.010	0.022
08/01/2020	0.00	89.27	5.10	6.34	5.32	9.00	19.84	0.03	0.03	1.07	0.009	0.011	0.023
15/01/2020	7.90	92.21	7.84	7.56	8.01	10.98	21.06	0.09	0.11	3.38	0.008	0.011	0.024
17/01/2020	3.90	91.84	7.16	7.34	7.21	11.08	20.86	0.11	0.13	4.01	0.019	0.025	0.025
22/01/2020	0.40	100.00	3.43	4.52	4.39	2.41	19.54	0.03	0.04	1.25	0.008	0.009	0.024
24/01/2020	0.30	100.00	5.49	5.57	5.64	3.16	19.72	0.03	0.04	1.18	0.008	0.009	0.022
29/01/2020	0.00	83.33	3.90	5.38	4.98	10.65	19.94	0.09	0.11	3.42	0.007	0.009	0.013
31/01/2020	0.00	92.46	6.93	6.10	10.27	12.59	19.95	0.05	0.05	1.74	0.008	0.009	0.045
05/02/2020	0.90	85.49	5.78	5.63	8.30	9.97	19.35	0.03	0.03	1.03	0.007	0.009	0.016
14/02/2020	0.00	86.70	5.24	5.43	7.21	10.42	20.34	0.04	0.04	1.39	0.006	0.007	0.010
21/02/2020	0.00	77.59	5.16	6.07	7.18	14.43	20.45	0.05	0.06	1.78	0.006	0.008	0.011
28/02/2020	7.70	92.17	3.83	5.17	5.28	11.85	21.19	0.13	0.15	4.71	0.006	0.008	0.012

Table C 3 Physico-chemical parameters of water samples measured *in situ* and in the lab.

Sampling point	Date	Metaldehyde concentration (μg L^{-1})	pH	Electrical conductivity (μS cm^{-1})	Dissolved oxygen (% Saturation)	Temperature (°C)	Nitrite (μg L^{-1})	Nitrate. (μg L^{-1})	Nitrate+ Nitrite (mg L^{-1})	Ammonia (μg L^{-1})	Phosphate (μg L^{-1})	Total P (μg L^{-1})
Point 1	16/01/2019	0.002	6.89	614.00		8.23	47.81	25.25	25.30	126.13	70.52	121.7
Point 2	16/01/2019	0.005	6.78	542.33		8.13	76.84	4.64	4.72	1111.43	179.05	397.6
Point 3	16/01/2019	0.002	6.50	503.33		8.20	20.05	1.82	1.84	179.09	84.56	54.2
Point 4	16/01/2019	0.004	6.84	590.00		8.37	44.68	4.14	4.19	1112.63	137.92	343.1
Point 5	16/01/2019	0.005	6.58	583.67		8.10	65.20	5.49	5.56	121.91	177.85	169.4
Point 1	30/01/2019	0.009	6.78	1056.00	85.27	5.33	48.04	5.88	5.93	273.84	110.34	117.0
Point 2	30/01/2019	0.008	7.00	615.67	75.27	4.93	27.96	5.35	5.38	386.23	138.72	182.6
Point 3	30/01/2019	0.006	6.76	676.33	88.37	4.80	15.75	3.59	3.61	164.50	81.76	72.2
Point 4	30/01/2019	0.007	6.58	941.00	86.73	5.20	21.53	5.83	5.86	235.24	78.21	137.5
Point 5	30/01/2019	0.007	6.82	946.00	90.50	4.30	24.49	6.24	6.26	153.50	67.16	136.0
Point 1	13/02/2019	0.006	7.11	847.00	88.03	7.17	31.39	7.40	7.44	135.05	51.59	98.7
Point 2	13/02/2019	0.002	7.07	756.00	75.53	7.57	25.18	6.28	6.31	408.86	130.37	307.6
Point 3	13/02/2019	0.002	7.15	718.33	94.90	7.73	12.81	6.49	6.50	73.59	53.75	64.0
Point 4	13/02/2019	0.005	7.17	862.67	84.43	7.37	17.13	6.21	6.23	101.61	34.76	167.8
Point 5	13/02/2019	0.007	6.96	845.67	91.17	6.97	22.10	7.49	7.51	67.74	81.26	124.5
Point 1	27/02/2019	0.002	7.45	811.33	81.83	8.80	56.00	13.41	13.47	102.87	66.66	111.7
Point 2	27/02/2019	0.002	7.32	691.67	75.13	9.73	27.16	5.47	5.49	368.33	125.42	356.8
Point 3	27/02/2019	0.002	7.34	661.33	87.90	9.37	5.95	6.18	6.18	48.20	30.65	57.7
Point 4	27/02/2019	0.002	7.32	809.67	82.60	8.27	17.60	5.36	5.38	85.66	52.97	138.9
Point 5	27/02/2019	0.002	7.26	798.33	84.57	6.13	19.95	7.17	7.19	59.61	102.21	133.0
Point 1	29/03/2019	0.004	7.20	718.00	87.87	11.87	50.13	8.06	8.11	135.75	64.51	52.4
Point 2	29/03/2019	0.002	7.56	688.33	74.80	10.97	41.86	5.99	6.03	404.82	250.78	302.2
Point 3	29/03/2019	0.002	7.60	662.00	88.90	11.13	15.07	6.05	6.06	63.10	67.56	46.3
Point 4	29/03/2019	0.002	7.65	779.33	85.07	10.30	31.89	5.38	5.41	83.60	203.18	77.4
Point 5	29/03/2019	0.004	7.50	792.33	86.50	10.63	21.61	6.14	6.17	78.28	87.85	109.8

Point 1	30/04/2019	0.005	7.79	729.67	78.97	10.17	24.42	6.60	6.62	258.83	33.88	79.2
Point 2	30/04/2019	0.002	7.31	648.00	72.00	11.40	60.91	6.03	6.09	1126.64	354.45	427.4
Point 3	30/04/2019	0.002	7.51	622.00	84.60	9.93	25.18	4.26	4.29	80.85	73.12	45.0
Point 4	30/04/2019	0.006	7.41	833.00	79.27	9.17	138.34	3.48	3.62	270.34	705.75	423.2
Point 5	30/04/2019	0.006	7.72	705.33	81.67	8.63	18.98	3.62	3.64	45.29	159.5	187.2
Point 1	29/05/2019	0.008	6.50	762.67	57.93	13.00	17.38	3.94	3.95	88.44	38.89	116.1
Point 2	29/05/2019	0.005	7.07	622.33	53.57	14.27	118.01	4.51	4.62	1129.73	496.84	773.7
Point 3	29/05/2019	0.002	7.53	598.33	57.43	13.47	15.94	4.40	4.41	50.21	36.7	107.8
Point 4	29/05/2019	0.010	7.68	794.33	66.43	12.83	34.59	1.98	2.02	65.32	142.54	294.7
Point 5	29/05/2019	0.010	7.62	759.33	68.00	12.73	7.36	1.22	1.23	43.26	55.47	261.5
Point 1	13/06/2019	0.004	7.69	760.67	74.37	13.50	38.07	5.31	5.35	302.05	34.26	201.1
Point 2	13/06/2019	0.004	7.37	783.00	71.27	14.97	253.33	3.93	4.18	628.16	363.06	631.3
Point 3	13/06/2019	0.010	7.24	780.33	83.07	13.77	24.75	6.52	6.54	81.24	47.61	122.2
Point 4	13/06/2019	0.012	6.93	815.00	83.40	13.60	59.59	3.19	3.25	166.63	194.66	292.5
Point 5	13/06/2019	0.015	6.93	693.33	83.93	13.40	15.72	4.04	4.05	71.89	71.44	183.2
Point 1	26/06/2019	0.005	7.36	588.00	70.53	16.03	32.58	4.32	4.36	88.12	45.8	99.5
Point 2	26/06/2019	0.002	7.28	670.00	52.83	17.17	160.83	3.88	4.04	1137.86	368.31	679.9
Point 3	26/06/2019	0.006	7.36	646.00	76.10	16.33	21.47	5.03	5.05	67.15	65.1	120.4
Point 4	26/06/2019	0.008	7.04	753.00	73.80	15.63	16.25	2.84	2.86	56.11	111.87	167.6
Point 5	26/06/2019	0.009	6.31	715.33	76.60	15.53	18.78	2.42	2.44	53.85	163.4	210.3
			7.44	1302.00	54.13	17.20	255.86	1.80	2.06	1140.38	2043.98	3906.45
Point 1	31/07/2019	0.008										x
Point 2	31/07/2019	0.002	7.44	678.67	72.47	18.27	268.04	3.30	3.56	1141.01	390.82	1191.9
Point 3	31/07/2019	0.002	7.41	741.67	74.00	17.60	33.66	6.12	6.16	216.04	17.38	109.1
Point 4	31/07/2019	0.006	7.35	817.67	79.67	17.13	31.27	3.32	3.35	103.56	162.27	228.7
Point 5	31/07/2019	0.005	6.45	810.33	80.00	16.80	19.26	2.46	2.48	187.95	297.88	217.1
Point 1	04/09/2019	0.006	7.19	780.67	33.90	16.40	406.32	0.73	1.14	1143.55	1378.98	212.8
Point 2	04/09/2019	0.006	7.38	643.33	43.60	17.03	184.99	2.90	3.08	1144.19	726.7	1596.1
Point 3	04/09/2019	0.002	7.47	733.00	49.10	16.07	90.34	6.05	6.15	362.63	155.7	1020.3
Point 4	04/09/2019	0.009	7.44	384.67	62.23	17.00	34.34	1.84	1.87	168.01	104.71	260.5
Point 5	04/09/2019	0.007	7.32	246.33	64.07	16.83	64.85	2.20	2.27	338.13	198.8	170.0
Point 1	02/10/2019	0.020	6.93	512.33	72.30	13.50	39.39	3.85	3.89	188.69	187.95	193.3

Point 2	02/10/2019	0.015	7.26	756.00	61.07	13.40	98.73	4.34	4.44	423.48	283.01	188.7
Point 3	02/10/2019	0.036	7.12	698.33	77.87	11.60	15.94	4.69	4.71	43.07	65.61	778.0
Point 4	02/10/2019	0.038	7.21	570.67	76.63	12.67	48.77	3.64	3.69	614.83	166.55	107.6
Point 5	02/10/2019	0.039	7.19	541.00	78.73	12.00	50.03	2.63	2.68	227.76	144.63	231.4
Point 1	16/10/2019	0.009	7.34	635.00	79.40	14.10	29.45	5.16	5.19	118.27	33.62	247.5
Point 2	16/10/2019	0.005	7.28	746.67	56.10	14.40	129.57	4.23	4.36	629.62	354.08	107.3
Point 3	16/10/2019	0.035	7.33	815.33	75.30	13.90	22.47	4.90	4.93	52.46	20.5	895.2
Point 4	16/10/2019	0.025	7.39	747.67	71.57	14.30	69.39	2.89	2.96	263.99	91.37	74.9
Point 5	16/10/2019	0.018	7.23	802.33	79.00	13.97	48.43	3.82	3.87	111.95	120.62	147.9
Point 1	31/10/2019	0.006	7.63	579.67	54.13	10.80	173.41	2.84	3.01	1142.57	930.91	169.1
Point 2	31/10/2019	0.005	7.38	560.67	52.90	11.00	148.16	4.62	4.77	615.26	331.85	1780.4
Point 3	31/10/2019	0.016	7.36	605.67	76.10	10.30	21.89	4.71	4.73	67.24	47.84	248.4
Point 4	31/10/2019	0.018	7.62	641.67	66.93	10.63	67.03	3.93	4.00	973.55	150.2	60.4
Point 5	31/10/2019	0.016	7.53	632.33	81.43	9.80	57.88	5.06	5.12	159.90	104	219.3
Point 1	13/11/2019	0.007	7.17	521.00	68.63	9.77	29.44	6.77	6.80	83.02	50.8	302.3
Point 2	13/11/2019	0.005	7.23	581.67	61.87	9.60	103.67	4.88	4.99	601.48	354.28	90.4
Point 3	13/11/2019	0.017	7.29	594.00	80.67	9.20	10.26	5.04	5.05	36.89	27.46	749.9
Point 4	13/11/2019	0.018	7.45	624.00	68.67	9.13	33.99	4.92	4.95	206.26	61.11	73.0
Point 5	13/11/2019	0.017	7.44	615.00	78.67	8.30	38.69	5.10	5.14	81.43	74.36	149.6
Field drain WSB	13/11/2019	0.008	7.02	540.67	61.00	9.30	3.54	12.45	12.46	21.85	111	158.1
Field drain Runkin's C.	13/11/2019	0.006	6.55	566.67	79.97	9.23	8.67	6.16	6.17	34.56	21.16	197.5
Culvert Runkin's C.	13/11/2019	0.012	7.81	559.67	76.97	9.07	8.77	4.27	4.28	37.92	16.23	99.8
Point 1	28/11/2019	0.012	7.18	451.00	74.27	10.07	8.49	6.71	6.72	279.57	30.79	30.0
Point 2	28/11/2019	0.006	7.20	476.67	62.93	10.40	20.77	4.85	4.87	132.41	66.45	128.0
Point 3	28/11/2019	0.026	7.00	451.00	65.40	9.83	20.89	6.69	6.71	66.64	39.18	410.5
Point 4	28/11/2019	0.023	7.04	437.67	70.80	9.87	22.75	5.91	5.93	166.65	65.39	123.2
Point 5	28/11/2019	0.022	7.19	409.00	83.67	9.80	26.76	4.50	4.53	119.01	76.63	167.8
Field drain WSB	28/11/2019	0.012	7.01	450.33	53.07	9.70	7.53	7.87	7.88	50.96	67.18	59.7
Field drain Runkin's C.	28/11/2019	0.012	6.60	496.33	61.13	10.20	13.85	9.64	9.65	85.23	43.13	196.4
Culvert Runkin's C.	28/11/2019	0.012	7.31	445.00	65.23	9.97	2.68	12.18	12.18	23.85	17.96	152.6

Point 1	13/12/2019	0.015	7.12	609.33	69.83	7.90	8.62	4.81	4.82	1000.68	55.08	84.0
Point 2	13/12/2019	0.007	7.11	677.33	68.17	8.03	10.70	4.25	4.27	91.00	38.97	256.0
Point 3	13/12/2019	0.016	7.09	503.00	76.93	8.33	23.64	1.96	1.99	115.04	103.83	342.7
Point 4	13/12/2019	0.017	7.17	506.67	68.97	7.83	16.63	3.30	3.32	138.83	28.32	266.9
Point 5	13/12/2019	0.017	7.09	477.67	79.60	7.20	15.11	5.14	5.16	112.16	15.1	689.3
Field drain WSB	13/12/2019	0.010	6.76	457.40	67.67	7.73	19.40	2.84	2.86	65.22	211.77	261.6
Field drain Runkin's C.	13/12/2019	0.015	6.90	623.33	73.00	7.73	8.03	6.16	6.17	42.05	13.76	280.5
Culvert Runkin's C.	13/12/2019	0.016	7.14	659.00	74.43	8.07	3.30	7.90	7.90	29.69	35.07	197.8
Point 1	03/01/2020	0.008	7.29	569.33	77.67	8.13	27.66	6.07	6.10	78.12	32.25	196.1
Point 2	03/01/2020	0.005	7.19	494.33	74.33	8.60	6.85	4.90	4.91	67.24	12.65	262.2
Point 3	03/01/2020	0.011	7.15	508.67	74.93	8.60	34.81	4.61	4.64	109.82	99.4	54.6
Point 4	03/01/2020	0.008	7.15	440.33	73.27	8.90	19.90	3.38	3.40	188.78	58.9	185.0
Point 5	03/01/2020	0.008	7.01	488.00	67.80	9.10	15.08	3.75	3.76	109.34	39.31	107.4
Field drain WSB	03/01/2020	0.008	6.99	529.67	59.10	8.23	5.73	6.71	6.72	36.20	62.18	123.1
Field drain Runkin's C.	03/01/2020	0.004	6.52	541.33	73.70	8.40	31.70	3.67	3.70	100.07	46.85	63.7
Culvert Runkin's C.	03/01/2020	0.006	7.34	522.33	71.90	8.20	7.18	3.80	3.81	36.65	23.84	37.7
Point 1	17/01/2020	0.012	7.25	563.33	70.60	8.43	31.79	7.53	7.56	67.59	75.99	77.8
Point 2	17/01/2020	0.010	7.17	519.33	66.73	8.70	6.65	2.44	2.45	64.76	13.9	170.8
Point 3	17/01/2020	0.013	7.10	489.00	65.97	9.30	8.92	4.82	4.83	56.27	34.25	161.0
Point 4	17/01/2020	0.012	7.13	461.00	69.80	9.40	15.72	3.66	3.68	80.81	51.44	97.8
Point 5	17/01/2020	0.014	7.40	456.00	77.47	9.63	42.23	1.90	1.94	117.41	92.82	119.1
Field drain WSB	17/01/2020	0.008	7.06	546.67	62.53	9.93	4.81	7.87	7.88	24.10	31.3	86.6
Field drain Runkin's C.	17/01/2020	0.007	6.60	541.33	67.80	9.03	9.16	6.10	6.11	87.84	24.22	74.0
Culvert Runkin's C.	17/01/2020	0.010	7.40	522.33	68.87	8.83	6.26	3.84	3.85	41.14	34.56	67.2
Point 1	29/01/2020	0.008	7.23	559.67	77.53	7.50	29.21	8.95	8.98	73.96	30.09	62.1
Point 2	29/01/2020	0.005	7.22	470.00	76.67	8.20	11.08	4.09	4.11	74.07	37.95	200.9
Point 3	29/01/2020	0.009	7.33	511.00	76.17	7.27	19.64	5.99	6.01	102.91	45.23	74.8
Point 4	29/01/2020	0.009	7.32	512.33	79.07	7.47	35.03	3.67	3.71	125.09	52.2	101.2
Point 5	29/01/2020	0.009	7.31	522.00	78.33	7.80	15.92	5.41	5.43	74.25	46.37	220.2

Field drain WSB	29/01/2020	0.004	6.99	506.67	71.47	7.77	5.48	7.72	7.73	57.34	39.76	89.1
Field drain Runkin's C.	29/01/2020	0.007	6.60	528.00	75.67	7.80	9.26	7.92	7.93	52.09	34.67	55.9
Culvert Runkin's C.	29/01/2020	0.007	7.27	495.33	76.30	6.97	2.58	7.67	7.67	36.31	16.81	14.4
Point 1	14/02/2020	0.007	7.46	720.00	92.27	7.90	17.99	7.94	7.96	100.47	25.57	58.5
Point 2	14/02/2020	0.002	7.34	636.33	88.13	8.40	6.58	4.46	4.47	85.49	25.8	193.8
Point 3	14/02/2020	0.006	7.24	623.00	93.53	9.10	14.77	5.30	5.32	90.38	12.32	92.9
Point 4	14/02/2020	0.007	7.29	670.33	96.03	9.00	6.98	4.34	4.35	58.45	23.96	96.6
Point 5	14/02/2020	0.007	6.93	679.00	89.60	8.13	12.95	5.25	5.26	69.77	38.43	136.4
Field drain WSB	14/02/2020	0.006	7.07	652.00	79.50	8.63	2.32	8.41	8.41	28.56	61.17	109.2
Field drain Runkin's C.	14/02/2020	0.002	6.60	667.67	91.60	8.77	7.82	6.43	6.43	38.46	20.14	61.3
Culvert Runkin's C.	14/02/2020	0.005	7.33	681.00	86.93	7.90	3.80	10.95	10.95	28.61	9.92	67.9
Point 1	28/02/2020	0.005		756.33		6.80	18.81	5.59	5.60	95.67	10.67	153.9
Point 2	28/02/2020	0.004		413.33	79.93	6.33	7.93	1.57	1.57	33.82	11.6	648.3
Point 3	28/02/2020	0.008		477.00	80.47	6.10	5.47	2.18	2.18	67.52	6.49	225.7
Point 4	28/02/2020	0.005		630.33	90.87	6.73	13.77	4.06	4.07	86.55	11.42	156.4
Point 5	28/02/2020	0.007		682.67	90.37	6.63	15.45	5.28	5.29	84.58	54.8	160.7
Field drain WSB	28/02/2020	0.006		646.00	78.80	6.63	4.21	6.43	6.43	39.20	42.44	115.3
Field drain Runkin's C.	28/02/2020	0.004		431.67	82.67	6.83	8.52	3.44	3.45	44.69	11.59	168.8
Culvert Runkin's C.	28/02/2020	0.005		624.67	82.67	6.87	10.35	1.25	1.26	79.02	10.46	117.5

Table C 4 Metaldehyde concentrations in precipitation.

Date	Metaldehyde concentration (µg L–1) at RW (rainwater) Ardleigh	Metaldehyde concentration (µg L–1) at RW (rainwater) Colchester	Precipitation (mm) at Ardleigh	Precipitation (mm) at Colchester
27/02/2019	< 0.004	0.008	23	24
29/03/2019	< 0.004	0.004	52	47
30/04/2019	0.018	No data	14	No data
30/05/2019	0.022	0.025	69	65
26/06/2019	0.018	0.025	54	45
31/07/2019	< 0.004	0.012	57	45
04/09/2019	0.014	0.04	47	43
02/10/2019	0.041	0.052	84	50
31/10/2019	0.052	0.038	97	132
28/11/2019	0.03	0.035	78	63
03/01/2019	0.014	0.012	139	115
29/01/2020	0.008	0.007	44	43
28/02/2020	< 0.004	< 0.004	80	64

Table C 5 Metaldehyde load values calculated for the mass budget model.

	Input flux (load, g)						
Date	REG1	REG2	REG3	Atmospheric deposition (load, g)	Input flux total (load, g)	Output flux (loss, g)	Metaldehyde flux retained in the reservoir (g)
01/01/2019	0.44	0.32	5.73	0.00	6.48	14.91	46.20
01/02/2019	0.45	0.44	3.99	0.00	4.87	10.96	36.34
01/03/2019	0.37	0.46	4.75	0.00	5.57	9.29	31.22
01/04/2019	0.20	0.32	5.24	0.11	5.86	7.93	29.65
01/05/2019	0.22	0.45	7.08	0.66	8.42	8.47	29.51
01/06/2019	0.26	0.45	14.15	0.43	15.30	8.12	31.56
01/07/2019	0.15	0.20	9.53	0.00	9.87	11.15	36.63
01/08/2019	0.15	0.18	5.93	0.27	6.53	10.22	31.79
01/09/2019	0.17	0.26	6.55	1.24	8.22	9.58	27.64
01/10/2019	0.55	1.24	15.47	1.99	19.25	12.89	39.78
01/11/2019	0.81	1.54	15.33	0.98	18.65	10.48	37.72
01/12/2019	3.13	4.12	10.23	0.81	18.29	14.84	47.36

Appendix D: Published papers

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Ubiquity of microbial capacity to degrade metaldehyde in dissimilar agricultural, allotment and garden soils

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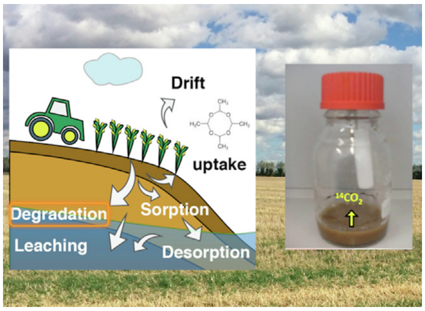
HIGHLIGHTS

- Results indicated ubiquitous catabolic competence to degrade metaldehyde in dissimilar soils.
- Metaldehyde catabolic competence was evident in garden, allotment and field soils.
- Metaldehyde mineralisation ranged from 17.7 to 60.0%
- Higher levels of catabolic competence were observed in the lighter soil textures.
- Pre-exposure to metaldehyde sometime, but not always, resulted in higher catabolic competence.

GRAPHICAL ABSTRACT



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ABSTRACT

Metaldehyde is a molluscicide used to control slugs and snails. Despite its extensive use, very little is known about the capacity of soil microbial communities to degrade this chemical. This research provides a synopsis of the latent capacity of soil microbial communities, present in agricultural (n=14), allotment (n=4) and garden (n=10) soils, to degrade metaldehyde. Extents of ^{14}C-metaldehyde mineralisation across all soils ranged from 17.7 to 60.0%. Pre-exposure (*in situ*, in the field) to metaldehyde was not observed to consistently increase extents of metaldehyde mineralisation. Where soils were augmented, (*ex situ*, in the laboratory) with metaldehyde (28 mg kg^{-1}), the mineralisation capacity was increased in some, but not all, soils (uplift ranged from +0.10 to +16.9%). Results indicated that catabolic competence to degrade metaldehyde was evident in both surface (16.7–52.8%) and in sub-surface (30.0–66.4%) soil horizons. Collectively, the results suggest that catabolic competence to degrade metaldehyde was ubiquitous across a diverse range of soil environments; that varied in texture (from sand to silty clay loam), pH (6.15–8.20) and soil organic matter (SOM) content (1.2%–52.1%). Lighter texture soils, in general, were observed to have higher capacity to mineralise metaldehyde. Weak correlations between catabolic competence and soil pH and soil organic matter content were observed; it was noted that above a SOM threshold of 12% metaldehyde mineralisation was always >34%. It was concluded that the common occurrence of metaldehyde in EU waters is *unlikely* the consequence of low potential for this chemical to be degraded in soil. It is more likely that application regimes (quantities/timings) and meteorological drivers facilitate the transport of metaldehyde from point of application into water resources.

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1. Introduction

Slugs, snails and other gastropods are significant pests to a range of crops, including agricultural, horticultural and garden plants (Rae et al., 2009). Metaldehyde (2,4,6,8-tetramethyl-1,3,5,7 -tetraoxcane) is a widely used molluscicide in agriculture and domestic settings globally (including the UK, Europe, the United States and China (EPA, 2011; Gavin et al., 2012; Ma et al., 2012; Zhongguo et al., 2013; EC, 2019)).

This pesticide is normally applied to crops in autumn and winter (Environment Agency, 2009). The maximum recommended application rate of metaldehyde in the UK is currently 210 g active substance/ha (from 1st August to 31st December); 700 g active substance/ha is the maximum total dose per calendar year (Metaldehyde Stewardship Group (MSG), 2019). Similar application rates are evident across Europe; allowing a maximum of 350 g active substance/ha per single treatment, with up to two treatments per year (EFSA, 2010). In the United States the recommended single application rate should not exceed 2240 g active substance/ha with a maximum of 6 applications per year (EPA, 2011).

Bait pellets release metaldehyde, under moderately moist conditions, for approximately 10 days (Puschner, 2006). Metaldehyde is relatively water soluble (190 mg L^{-1}; PPDB, 2017) and has as low K_{OW} value (0.12; Hall, 2010). Owing to, i) its physicochemical properties (Table 1 in Supplementary Material), ii) application times that often coincide with wetter periods (when molluscs are more prevalent, compared to dry weather conditions) and, iii) the prevailing wet autumn/winter weather in the UK and northern EU countries, metaldehyde is mobile in the environment. This mobility serves to transfer metaldehyde from soil to both ground- and surface waters. Thus, metaldehyde presence in surface water and groundwater has been reported with high frequency (Busquets et al., 2014; Hillocks, 2012).

Kay and Grayson (2014) reported peak concentrations of metaldehyde in the range 0.4–0.6 μg L^{-1} and highlighted that metaldehyde has been detected above the maximum allowable concentration for drinking water of 0.1 μg L^{-1} (Council of the European Communities, 2000) during the October–December periods, when slug pellets are typically applied. These findings agree with metaldehyde concentration trends, observed by Castle et al. (2018), who reported peak concentrations of metaldehyde in the stream water of the River Thames Catchment to vary between 0.1 and 0.35 μg L^{-1} during September–January 2017. The maximum concentration of 5 μg L^{-1} was recorded in November, and no metaldehyde concentrations above 0.1 μg L^{-1} were recorded during the February–August period (Castle et al., 2018). Concentrations up to 1.5 μg L^{-1} were reported in stream water of the same catchment by Lu et al. (2017). Metaldehyde concentrations up to 2.2 μg L^{-1} were reported in a UK chalk aquifer by Bullock 2014, with peak concentrations observed in January and February. Metaldehyde presence in the aquatic environment has been reported in other countries. Calumpang et al. (1995) reported maximum metaldehyde concentrations of 1.57 mg L^{-1}, in rice paddy water in the Philippines, following application; concentrations fell to below the detection limit within nine days (Calumpang et al., 1995). Metaldehyde concentrations up to 6.98 μg L^{-1} were observed in runoff water from fish farming ponds in northern France within the Moselle River Basin (Lazartigues et al., 2012).

A key factor underpinning metaldehyde fate and mitigating its transport is the latent capacity of soil microbial communities to degrade this pesticide. Yet, literature relating to microorganisms capable of metaldehyde degradation is limited to three studies. Thomas et al. (2013, 2017) reported several metaldehyde-degrading bacterial strains that were isolated from domestic soils (liquid cultures contained 100 mg L^{-1} metaldehyde); *acinetobacter* E1 was reported to degraded metaldehyde present in solution at concentrations <1 nM (0.16 μg L^{-1}), other *acinetobacter* strains were reported to be unable to degrade the pesticide. A laboratory study (EFSA, 2010), reported metaldehyde to be mineralised (50–78%) by soil microbial communities under aerobic conditions; while under anaerobic conditions metaldehyde was observed to be stable.

However, to date, no reports have been published that account the capacity (assessed using ^{14}C-respirometry) of dissimilar soils from contrasting settings, to degrade metaldehyde. Thus, this current research sought to establish the level of catabolic competence of soil microbial communities to degrade metaldehyde (i.e. the competence of the microbial community to break down metaldehyde molecules into smaller units that are subsequently oxidised/mineralised to carbon dioxide). The current research considered soils obtained from three contrasting settings: agricultural fields, allotments and gardens (and both surface and subsurface regimes). The research sought to establish intrinsic metaldehyde mineralisation potential of the microbial community within these soils and the directing influence of metaldehyde augmentation in terms of inducing metaldehyde degradation. Furthermore, it was hypothesised that soil attributes, include texture, SOM and pH would have a shaping influence upon levels of metaldehyde catabolic competence. These original lines of enquiry provide a synopsis of metaldehyde biodegradation in dissimilar soils from contrasting settings.

2. Materials and methods

2.1. Chemicals

Metaldehyde pellets (1.5% active ingredient) were manufactured by Bayer. ^{14}C-metaldehyde (UL-^{14}C; 5.1 mCi $mmol^{-1}$) was obtained from American Radiolabeled Chemicals Inc. St Louis, USA. Ultima Gold and Ultima Gold XR liquid scintillation fluids were purchased from Perkin Elmer, UK. Calcium chloride, ethanol, methanol and sodium hydroxide were supplied by Fischer Scientific, UK; and dichloromethane provided by Sigma Aldrich, UK. Mineral Basal Salt (MBS) components (namely: NaCl, $(NH_4)_2SO_4$, KNO_3, KH_2PO_4, K_2HPO_4 and $MgSO_4{\cdot}7H_2O$) were obtained from BDH, UK.

2.2. Soils

Soils were collected from three contrasting settings: agricultural fields, allotments and gardens. Soils were collected in Norfolk and Essex, UK (Table 1). Soil samples (200 g) were collected using a Dutch auger (0–10 cm for topsoil; and, 40–50 cm for subsoil samples); four auger heads were combined to produce a single composite sample at each sampling point and a given location was sampled in triplicate (within 5 m of each other). Between sampling the auger head was thoroughly cleaned (washed with water and a tissue, then sprayed with 70% ethanol solution that was allowed to evaporate). Soils were transported to the laboratory and stored (4 °C) in sealed plastic bags, for no >2 days, prior to assessment of catabolic competence.

Soils were characterised in terms of their: SOM content (mass loss on ignition in a muffle furnace (450 °C) for 12 h; 10 g (n=3)) (Ghabbour et al., 2014); pH (samples (3 g (n=3) were combined with 30 mL of distilled water in a centrifuge tube, tubes were then shaken (reciprocal shaker (IKA Labortechnik KS501)) at 100 r.p.m for 14 h and the soil water pH was measured using an electrode (Jenway) and meter (Mettler Toledo FE20 Five Easy Benchtop pH Meter), and texture (samples of soil were moistened and kneaded into a ball and texture determined following the hand-texture

Table 1
Field, Allotment and Garden soil properties.

Soil Code	Setting	Texture	Metaldehyde application	OM (%)	pH
FT(n)1	Field 1	Sand	>4 years ago	3.49 ± 0.1	6.68 ± 0.23
FT(n)2	Field 2	Loamy Sand	>4 years ago	3.08 ± 0.2	7.55 ± 0.5
FS(n)2	Field 2	Sand	>4 years ago	1.82 ± 0.4	7.55 ± 0.2
FT(n)3	Field 3	Sandy Loam	>4 years ago	2.53 ± 0.1	6.57 ± 0.1
FT(n)4	Field 4	Sandy Loam	>4 years ago	3.85 ± 0.03	6.35 ± 0.1
FS(n)4	Field 4	Sand	>4 years ago	2.38 ± 0.1	7.21 ± 0.4
FT(n)5	Field 5	Sandy Loam	>4 years ago	4.52 ± 0.3	7.19 ± 0.3
FT(p)6	Field 6	Sandy Loam	Seasonal (ongoing)	2.79 ± 0.2	8.2 ± 0.1
FT(p)7	Field 7	Silty Loam	Seasonal (ongoing)	3.89 ± 0.1	7.24 ± 0.1
FT(n)8	Field 8	Loam	>4 years ago	4.02 ± 0.3	6.15 ± 0.1
FT(p)9	Field 9	Loam	Seasonal (ongoing)	3.4 ± 0.1	7.11 ± 0.2
FT(p)10	Field 10	Loam	Seasonal (ongoing)	2.67 ± 0.1	7.73 ± 0.2
FT(p)11	Field 11	Sandy Clay Loam	Seasonal (ongoing)	3.96 ± 0.3	6.44 ± 0.02
FT(p)12	Field 12	Silty Clay Loam	Seasonal (ongoing)	4.02 ± 3.9	7.29 ± 0.2
AT(n)1	Allotment 1	Loamy Sand	No previous application	7.91 ± 0.4	7.58 ± 0.01
AS(n)1	Allotment 1	Sand	No previous application	1.36 ± 0.3	7.05 ± 0.2
AT(p)2	Allotment 2	Loamy Sand	Seasonal (ongoing)	5.24 ± 0.1	7.44 ± 0.5
AS(p)2	Allotment 2	Sand	Seasonal (ongoing)	1.17 ± 0.1	7.18 ± 0.1
GT(n)1	Garden 1	Sandy Loam	>6 years ago	52.1 ± 1.0	7.1 ± 0.03
GT(n)2	Garden 2	Loamy Sand	>6 years ago	7.2 ± 0.2	7.54 ± 0.03
GT(n)3	Garden 3	Loamy Sand	>6 years ago	25.3 ± 0.2	6.92 ± 0.02
GT(n)4	Garden 4	Loamy Sand	>6 years ago	16.2 ± 0.3	7.49 ± 0.04
GT(n)5	Garden 5	Loamy Sand	>6 years ago	11.8 ± 0.5	8.02 ± 0.02
GT(n)6	Garden 6	Loamy Sand	>6 years ago	11.4 ± 0.4	8.01 ± 0.01
GT(n)7	Garden 7	Sandy Clay Loam	>6 years ago	10.2 ± 0.1	7.65 ± 0.01
GT(n)8	Garden 8	Sandy Clay Loam	>6 years ago	12.4 ± 0.4	7.52 ± 0.01
GT(n)9	Garden 9	Sandy Clay Loam	>6 years ago	5.5 ± 0.1	8.15 ± 0.01
GT(n)10	Garden 10	Sandy Clay	>6 years ago	8.6 ± 0.3	7.7 ± 0.02

framework of McDonald et al. (1998)). Soil characteristics are listed in Table 1, and its expanded version could be found within the Supplementary Material.

2.3. ^{14}C-radiorespirometry assessment of intrinsic and induced catabolic competence

Prior to undertaking the respirometry, soils were transferred to the laboratory incubator for 24 h to bring them back to a temperature of 18 °C. Soil samples (10 g) were added to sterile Duran Schott bottles (250 mL) containing sterile MBS (30 mL) (0.3 g NaCl, 0.6 g $(NH_4)_2SO_4$, 0.6 g KNO_3, 0.25 g KH_2PO_4, 0.75 g K_2HPO_4 and 0.15 g $MgSO_4{\cdot}7H_2O$ dissolved in 1 L of deionised water) (Hickman et al. (2008)). To each bottle ^{14}C-metaldehyde was added (100 Bq in 100 μL of ethanol). To capture $^{14}CO_2$ generated from the mineralisation of ^{14}C-metaldehyde, a glass scintillation vial (7 mL) containing 1 M NaOH (1 mL) was suspended (using a stainless-steel clip) from the top of a Teflon^{TM} lined respirometer lid. Bottles were continuously shaken on an orbital shaker (IKA Labortechnik KS501) at 100 r.p.m and the vials were removed and replaced periodically over the 120 h (5 d) assay time. Removed vials were wiped with a tissue, and Ultima Gold scintillation fluid (6 mL) added. Vials were sealed, shaken and stored in the dark (for a minimum of 24 h) and then analysed by liquid scintillation counting (Perkin-Elmer TriCarb 2900TR liquid scintillation analyser; count time 10 mins). Results were corrected for background radiation using un-spiked respirometers (Reid et al., 2001). The respirometer system was previously validated by Reid et al. (2001), who reported that up to 400 μmol CO_2 could be accommodated in a single trap and a ^{14}C activity balance of 101 ± 8.9%.

In order to assess the inducible capacity of soil microbial communities in response to metaldehyde augmentation the above procedure was repeated with the addition of a metaldehyde pellet to each respirometer bottle. Each pellet had a mass of 0.028 g and a metaldehyde content of 1.5%. Thus, each respirometer was dosed with the equivalent of 28 mg metaldehyde kg^{-1} soil. Sterile respirometers, containing MBS (30 mL), were spiked with ^{14}C-metaldehyde to evaluate abiotic degradation and volatilisation of ^{14}C-metaldehyde. All respirometer assays were run in triplicate.

2.4. Sample codes

Samples have been coded to indicate: land use regime, Field (F), Allotment (A) and Garden (G); the location qualifier (1–10; see Table 1); if samples were top soil (T) or subsoil (S); if the *in situ* regime had metaldehyde application (p) or no metaldehyde application for at least the last 4 years (n), and; if the *ex situ* laboratory assay was conducted in the presence of a slug pellet (+) or its absence (-). For example, F2Tp+ corresponds to Field 2, a topsoil sample that was exposed to metaldehyde *in situ* and was screened for catabolic competence in the presence of a metaldehyde pellet. In presenting the data, soils have been organised with lighter (sandier) textures presented first and heavier (clay) textures presented last.

2.5. Statistics

Significant differences between intrinsic and induced mineralisation levels were established using ANOVA *post hoc* Tukey Tests (SPSS Statistics 22); a significance level of 0.05 (95% level of confidence). Pearson's correlation test was applied to determine linear correlation between mineralisation and pH/SOM values, a significance level of 0.05.

3. Results

3.1. Control flasks and blanks

Abiotic degradation/volatilisation of ^{14}C-metaldehyde was evident at a modest level (7.8 ± 3.9%). This value was commensurate with a fugacity (Mackay, 2001) driven pseudo-equilibrium (theoretical value = 9.5%), where: the respirometer MBS media volume was 30 mL, the trap volume was 1 mL and the trap was changed three times over the assay period. Background ^{14}C-radiation was negligible (0.06% of the activity delivered in the respirometer spike).

3.2. Agricultural Field soils (FT, FS)

Intinsic catabloic competence (i.e. in asays with no metaldehyde pellet added (-)) was ubiquitous across all Agricultural Field soils; mineralisation varied between 17.6% (FT(p)7) and 31.0% (FT(n)1) (Fig. 1).

In most instances soils with light texture (FT(n)1, FS(n)2, FS(n)4 – sand, FT(n)2 – loamy sand, FT(n)3 – FT(p)6 – sandy loam, FT(p)7 – silty loam), were observed to have higher intrinsic capacites to mineralise ^{14}C-metaldehyde. Soils with heavier texture (FT(n)8, FT(p)9 and FT(p)10 – loam, FT(p)11 – sandy loam clay, FT(p)12 – silty clay loam) were observed to have lower intinsic catabloic competence (Fig. 1).

Similarly, induced (with pellet present (+)) catabloic competence was observed to be higher in lighter textured soils (FT(n)1 – FT(p)7) than in heavier textured soils (FT(n)8 – FT(p)12). This was also the case for the Field Subsoil samples (FS(n)2, FS(n)4 – sandy texture), where an uplift in induced mineralisation was observed (+8.9% and +0.1%) (Fig. 1). The extent of induced mineralisation in FT (where a pellet was added to the respirometer) varied from 16.5% (FT(n)8) to 30.3% (FT(n)3) (Fig. 1); this range was almost identical to the intrinsic catabloic competence range, suggesting that catabolism of metaldehyde was operating at its maximum capacity before the pellet was added.

With the exception of FT(n)1 (light sandy texture) and FT(n)8 (medium loamy texture), all Agricultural Field soils that were not exposed to metaldehyde *in situ* (n) were observed to show an uplift of catabolic competnce following the addition of a metaldehyde pellet (+) (FS(n)2 – FT(n)5). Lighter FT soil textures included sand (FS(n)2, FS(n)4), loamy sand (FT(n)2), sandy loam (FT(n)3 – FT(n)5). The same outcome was observed for light soils where metaldehyde was used *in situ* (p) (FT(p)6 – sandy loam, FT(p)7 – silty loam).

FS(n)2 was the only sample among all Agricultural Field soils in which a significant difference between intrinsic and induced mineralisation was observed ($P < 0.05$) (+8.9%) (Fig. 1). The maximum level of observed catabolic activity did not exceed 38.9% (induced mineralisation in FS(n)2 sample) in the Agricultural Field soils (Fig. 1).

3.3. Allotment soils (AT, AS)

Intinsic (-) catabloic competence was ubiquitous across all Allotment soils; mineralisation varied between 34.3% (AT(p)2) and 60.0% (AS(n)1) (Fig. 2). Similar to the Field soils, Allotment soils with lighter texture (sand) exhibited higher intrinsic mineralisation capacities when compared to soils with slightly heavier texture (loamy sand) (Fig. 2).

Relative difference between intrinsic (-) and induced (+) mineralisation in lighter textured subsoils were also higher, particularly in soil with previous *in situ* metaldehyde application history (p) (AS(p)2) (Fig. 2). Sandy Subsoil sample (AS(n)1) with no previous metaldehyde application had the highest metaldehyde mineralisation (both induced and intrinsic).

Like Field soils, Allotment soils exhibited elevated mineralisation levels in the presence the of metaldehyde (Fig. 2). In the presence of metaldehyde, the extent of mineralisation varied from 35.7% (AT(p)2) to 66.4% (AS(n)1) (Fig. 2).

Only in the case of AS(p)2, intrinsic and induced levels of ^{14}C-metaldehyde mineralisation were significantly different ($P < 0.05$) (a +9.9% uplift in mineralisation was observed). The maximum level of observed catabolic activity did not exceed 66.4% (induced mineralisation in AS(n)1 sample) (Fig. 2).

3.4. Garden soils (GT)

As observed for Field and Allotment soils, competence to degrade metaldehyde in garden soils was ubiquitous across soil types (Fig. 3). In the absence of a metaldehyde pellet, the extent of intrinsic metaldehyde mineralisation varied from 28.9% (GT(n)7) to 52.8% (GT(n)6) (Fig. 3).

In general, as was the case with Field soils (Fig. 3), lighter textures (sandy loam and loamy sand); GT(n)1 through GT(n)6) indicated higher levels of catabolic competence to mineralise metaldehyde when compared to heavier textures (sandy clay loam and sandy clay) (Fig. 3).

In the presence of metaldehyde all soils showed elevated levels of mineralisation (Fig. 3); the extent of mineralisation varied from 39.9% (GT(n)2) to 53.0% (GT(n)6). Uplift in mineralisation, in the presence of a metaldehyde pellet (+), was greatest for soils observed to have lower intrinsic catabolic competence; conversely, where soils were observed to already have high catabolic

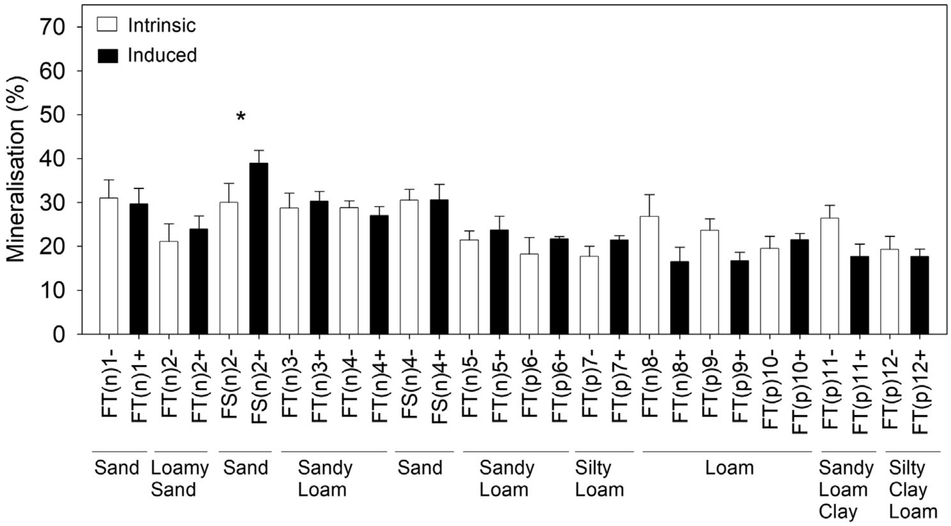

Fig. 1. Catabolic competence (^{14}C-metaldehyde mineralisation (%) after 5 days assay time) in Field topsoil (FT(n)1-FT(p)12) and Field subsoil (FS(n)2, FS(n)4): soil only treatments (white bars) and soil with metaldehyde addition (black bars). Soil types are ordered by texture and then by mineralisation (%) for each texture class. Error bars are standard error of the mean (n=3). A star indicates significant difference ($p < 0.05$) between soil only (-) and soil with metaldehyde (+) couplets.

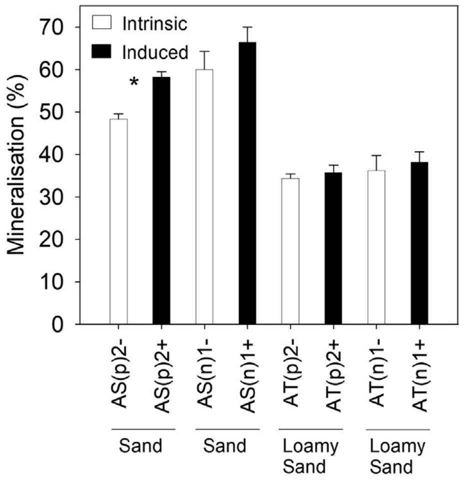

Fig. 2. Catabolic activity (^{14}C-metaldehyde mineralisation (%) after 5 days assay time) in Allotment soils (AT – Allotment topsoil, AS – Allotment subsoil): soil only treatments (white bars) and soil with metaldehyde addition (black bars). Soil types are ordered by texture and then by mineralisation (%) for each class. Error bars are standard error of the mean (n=3). A star indicates significant difference (p <0.05) between soil only (-) and soil with metaldehyde (+) couplets.

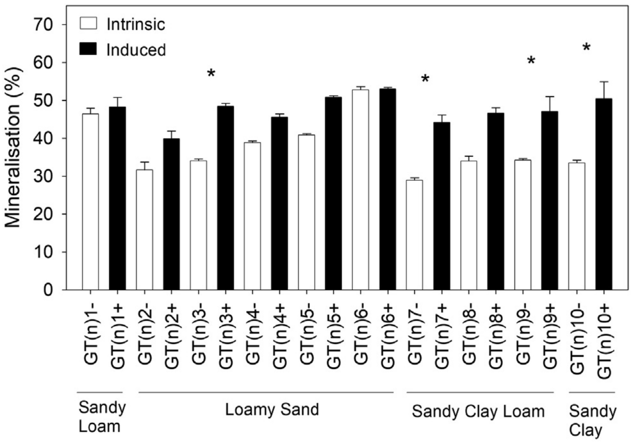

Fig. 3. Catabolic activity (^{14}C-metaldehyde mineralisation (%) after 5 days assay time) in Garden soils (GT(n)1-GT(n)10): soil only treatments (white bars) and soil with metaldehyde addition (black bars). Soil types are ordered by texture and then by mineralisation (%) for each class. Error bars are standard error of the mean (n=3). Stars indicate significant difference (p <0.05) between soil only (-) and soil with metaldehyde (+) couplets.

competence only small increases (a few %) in mineralisation were observed following metaldehyde augmentation (e.g. GT(n)1 and GT(n)6; Fig. 3).

In several instances the augmentation resulted in significant (P <0.05) increases in mineralisation GT(n)3, GT(n)7, GT(n)9 and GT(n)10; +14.4%, +15.3%, +12.8% and +16.9%, respectively). Again, as observed for Field and Allotment soils, the maximum catabolic capacity of 50–55% appeared to be a ceiling, beyond which catabolic capacity was not exceeded.

4. Discussion

The degradation of any pesticide depends upon its physical and chemical characteristics, e.g. aqueous solubility and inherent recalcitrance (Semple et al., 2003), and the physical, chemical and biological properties of the soil (Rao et al., 1983), such as pH, redox conditions, matrix attributes, carbon:nitrogen:phosphorus (C:N:P) elemental ratio, temperature, moisture content (Arias-Estévez et al., 2007). Presence/absence/activity of catabolic enzymes in soils affect pesticide degradation directly (Deng et al., 2016), while pesticide bioavailability/bioaccessibility indirectly influence pesticide degradation (Arias-Estévez et al., 2007). Additionally, pesticide transport, biological degradation and chemical transformation processes are affected by application regime (rates/methods and timing), as well as hydrological and weather conditions (Borgesen et al., 2015). Thus, site-specific physical, chemical and biological properties control the fate and transport of pesticides in the environment and determine the variation in spatial distribution of pollutants.

4.1. Soil microbe response to chemicals inputs

The ability of microbial communities to respond to organic compounds (e.g. pesticides) presence/augmentation is well documented for a range of compound classes, including: several semi-volatile hydrocarbon pollutants (Kelsey and Alexander 1997; Reid et al., 2002; Springael and Top, 2004; Hickman et al., 2008), pesticides (Duah-Yentumi and Johnson, 1986; Reid et al., 2005; Bending et al., 2006; Posen et al., 2006; Trinh et al., 2012; Reid et al., 2013) and antibiotics (Islas-spinosa et al., 2012; Bennet et al., 2017). These studies confirm the capacity of microbial communities to respond to organic compound input by becoming more catabolically competent (Reid et al., 2005; Bending et al., 2006; Posen et al., 2006; Reid et al., 2013). For example, Reid et al. (2005) reported soil microbial communities, of initially low catabolic competence, to degrade the herbicide isoproturon, (mineralisation C. 5%); their competence was increased following the incubation of soil with a low ($0.05\ \mu g\ kg^{-1}$) application of the herbicide (mineralisation increased to C. 40%). In column studies, Trinh et al. (2012) reported three phases of attenuation/degradation of these herbicides isoproturon and MCPA: an initial sorption phase, followed by an acclimatisation/adaptation phase and a final rapid degradation phase (resulting in complete removal of the herbicides).

Several studies on biodegradation of metaldehyde have been reported, for example, Thomas et al. (2013, 2017) isolated and characterised metaldehyde-degrading bacteria in domestic soils. They reported Acinobacter E1 strain to be able to degraded metaldehyde to a concentration below 1 nM. However, to date, the response of soil microbial communities, present in agricultural, allotment and garden soils, to metaldehyde augmentation has not been reported. Thus, our results confirm the potential for soil microbial communities to increase in their competence to degrade metaldehyde following exposure. In keeping with observations for other compounds, metaldehyde catabolic competence was observed to increase significantly, following slug pellet addition (in some cases increasing by a factor of 2). Largest increases in catabolic competence following metaldehyde augmentation were observed for FS(n)2 (+8.9%), AS(p)2 (+9.9%), GT(n)3, GT(n)7, GT(n)9 and GT(n)10 (+14.4%, +15.3%, +12.8% and + 16.9%, respectively).

In contrast to other pesticides, where low catabolic competence is exhibited in unexposed soils, high levels of intrinsic catabolic competence to degrade metaldehyde were observed (up to 66.0%). Metaldehyde is a cyclic tetramer of sub-units that can depolymerise, through microbial activity, into acetaldehyde (Castle et al., 2017; Tomlin, 2003). High levels of metaldehyde degradation in the soil environment have been reported in the literature. For example, Bieri (2003) reported fast degradation rates of metaldehyde in agricultural soils in Germany; with, DT$_{50}$ values ranging from 5.3 to 9.9 days. Coloso et al. (1998) reported metaldehyde concentration in pond sediment to rapidly decrease from an initial concentration of 80 $mg\ kg^{-1}$ to 1 $mg\ kg^{-1}$ after 15 days. Ma et al. (2012) studied metaldehyde residues in agricultural soils in China and reported metaldehyde residue of up 9 mg kg^{-1} to decrease below 0.3 mg kg^{-1} over 7 days. While Calumpang et al. (1995) reported metaldehyde concentrations in paddy soil to fall from 0.13 mg kg^{-1} to below the analytical detection level within 22 days.

We suggest the ubiquity of high levels of catabolic competence observed in our research are likely due to the degradation of the simple metaldehyde molecule to acetaldehyde (the primary degradation product), and the subsequent degradation of acetaldehyde to acetate; this being assimilated into Krebs tricarboxylic acid (TCA) Cycle (Tomlin, 2003) and respired as carbon dioxide.

4.2. Catabolic competence and its relationship with soil properties

All soil types, drawn from all settings (Field, Allotment and Garden), were observed to exhibit significant levels of catabolic competence. As already highlighted, soil texture had a shaping influence on the extent of ^{14}C-metaldehyde mineralisation; with sandy soils supporting, in general, higher level of catabolic competence. It is widely recognised that soil texture has a substantial influence on the soil environment. It controls soil porosity, and thus, has a directing influence on soil hydrology (Luna et al., 2017) and soil atmosphere (Pagliai et al., 2004). In turn, these drivers exert a shaping influence on soil microbial community structure (Fierer, 2017). Schroll et al. (2006) reported optimum pesticide mineralisation at a soil water potential of -0.015 MPa; pesticide mineralisation was markedly reduced when soil moisture approached soil water holding capacity.

Acknowledging the considerable influence soil texture has on soil moisture conditions, it is unsurprising that levels of catabolic competence observed have been influenced by soil texture. We suggest that the higher levels of catabolic competence for metaldehyde, observed in the lighter soil textures, could be linked to a higher redox potential in these more freely drained soils (Voroney and Heck, 2015). These conditions would, putatively, support a more active microbial community with greater capacity to degrade organic substrates (including metaldehyde). In general, pesticide degradation (Fenner et al., 2013), and metaldehyde degradation specifically (EFSA, 2010), have been reported to be faster under aerobic conditions.

Beyond its influence on soil, physical, hydrological and biological attributes soil texture also controls pesticide bioavailability (Gavrilescu, 2005). Numerous studies have sustained the general trend that lighter sandy soil textures assist biodegradation by maintaining high pesticide bioavailability and, in contrast, heavier clay textures tend to facilitate greater sorption and entrapment of pesticide (e.g. Reid et al., 2000; Gavrilescu, 2005). Thus, heavier clay textures tend to decrease the potential for degradation though stronger sorption. These strong interactions have been reported to preclude the opportunity for pesticides to induce catabolic competence (Reid et al., 2013).

In addition to their texture, the dissimilar soils also varied in their SOM content. SOM has been reported to influence the fate, behaviour and biodegradation of pesticides (Hatzinger and Alexander, 1995). However, to date, there have been no reports accounting how soil properties (specifically, SOM and pH) influence the biodegradation of metaldehyde by soil microbial communities. To elucidate any such relationships, SOM and soil pH were correlated with ^{14}C-metaldehyde mineralisation under intrinsic and induced regimes and across all settings (Fig. 4).

SOM varied (from 1.17% to 52.14%) across the dissimilar soil types obtained from contrasting settings (Table 1) and extent of mineralisation in these soils also varied greatly (from 16.51% to 66.44%). Considering all soils, ^{14}C-metaldehyde mineralised was observed to increase with increasing SOM for both intrinsic and induced assessments (Fig. 4A). While the correlations between mineralisation extent and SOM were not significant (r=0.34, p=0.08; intrinsic and induced mineralisation vs. SOM); the data supports the conclusions that i) beyond a SOM content of 12% metaldehyde mineralisation was consistently >34%, and, ii) where SOM content was <12% metaldehyde mineralisation was observed across a very broad range (from 16.5 to 60%) (Fig. 4A). These results suggest that efforts to sustain SOM levels in soil could assist in promoting higher levels of metaldehyde degradation, and thus, reduce the opportunity for metaldehyde to transfer to water resources.

On the one hand, SOM controls sorption of pesticides in soil (Chiou et al., 1983). Sorption is responsible for retention of pesticides in soil, preventing leaching and decreases pesticide bioavailability (Singh, 2008). While, on the other hand, SOM is the cornerstone of soil food webs, and its amount and quality underpin microbial diversity and its capacity to utilise a broad range of substrates (Neumann et al., 2014). With regards to metaldehyde, as a relatively water soluble compound (190 mg L^{-1}) and as a labile carbon source (Bieri 2003; EFSA, 2010), we suggest sorption onto SOM is unlikely to be a significant influence on biodegradation. It more likely that SOM has a synergistic influence on metaldehyde biodegradation as it acts as a primer for microbial activity. The higher levels of catabolic competence observed to be synonymous with SOM content of >12% (Fig. 4A) support this linkage.

Where pH was correlated with mineralisation across all soil types and regimes, no relationship was observed for intrinsic mineralisation (r=0.19, p=0.34) (Fig. 4B). A slightly positive correlation was observed between increasing pH and induced mineralisation (r=0.44, p=0.02) (Fig. 4B). More useful, perhaps, is the observable distinction between soils of pH lower than 6.9, where mineralisation never exceed 30%, and soils where pH was >6.9, and mineralisation was more often observed to be >35% (Fig. 4B). Thus, while pH influence on pesticide degradation has been reported for other compounds (e.g. atrazine (Houot et al., 2000) and pirimicarb and metsulfuron-methyl (Kah et al., 2007)), its influence upon metaldehyde mineralisation was inconsistent.

4.3. Wider context

The results reported herein highlight soil microbial communities, in dissimilar soils under Agriculture, Allotment and Garden regimes, to all have a considerable latent capacity to degrade metaldehyde (Figures 1–3). Our results suggest that soil microbial communities across these regimes, and present in both topsoil and subsoil, are well predisposed to degrade metaldehyde. We suggest that it is unlikely that the, at times, high levels of metaldehyde detected in water (Castle et al., 2017; Kay and Grayson, 2014) are due to low degradation capacity in the soil system. It is more likely that runoff and fast leaching of metaldehyde is the main driver underpinning the high incidence and high concentrations of metaldehyde sometimes reported in water resources (Calampung et al., 1995; Coloso et al., 1998; Council of the European Communities, 2000; Bieri 2003; Hillocks, 2012; Ma et al., 2012; Busquets et al., 2014; Lu et al., 2017).

With metaldehyde being applied in autumn and winter, when slug populations are higher due to wet weather (and when young crops are most vulnerable), the opportunity for metaldehyde transport is increased. The situation is further antagonised by metaldehyde having a relatively high aqueous solubility (190 mg L^{-1}). In support of this view there is considerable evidence that pesticides applied to the soil surface can be transported rapidly, bypassing the unsaturated soil zone, to groundwater (Arias-Estévez et al., 2007; Johnson et al., 1995; Lopez-Perez et al., 2006). Indeed, metaldehyde has frequently been detected in groundwater at levels higher than the EU Drinking Water Framework Directive limit (0.1 μg L^{-1}) (EC, 1998); in some cases, concentrations of metalde-

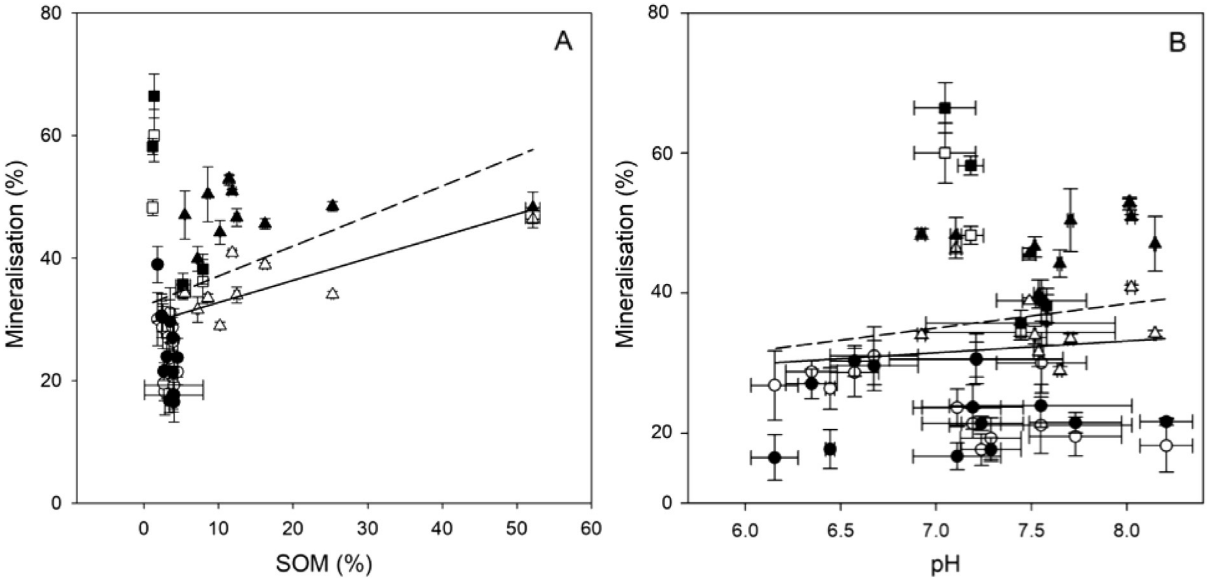

Fig. 4. Correlation of intrinsic (black), and induced (white), catabolic activity (% mineralisation) with: OM (A) and pH (B); for, Field soils (○), Allotment soils (□) and Garden soils (△). Errors bars are ± 1 standard deviation (n=3). Lines of best fit indicates correlations between intrinsic (solid) and induced (dashed) mineralisation capacity and SOM (A) and pH (B).

hyde of up to ten times this limit have been reported (UKWIR, 2013).

Given its ubiquity in water resources, metaldehyde has been subject to scrutiny, voluntary initiatives and evolving regulation. Specifically, in the UK the Get Pelletwise campaign of the Metaldehyde Stewardship Group (MSG, formed in 2008), aimed to promote sustainable use of metaldehyde by applying principles of Integrated Pest Management and introducing guidelines for metaldehyde application (MSG, 2019). This guidance recommended the use of the minimum amount of active compound per hectare; that soil conditions, topography and fields proximity to watercourses are factors to be considered in assessing the risk of metaldehyde loss to streams, and that metaldehyde application is discouraged during heavy rain events and if field drains are flowing (MSG, 2019). However, metaldehyde is still regularly detected at the concentrations above the DWD limit of 0.1 $\mu g\ L^{-1}$ (Castle et al., 2017; Lu et al., 2017). Thus, in order to mitigate metaldehyde transfer, a further reduction in the nominal loading of metaldehyde in pellets (e.g. from 3% to 1.5% active ingredient) and the development of pellets that afford stronger metaldehyde attenuation might offer further opportunity for improvements.

We highlight that soil itself is likely to be a significant reservoir of metaldehyde. With respect to this soil burden, the results reported herein suggest that there is good prospect that, given time, the indigenous soil microbial communities will degrade this reservoir of metaldehyde. However, further research regarding the levels of microbial catabolic activity, specifically under lower substrate concentrations, should be undertaken.

5. Conclusions

Results indicate substantial catabolic competence to degrade metaldehyde in soils with various texture (from sand to silty clay loam), pH (6.15–8.20) and organic matter content (1.2–52.1%). Ubiquitous catabolic competence was observed in both topsoil (16.7–52.8%) and subsoil horizons (30.0–66.4%). In general, soils with lighter texture (sand, sandy loam and loamy sand; average mineralisation 37.3%) had higher levels of ^{14}C-metaldehyde mineralisation when compared to soils with heavier texture (sandy clay, sandy clay loam and silty clay loam; average mineralisation 33.3%). When soils were augmented with metaldehyde (in the laboratory) an increase in mineralisation was observed in some, but not all soils (up to 16.9% increase in the Garden Soil GT(n)10 (sandy clay)). Overall, pH and organic matter content were weakly correlated with ^{14}C-metaldehyde mineralisation. However, soils with higher SOM (>12%) were, in general, observed to support higher levels of metaldehyde mineralisation. It is suggested that the higher SOM status of these soils exerted a beneficial shaping influence upon soil microbial communities and their capacity to degrade metaldehyde. Collectively, results suggest that the concentrations of metaldehyde (that are at times high), detected in water, are unlikely due to insufficient microbial capacity to degrade this pesticide. It is suggested that application regime (rate and timing), the high mobility of metaldehyde and its loss to the watercourses via runoff and leaching are the driving factors underpinning the ubiquity of metaldehyde in surface and ground water resources. To reduce metaldehyde runoff to watercourses, the application timing should not coincide with wet weather conditions. The use of pellets with reduced concentrations of metaldehyde and development of the pellet products with stronger attenuation capacity could further assist in the effort to reduce metaldehyde transfer to the aquatic environment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.135412.

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Trends in metaldehyde concentrations and fluxes in a lowland, semi-agricultural catchment in the UK (2008–2018)

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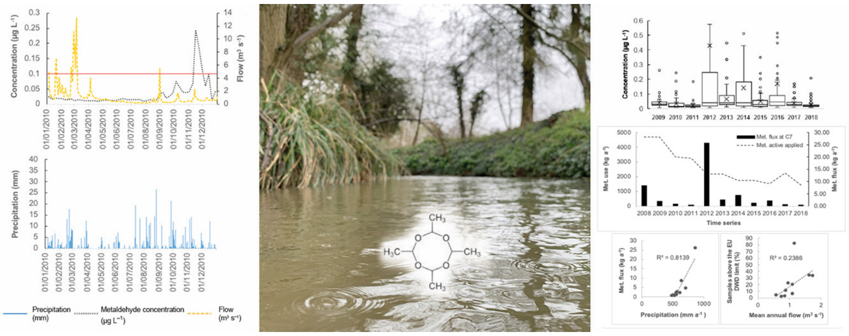
HIGHLIGHTS

- Peaks in metaldehyde concentration mainly occurred during the autumn-winter application season.
- Concentrations above the EU DWD limit of 0.1 μg L^{-1} in the river water were short-lived.
- Metaldehyde is highly mobile, runoff-driven transport of metaldehyde serves as a major pathway.
- Losses from point of application to surface water varied between 0.01 and 0.25%, maximum of 1.18% (2012).
- Concentrations is watercourses are likely to be below 0.1 μg L^{-1} following metaldehyde ban in the UK.

GRAPHICAL ABSTRACT



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ABSTRACT

Metaldehyde, a widely used molluscicide, is one of the most commonly detected pesticides in aquatic environments in the UK. In this study, metaldehyde concentrations and fluxes in stream water over a ten-year period (2008–2018) are reported for the River Colne catchment (Essex, southeast England), and the influence of hydrological conditions and application regimes are assessed.

In general, peaks in metaldehyde concentration in river water occasionally exceeded 0.25 μg L^{-1}, and concentrations did not typically exceed the European Union Drinking Water Directive (EU DWD) regulatory limit of 0.1 μg L^{-1}. Metaldehyde concentration peaks displayed a seasonal pattern. Metaldehyde concentrations during periods when the molluscicide was not applied to agricultural land (January, July) and during the spring-summer application period (February to June) were generally low (0.01–0.03 μg L^{-1}). Peaks in metaldehyde concentration mainly occurred during the autumn-winter application season (August to December), and were typically associated with high intensity hydrological regimes (daily rainfall ≥10 mm; stream flow up to 18 $m^3 s^{-1}$). Where metaldehyde concentrations exceeded the EU DWD regulatory limit, this was short-lived.

The annual flux at the top of the Colne catchment (0.2–0.6 kg a^{-1}) tended to be lower than in the middle of the catchment (0.3–1.4 kg a^{-1}), with maximum flux values observed at the bottom of the catchment (0.5–25.8 kg a^{-1}). Metaldehyde losses from point of application to surface water varied between 0.01 and 0.25%, with a maximum of 1.18% (2012). Annual flux was primarily controlled by the annual precipitation and stream flow ($R^2 = 0.9$) rather than annual metaldehyde use (kg active applied). Precipitation explained 37% and 81% of variability in metaldehyde concentration and flux, respectively.

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Annual ranges in metaldehyde concentration were greater in the years 2012 and 2014 with an overall reduction in the range of metaldehyde concentrations evident over the period 2015–2018. It is the expectation that metaldehyde concentrations in stream water will continue to decrease following the withdrawal of metaldehyde for outdoor use in the UK from March 2022.

1. Introduction

Pesticides are widely present in surface water (e.g. Sandin et al., 2018; Metcalfe et al., 2019), affecting the ecological status of water bodies (Palma et al., 2004). Pesticide presence in watercourses is a challenge for environmental risk regulators tasked with achieving good water quality status (Holvoet et al., 2007) under the European Union Drinking Water Directive (EU DWD) (Directive 98/83/EC; EC, 1998) and the European Union Water Framework Directive (Directive 2000/60/EC; EC, 2000).

These pollutants enter aquatic environments via diffuse pathways (runoff, drains and groundwater flow, and atmospheric deposition), and via point sources, often associated with pesticide handling procedures (Fait et al., 2007). The amount of pesticide loss to surface water depends on a number of factors, including topography, land use, hydrological conditions, pesticide application regime (timing of application and the amounts applied), as well as physiochemical properties of the substance (Morvan et al., 2006; Gevaert et al., 2008; Villamizar and Brown, 2017).

Metaldehyde – the cyclic tetramer of acetaldehyde with the formula $(CH_3CHO)_4$, has regularly been detected in water supplies in the UK over the past decade (Stuart et al., 2012). This molluscicide is commonly used in agriculture to control populations of snails and slugs, and is widely applied in the months August–December to protect winter cereals and winter oilseed rape crops (Environment Agency (EA), 2016). Wet weather conditions typical for the autumn period create a favourable environment for slugs, and slug control becomes a priority. With increased precipitation and runoff during the application season, exceedances of metaldehyde concentrations above the EU DWD limit of 0.1 μg L^{-1} (EC, 1998) have been regularly recorded (Castle et al., 2017) since 2008, when intensive regulatory monitoring of metaldehyde began nationwide. Overland and subsurface runoff is known to be a major input pathway for pesticides found in watercourses (Huber et al., 1998; Larsbo et al., 2016). Coupled with the physiochemical characteristics of metaldehyde, a relatively water-soluble substance (188–190 mg L^{-1} at 20 °C) with low adsorption potential (K_{oc} of 35 L kg^{-1}) (PAN, 2020; PPDB, 2020), there is a high potential of increased mobility of metaldehyde in the environment (Lu et al., 2017; Asfaw et al., 2018). Due to its physico-chemical properties, metaldehyde is susceptible to surface runoff during rainfall events; it is likely to be mobile in the soil zone (Castle et al., 2017) and transported rapidly to groundwater (Balashova et al., 2020).

Furthermore, due to its physico-chemical properties, metaldehyde cannot be removed from raw water using conventional methods employed at water treatment works, including granular activated carbon, chlorination and ozonation (Kay and Grayson, 2014).

Not only do the increasing amounts of metaldehyde contamination in surface waters give cause for concern, the adverse effects of metaldehyde on aquatic ecosystems and non-target organisms are also problematic, and non-target effects of metaldehyde on aquatic organisms and small mammals have been reported (Moreau et al., 2015; Hallet et al., 2016; De Roma et al., 2017). Due to the risk that metaldehyde poses to wildlife, including birds and mammals, the outdoor use of metaldehyde in the UK will cease from March 2022. This decision was made following advice from the Health and Safely Executive (ECP) and the UK Expert Committee on Pesticides (ECP) (DEFRA, 2020).

In light of these recent changes in UK policy, research regarding temporal trends in metaldehyde concentrations in aquatic systems is particularly important, not least as a benchmark for the pre-withdrawal situation. Yet, peer-reviewed studies of metaldehyde levels in surface water are limited (e.g. Calumpang et al., 1995; Coloso et al., 1998), and only a few studies are available on patterns of metaldehyde concentrations at the catchment scale. For example, Kay and Grayson (2014) quantified metaldehyde levels in surface water of the River Ouse catchment in Yorkshire, UK using concentration data collected over a period of 2.5 years (2008–2011). Kay and Grayson (2014) also studied the effect of catchment characteristics (slope, soil type and crop coverage) on metaldehyde levels in rivers and found no significant relationships and concluded that metaldehyde application regime at the individual farm level (such as application rate, timing and technique; although data were not available) may be the driving factor transporting metaldehyde to surface water. Lu et al. (2017) used metaldehyde concentration data collected over a period of 5 years (2011–2015) in the River Thames catchment as input data to a process–based hydrobiochemical transport model (INCA). Their results highlighted that increased metaldehyde concentrations in the watercourse network were directly linked to excessive application (Lu et al., 2017). Asfaw et al. (2018) developed a surface runoff transport model to describe short-term metaldehyde dynamics in the River Leam catchment (central England, UK) using high resolution metaldehyde concentration data and precipitation data for four separate rainfall events (9–35 h duration). Castle et al. (2018) compared metaldehyde levels in surface water using two monitoring approaches (automated passive and spot sampling) in the River Dee and the River Thames catchments during a 1-year period (January 2016–January 2017). Additionally, metaldehyde concentrations in surface water samples were examined in the Mimmshall Brook catchment (Hertfordshire, UK) using similar approaches, with samples collected during a 3-month period (October–December 2017) (Castle et al., 2019). Most of these studies are short-term, and there is currently the knowledge gap when it comes to understanding of metaldehyde trends over the longer time periods.

The aim of the current research was to review long-term and seasonal trends in metaldehyde concentrations and fluxes in a lowland, semi-agricultural UK catchment (the River Colne). To meet this aim, the first objective was to quantify and evaluate long-term and seasonal metaldehyde concentration and flux patterns using metaldehyde concentration data collected over a period of 10 years and 7 months (June 2008–December 2018). The second objective was to evaluate the impact of hydrological conditions (precipitation and stream discharge (flow)) and metaldehyde application regime (application timing and annual application rates) on concentrations of metaldehyde in the stream network of the study catchment. The final objective was to achieve a better understanding of metaldehyde pathways/sources and their scale within the study catchment. Collectively, these objectives are aimed to provide a prognosis regarding long-term levels and persistency of metaldehyde in the environment. Such a prognosis will help support informed design of water quality policy.

2. Materials and methods

2.1. Study area

The study area is located in southeast Essex in East Anglia and incorporates the River Colne catchment (Fig. 1). The River Colne has a catchment area of 242 km^2, comprising six sub-catchments and the catchment outlet: Stambourne Brook and River Colne at Nuns Walk, Great Yeldham (C1, 14 km^2); River Colne at Highfields Close, Great Yeldham (C2, 17 km^2); Toppesfield Brook (C3, 26 km^2); River Colne at

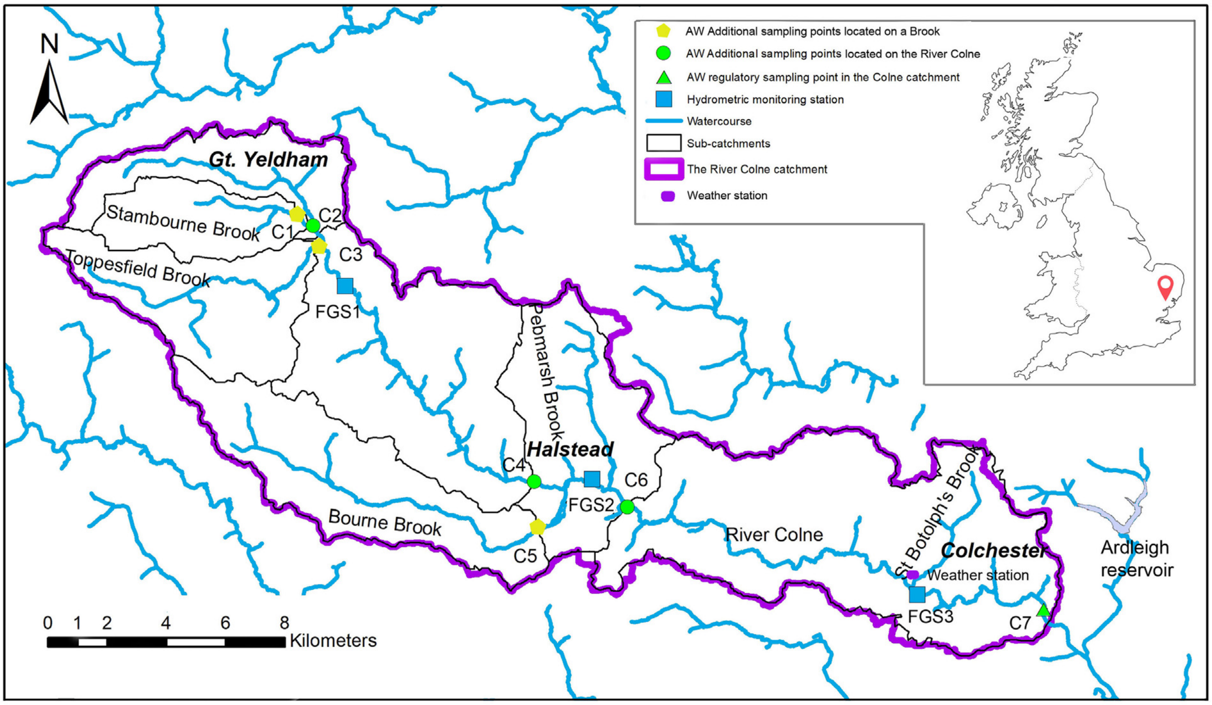

Fig. 1. Geographical location of the study sites indicating major settlements. The hydrological network of the study area includes the locations of sampling points and gauging stations.

Langley Mill, Earls Colne (C4, 49 km^2); Bourne Brook (C5, 35 km^2); Pebmarsh Brook and River Colne at Earls Colne Road (C6, 31 km^2); and the River Colne outlet at Eastmill (C7, 70 km^2) (Fig. 1, Table 1). The length of the stream network within the Colne catchment is 50 km with the average stream flow increasing downstream from 0.29 m^3 s^{-1} and 0.73 m^3 s^{-1} at the upper and middle sub-catchment gauging stations (37012 and 37024) to 1.07 m^3 s^{-1} at the lower sub-catchment gauging station (37005) near Lexden and Colchester for the period 1959–2017. Base Flow Index (BFI) values gradually increase from 0.28 in the upper part of the catchment (station 37012) to 0.43 and 0.52 (stations 37024 and 37005, respectively) in the middle and the lower parts of the study area (Fig. 1; NRFA, 2019a, 2019b, 2019c). The River Colne has a number of abstractions along its reach for irrigation use in arable farming. The water from the river is also abstracted and pumped into the Ardleigh Reservoir in the adjacent catchment for drinking water supply (EA, 2019).

The superficial geology is represented by deposits of clay and silt diamicton and sand and gravel deposits of glacial origin. These deposits were formed during the Quaternary period, the Pleistocene epoch (British Geological Survey (BGS), 2019). Bedrock material underlying the catchment area consists of silt, and silty and sandy clay that belong to the London Clay Formation of the Thames Group, formed during the Paleogene period in the Eocene epoch, followed by clay, silt, sand and gravel bedrock material of the Lambeth Group (56 to 66 Ma). The

Table 1
Key characteristics of the sub-catchments.

Sampling point	C1	C2	C3	C4	C5	C6	C7
Name	Stambourne Brook	River Colne at Nuns Walk, Great Yeldham	Toppesfield Brook	River Colne at Langley Mill, Earls Colne	Bourne Brook	Pebmarsh Brook and River Colne at Earls Colne	River Colne outlet
Area draining to the monitoring point	14	31	26	106	35	172	242
% Arable land	90	83	89	69	77	76	61
% Oilseed rape and cereals	37	81	82	59	61	61	51
Soil characteristics	Slowly permeable lime-rich clayey and loamy soils.	Slowly permeable lime-rich clayey and loamy soils.	Slowly permeable lime-rich clayey and loamy soils; fine loamy over clayey soils with slowly permeable subsoils.	Fine and coarse loamy soils with high drainage capacity. Fine loamy over clayey, and fine silty over clayey soils that have subsoils with low permeability, subject to seasonal waterlogging.	Fine and coarse loamy soils with high drainage capacity and fine silty over clayey soils that have subsoils with low permeability, subject to seasonal waterlogging.	Fine and coarse loamy soils with high drainage capacity. Fine loamy over clayey with low permeability, subject to seasonal waterlogging.	Coarse loamy and clayey soils are located on the floodplain with naturally high groundwater levels.
Sampling point's location	Stambourne Brook	River Colne	Toppesfield Brook	River Colne	Bourne Brook	River Colne	River Colne

underlying deposits include Chalk of the Sussex White Chalk Formation formed in the Cretaceous period, the Late Cretaceous epoch (BGS, 2019).

The catchment includes nine soil associations of loamy and clayey soils, predominantly with slightly impeded drainage capacity. Loamy and clayey soils in the lower part of the catchment are located on the floodplain with naturally high groundwater levels (Cranfield Soil and AgriFood Institute, 2019) (Table 1).

The area is characterised by a temperate maritime climate with the mean annual temperature ranging between 9.5 °C to 10.5 °C. The mean annual precipitation for 1981–2010 is less than 700 mm; with the lowest and the highest mean monthly rainfall occurring in February (40.7 mm) and October (64.8 mm), respectively (Met Office, 2020).

Approximately 61% of the whole catchment is arable land, with more residential and industrial land use in the lower part of the catchment. Urban land use in the catchment comprises 11% of the total area (UK Centre for Ecology and Hydrology (UKCEH), 2017). Land use for arable crops includes mainly winter cereals and some other crops (UKCEH, 2018) (Table 1).

2.2. Data collection and analysis

2.2.1. Water sampling and analytical procedure

Water sampling and analysis were conducted by Anglian Water Services. Non-composite water samples were collected manually on a weekly basis from the stream network during the period June 2008–December 2018 at the regulatory point C7 at the Colne catchment outlet. Additionally, in the period July 2015–December 2018, samples were collected at monitoring points C1–C6 in the Colne catchment, giving a total of seven monitoring points (Fig. 1). Samples were collected in 500 mL brown plastic bottles (these were flushed with sample before being sealed) and refrigerated at 4^{o} C (within 24 h of collection). Determination of the metaldehyde concentration in water samples was conducted within 7 days of sample collection using liquid chromatography with mass spectrometric detection in line with the Drinking Water Testing Specification (method No CL/TO/046; UKAS, 2019). The method's limit of detection of metaldehyde is 0.004 $\mu g\ L^{-1}$, all data entries of the dataset are above the detection limit.

2.2.2. Hydrological parameters

Daily flow data ($m^3\ s^{-1}$) recorded during the investigation period at three gauging stations (37,012, 37,024 and 37,005 (FGS 1, 2 and 3) with UK National Grid references TL771364, TL855297 and TL962261, respectively) across the Colne catchment (Fig. 1) were obtained from the National River Flow Archive (NRFA, 2019a, 2019b, 2019c) and the Environment Agency. Daily precipitation (mm) data were retrieved from the UK Climate Projections (UKCP09) dataset covering the period June 2008–December 2016 for a weather station located in the Ardleigh Catchment, northeast of Colchester (TM025275), 6.5 km at 80 degrees from the FGS3 location (Met Office et al., 2017). Daily rainfall data recorded at the West Bergholt station located within the catchment (TL960267, 0.6 km at 343 degrees from location FGS3) during January 2017–February 2019 were provided by the Environment Agency. The collected data were used to calculate monthly and annual average precipitation and flow for the investigation period.

2.2.3. Catchment delineation

The Colne catchment was delineated into separate sub-catchments focused on the location of sampling points, with the outlets defined using the Hydrology Toolset in ArcGIS 10.7. Flow direction and accumulation were generated from the 50-m grid Digital Terrain Model (OS, 2019) to determine the contributing area following the application of the Watershed tool to define sub-catchments draining to individual sampling points. The total sub-catchment areas draining to the C2, C4, C6 and C7 sampling points incorporated the area of those sub-catchments located upstream. For example, the sub-catchment draining to point C4 incorporated the area of sub-catchments with outlets at the C1, C2 and C3 sampling points (Fig. 1, Table 1).

2.2.4. Calculations

The monthly metaldehyde fluxes (monthly load, ML) were calculated using the formula:

$$ML = Q \times C_i \times t_i \tag{1}$$

where Q is the average monthly stream flow during the period t_i ($L\ s^{-1}$), C_i is the average metaldehyde concentration in water samples collected within a month ($\mu g\ L^{-1}$), and t_i is the time period considered (seconds i.e. 60 × 60 × 24 × number of days in the month). The sum of monthly load values within each year represents the annual load (AL) of metaldehyde ($kg\ a^{-1}$) (Kreuger, 1998; Rabiet et al., 2010).

Annual metaldehyde application rates (active applied, $kg\ ha^{-1}$) were obtained from the Pesticide Usage Survey for the period 2008–2018 (FERA, 2018). Crop coverage area (ha) was retrieved from the UKCEH Land Cover plus Crop map (UKCEH, 2018). The total arable area (all crops excluding grassland) and the area of cereals and oilseed rape crops were estimated for the entire Colne catchment. To calculate the amount of metaldehyde applied annually in the Colne catchment (annual application (AA), $kg\ a^{-1}$), metaldehyde application rates were multiplied by the crop area within the catchment, as follows:

$$AA = r \times A_i \tag{2}$$

where r is metaldehyde application rate ($kg\ ha^{-1}$) for a given year, and A_i is the area of arable crops (ha). Annual application of metaldehyde was estimated for: (i) total arable area (all crops excluding grassland) to reflect application during the February–June months to protect rooted vegetables, maize and other spring/summer crops; and (ii) the area of cereals and oilseed rape crops in each sub-catchment. Cereals and oilseed rape crops are the predominant type of crops within the study area; metaldehyde is applied during the August–December period to protect these crops.

Metaldehyde transport from the point of application to the stream network was calculated using two calculation methods: (i) loss per hectare ($g\ ha^{-1}$) of arable crop, by dividing annual metaldehyde load (AL) by crop area; and (ii) the loss of metaldehyde as a percentage of the amount applied in a sub-catchment annually:

$$\text{Annual Loss} = (AL/AA) \times 100 \tag{3}$$

The loss values from the total crop area (excluding grassland) and from cereals and oilseed rape crops were established separately.

Simple and multiple forward stepwise linear regression models were completed to estimate the relationship between metaldehyde concentration, flux, precipitation, flow and metaldehyde use. JASP and Microsoft Excel software were used for the statistical analysis, including data visualization.

3. Results

3.1. Annual trends in metaldehyde levels

3.1.1. Spatial trends

Metaldehyde concentrations were observed to vary between monitoring points within the Colne catchment on an annual basis (Table 2). Median concentrations recorded in the stream network of the Colne catchment tended to be lower at the C4–C6 monitoring points situated in the middle part of the catchment compared to values at sites C1–C3 in the upper part of the catchment (up to 0.07 $\mu g\ L^{-1}$ at monitoring point C1 in 2015) (Table 2; Figs. S1 and S2 in the Supplementary Material). Metaldehyde concentrations above 0.1 $\mu g\ L^{-1}$ were detected each year during 2015–2018 at sites C1 and C3 (Figs. S1–S3). During the years 2016–2018, 2–13% and 12–25% of samples collected at C1 and C3,

Table 2
Summary of historic metaldehyde concentration (μg L^{-1}) data in the Colne catchment for the period 2008 to 2018.

Site	Year	Total number of samples	Concentration			Number of samples above the DWD limit	Percentile of samples above the DWD limit
			Minimum	Median	Maximum		
C7	2008[a, c]	22	0.030	0.521	2.630	18	82
	2009	52	0.005	0.031	0.262	3	6
	2010	52	0.010	0.015	0.244	3	6
	2011	51	0.005	0.015	0.185	1	2
	2012[a, c]	58	0.006	0.040	6.780	19	33
	2013	106	0.012	0.041	0.445	21	20
	2014[a, c]	77	0.008	0.041	2.020	26	34
C1[a]	2015[a, c]	23	0.016	0.073	0.703	8	35
C2		23	0.006	0.040	0.316	3	13
C4		37	0.005	0.028	0.439	7	19
C5		37	0.004	0.019	0.253	6	16
C6		38	0.024	0.026	0.395	8	21
C7		80	0.008	0.027	0.349	9	11
C1[a]	2016[c]	53	0.011	0.030	1.910	7	13
C2		53	0.008	0.019	2.140	11	21
C3[b]		53	0.004	0.023	1.480	13	25
C4		53	0.008	0.023	2.550	7	13
C5		53	0.007	0.023	0.220	7	13
C6		53	0.009	0.024	1.160	8	15
C7		112	0.010	0.046	2.280	25	22
C1[a]	2017	52	0.018	0.034	0.110	1	2
C2		52	0.008	0.021	0.084	0	0
C3[b]		52	0.004	0.026	0.190	7	13
C4		52	0.008	0.019	0.094	0	0
C5		52	0.004	0.020	0.157	1	2
C6		52	0.010	0.020	0.091	0	0
C7		136	0.010	0.028	0.175	5	4
C1[a]	2018	52	0.008	0.016	0.116	1	2
C2		52	0.004	0.010	0.054	0	0
C3[b]		52	0.004	0.014	1.570	6	12
C4		52	0.004	0.012	0.054	0	0
C5		52	0.004	0.012	0.032	0	0
C6		52	0.010	0.020	0.091	0	0
C7		148	0.007	0.019	0.207	4	3

All analysed samples were above the limit of detection (0.004 μg L^{-1}).

[a] Site where samples above the EU DWD limit (0.1 μg L^{-1}) were recorded in each year in the period 2015–2018.

[b] Site with the largest number of samples above the EU DWD limit in the period 2015–2018.

[c] Year with >20% of samples above the EU DWD limit (0.1 μg L^{-1}).

respectively, contained metaldehyde concentrations above the EU DWD limit (Table 2).

At the sub-catchment level, higher metaldehyde concentrations were observed at sites C1 and C3 at the top of the Colne catchment and also in the middle section of the catchment (points C4 and C6) during 2015–2018 (Table 2).

Highest concentrations and proportion of samples exceeding the EU DWD were observed at site C7 within the same time period (percentile range 2–34% of samples collected) (Table 2, Fig. S3). Median concentrations at site C7 were consistently higher than at the monitoring points within the catchment, and varied between 0.02 and 0.52 μg L^{-1} during 2008–2018 (Table 2). Similar to metaldehyde concentrations, metaldehyde flux at site C7 was consistently the highest among all monitoring points in each year during the period 2015–2018, and the flux values were highest in 2016 across all monitoring points, except at site C5. Collectively, the annual flux at the top of the Colne catchment (sites C1–C3) tended to be lower than in the middle part of the catchment (C4–C6). For example, in 2017 metaldehyde flux within the range 0.1–0.2 kg a^{-1} and 0.4–0.5 kg a^{-1} were recorded in C1–C3 and C4–C6 sites, respectively, with a maximum flux of 0.7 kg a^{-1} observed at C7 (Fig. 2).

3.1.2. Temporal trends

Metaldehyde concentrations above the EU DWD regulatory limit (0.1 μg L^{-1}) were detected at all monitoring points in 2008, 2012, 2013, 2015 and 2016 in the study area. The highest percentile of all samples with a metaldehyde concentration above 0.1 μg L^{-1} was in 2008 (82%), followed by 28% and 34% in 2012 and 2014, respectively (Table 2).

Maximum concentrations did not exceed 0.5 μg L^{-1} in all years except 2008, 2012, 2014 and 2016 (except at site C1 November 2015 (concentrations up to 1.57 μg L^{-1}) and at C3 in November 2018 (up to 1.57 μg L^{-1})). Concentration levels up to 2.63 μg L^{-1} were recorded in 2008, 2014 and 2016, with highest levels in 2012 (6.78 μg L^{-1}) at monitoring point C7 (Table 2; Fig. S3). The highest mean annual concentrations and variability in metaldehyde concentrations were observed in 2012, followed by the 2014 and 2016 time series at C7 when mean concentrations were above the EU DWD limit in these periods (Fig. 3). In 2016, the maximum concentration at the Colne catchment reached 2.28 μg L^{-1} (Figs. 3, 4, S3). Noticeable decreases in metaldehyde concentrations above the EU DWD limit took place in 2017 and 2018, when compared with concentration statistics for the 2015 and 2016 time series (Table 2, Figs. 3, 4). Annual ranges in metaldehyde concentration were greater in the years 2012 and 2014 with an overall reduction in the range of metaldehyde concentrations evident over the period 2015–2018.

Annual time series of metaldehyde fluxes were similar overall to trends in annual metaldehyde concentrations during the study period 2008–2018 (Fig. 2). When mean annual concentration values were compared to annual flux at C7, the data showed a strong positive relationship ($R^2 = 0.9$, $r = 0.7$, $p = 0.02$, $n = 22$). Maximum flux values were recorded in 2012 with up to 25.8 kg recorded at C7, followed by flux values of 8.37 kg in 2008 and 4.35 kg in 2014.

Metaldehyde loss to the stream network in g ha^{-1} varied across the catchment and was highest downstream to the C1 and C5 monitoring points, with up to 1.13 and 0.34 g ha^{-1} metaldehyde loss from cereal and oilseed rape crops in 2016, respectively (Table 3). Metaldehyde loss from cereal and oilseed rape crops in the Colne catchment recorded at C7 reached a maximum of 2.39 g ha^{-1} in 2012, followed by losses of 0.78 and 0.40 g ha^{-1} in 2008 and 2014, respectively. The lowest losses of metaldehyde were observed in 2011 and 2018 with 0.04 g ha^{-1} recorded at C7 (Table 3).

Similar trends were observed when metaldehyde loss was expressed as a percentage of annual metaldehyde application in the period of 2008–2018. Highest levels of metaldehyde loss from cereal and oilseed rape crops in the Colne catchment, at monitoring point C7, were equal to 1.57%, 0.33% and 0.24% in 2012, 2014 and 2008, respectively. Metaldehyde losses to surface water from all crops varied between 0.01 and 0.25%, with maximum 1.18% in 2012 (Table S1).

Metaldehyde use (kg a^{-1}) in the Colne catchment showed a decline from 4680 kg in 2008/2009 to 3326 kg in 2010 and 2189 kg in each of 2012 and 2013. Although the application of metaldehyde in 2012 and 2013 was similar to the metaldehyde use in 2014 and 2015 (1757 kg a^{-1}), a substantial increase of metaldehyde flux was observed in 2012 and 2014 (25.78 and 4.35 kg, respectively, at C7). Consequently, no relationship between application rates and metaldehyde concentration/flux was observed (Figs. 5, S4). Results of multiple linear stepwise regression demonstrated that precipitation and stream flow were the main factors controlling flux ($R^2 = 0.9$), while precipitation explains 37% and 81% of variability in metaldehyde concentration and flux, respectively (Figs. 5, S5; Table 4).

3.2. Seasonal variations in metaldehyde levels: comparison with hydrological conditions and application regime

3.2.1. Hydrological conditions

Concentration displayed a seasonal pattern with concentrations rising during September–December each year across all monitoring points. Such elevated levels often coincided with high-intensity

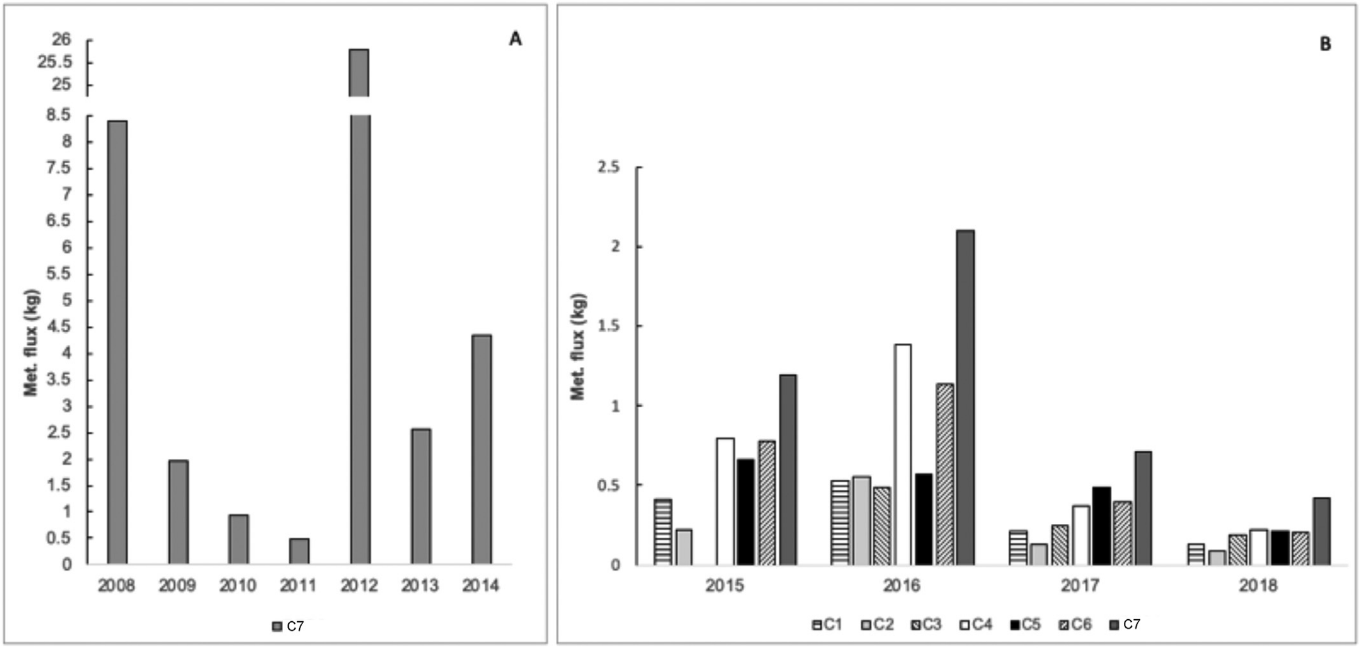

Fig. 2. Time series of annual metaldehyde flux (kg) at monitoring point C7 during 2008–2014 (A), and at sites C1–C7 during the period 2015–2018 (B).

precipitation events followed by increased stream discharge during September–December annually (Fig. 4; Figs. S1–S3). Highest metaldehyde concentrations frequently occurred following rainfall events with daily precipitation above 10 mm. For example, in 2012, concentrations within the 4.05–6.78 μg L^{-1} range were associated with 15–30 mm cumulative rainfall (4 days before the concentration peak was detected). 63% of all samples above the EU DWD limit (0.1 μg L^{-1}) were recorded when the 4-day cumulative rainfall was ≥10 mm. During the metaldehyde application period from August–December, elevated levels were also associated with rainfall events of lower intensity (up to 5 mm of daily precipitation) and under baseflow conditions (below 0.5 m^3 s^{-1}). For example, in October–November 2016, metaldehyde levels above the EU DWD limit were recorded. A significant positive relationship ($p < 0.001$) between average quarterly metaldehyde concentration and average flow during the period 2009–2018 was observed (Figs. 4, S1).

When average quarterly concentrations at site C7 are compared for the periods January–March, April–June, July–September and October–December in 2009, 2010 (dry years) and 2016 (a wet year), average metaldehyde concentrations across all seasons remained below the EU DWD limit across all seasons in 2009 and 2010. Average concentrations of metaldehyde at C7 were below 0.2 μg L^{-1} when an average flow of 2.7 m^3 s^{-1} (January–March) and cumulative precipitation of 210 mm (July–September) were recorded in 2010. A significant positive relationship ($R^2 = 0.76$, $r = 0.87$, $p < 0.001$, $n = 10$) between average metaldehyde concentration and stream flow was observed in the October–December months in 2009–2018. (Fig. 6).

Hydrological conditions of high intensity with daily rainfall ranging between 10 and 20 mm (for example, daily precipitation within the range 10–18 mm day^{-1} on 7, 8, 12 and 13 July 2012), and within 30–43 mm on several occasions (43 mm on 24 July 2015; 31 and 38 mm on 30 May and 22 June 2016, respectively; see Figs. 4, S1), and maximum daily flow up to 16 m^3 s^{-1} during February–July at the FGS3 were not associated with metaldehyde levels above 0.1 μg L^{-1}, except for those occasions in 2009, 2013 and 2017.

Three instances of EU DWD limit exceedance were recorded at C7 in January 2009 (Table 4); elevated but below the regulatory limit metaldehyde concentrations, up to 0.06 μg L^{-1}, were observed in February of the same year. Eight instances of regulatory limit exceedance (observed concentrations up to 0.22 μg L^{-1}) occurred in February–April 2013 and also a rise in metaldehyde concentrations in February 2017 (up to 0.12 μg L^{-1}) (Tables 4, S2, S3). Stream flows recorded at the FGS3 during these time periods varied between 1 and 7 m^3 s^{-1}. Additionally, one instance of the EU DWD limit exceedance (0.16 μg L^{-1}) was recorded at the C5 site on 9 February 2017 (Fig. S3 and Table S3). On 22 June 2016, concentrations increased at all monitoring points to varying extent, with peak concentrations ranging between 0.05 μg L^{-1} (C5) and 0.1 μg L^{-1} (C7) across the catchment (Figs. 4, S1).

In those instances when metaldehyde levels above the regulatory limit were detected during baseflow conditions during February–July, regulatory limit exceedances were localised and shortlived. These circumstances support probable point source pollution as the cause. For example, a metaldehyde concentration of 0.19 μg L^{-1} was recorded at C7 in April 2011 when only 3 mm of monthly precipitation and an average daily flow of 0.5 m^3 s^{-1} were recorded. Also, metaldehyde concentrations up to 0.1 μg L^{-1} were detected at C7 in the first two weeks of July 2018 when no rainfall fell and an average daily flow of 0.18 m^3 s^{-1} was recorded at the FGS3 (Fig. 4). No increase in metaldehyde concentrations was observed elsewhere across the catchment during July 2018 (Fig. S2).

3.2.2. Application regime

When periods of no metaldehyde application (January, July) were assessed, metaldehyde concentrations were typically in the range of 0.01–0.03 μg L^{-1} across all years observed. Elevated concentrations within the range 0.05–0.09 μg L^{-1} were observed on 23 instances at C7 in January ($n = 17$) and July ($n = 6$) during 2008–2018, accounting for 17% of samples collected during no-application months (Table S2). Metaldehyde concentrations above 0.1 μg L^{-1} were observed on eight occasions in January from 2008 to 2018 and on two occasions in July from 2008 to 2018, representing 7% of all samples collected in these two months (Table 5).

Concentrations during metaldehyde application periods to protect spring and summer crops (February–June) were within a similar range to concentration values observed during no application time periods, generally not exceeding 0.03 μg L^{-1}. Concentrations within the range 0.05–0.09 μg L^{-1} were observed on seven and 14 instances at C7 in February–March and April–June 2008–2018, respectively (9% of all samples collected in February–June 2008–2018) (Table S2). Twelve instances (5% of all samples) occurred when metaldehyde

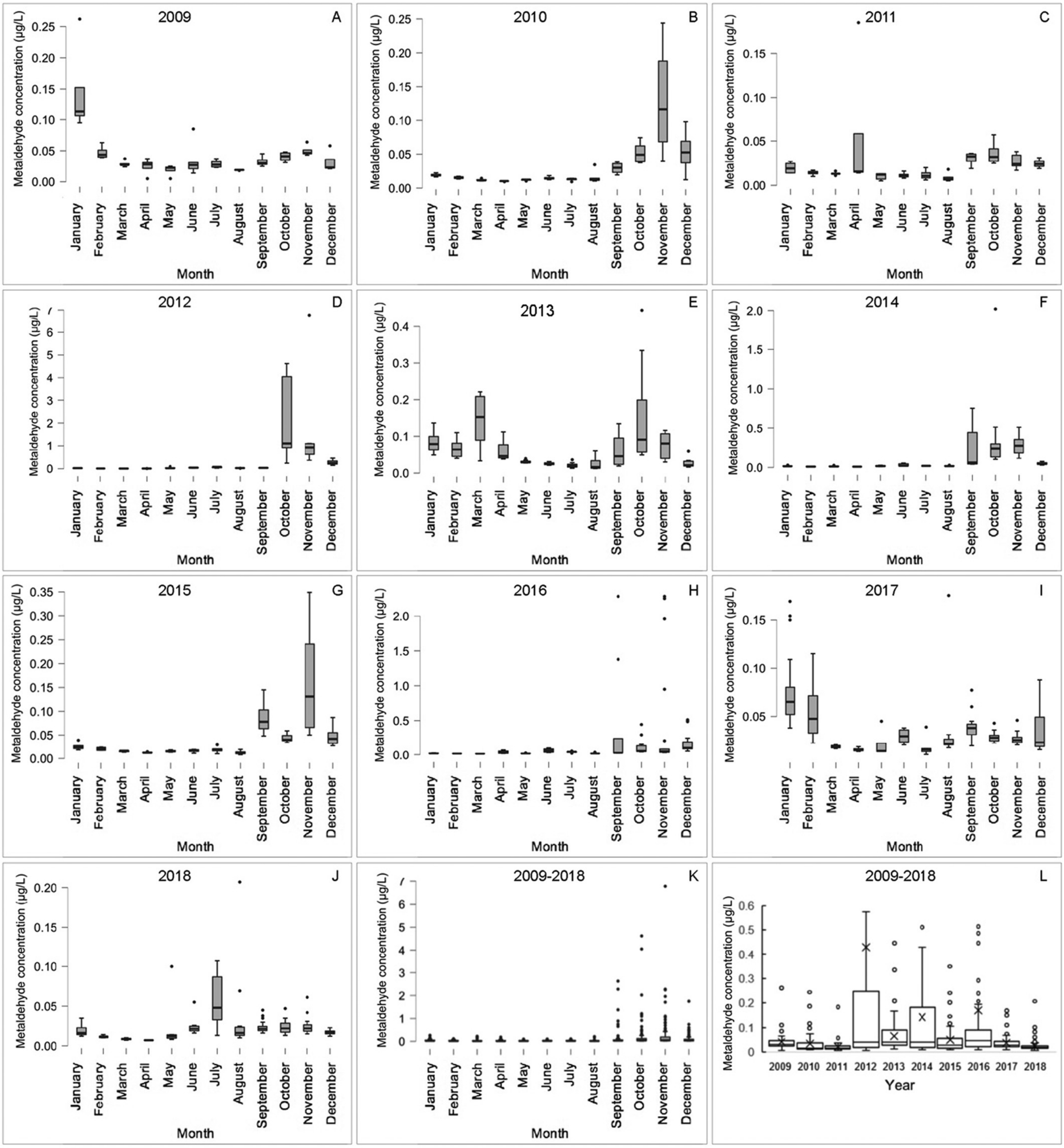

Fig. 3. Box plots representing the range in metaldehyde concentrations (μg L^{-1}) in the Colne catchment outlet (C7) during the period 2009 to 2018. Panels A–J show monthly range in metaldehyde concentrations for individual years. Panels K and L represent monthly range and annual range in concentrations over the 2009–2018 period. Circles represent outliers that are not included in the range data. Crosses and lines in each box indicate mean and median values, respectively; error bars display one standard deviation of the sample range. Whiskers (A–K) represent minimum and maximum values.

concentrations above 0.1 μg L^{-1} were observed at C7 during the spring/summer application period (Table 5). At the sub-catchment level, only five instances of metaldehyde concentrations above 0.1 μg L^{-1} were recorded during February–June in 2015–2018 across the C1–C6 monitoring points in the Colne catchment (see Table S3). For a comparison, 101 instances of regulatory limit exceedance were recorded during the whole period 2015–2018 at these monitoring points (C1–C6, Table 2).

In the autumn/winter application period (August–December) 2008–2018, 64% of the samples collected during these months had metaldehyde concentrations within the range 0.01–0.04 μg L^{-1}. At C7, elevated levels of metaldehyde within the range 0.05–0.09 μg L^{-1} were observed in 14% of samples collected between August–December 2008–2018. The autumn/winter application period was associated with the highest number of concentrations above 0.1 μg

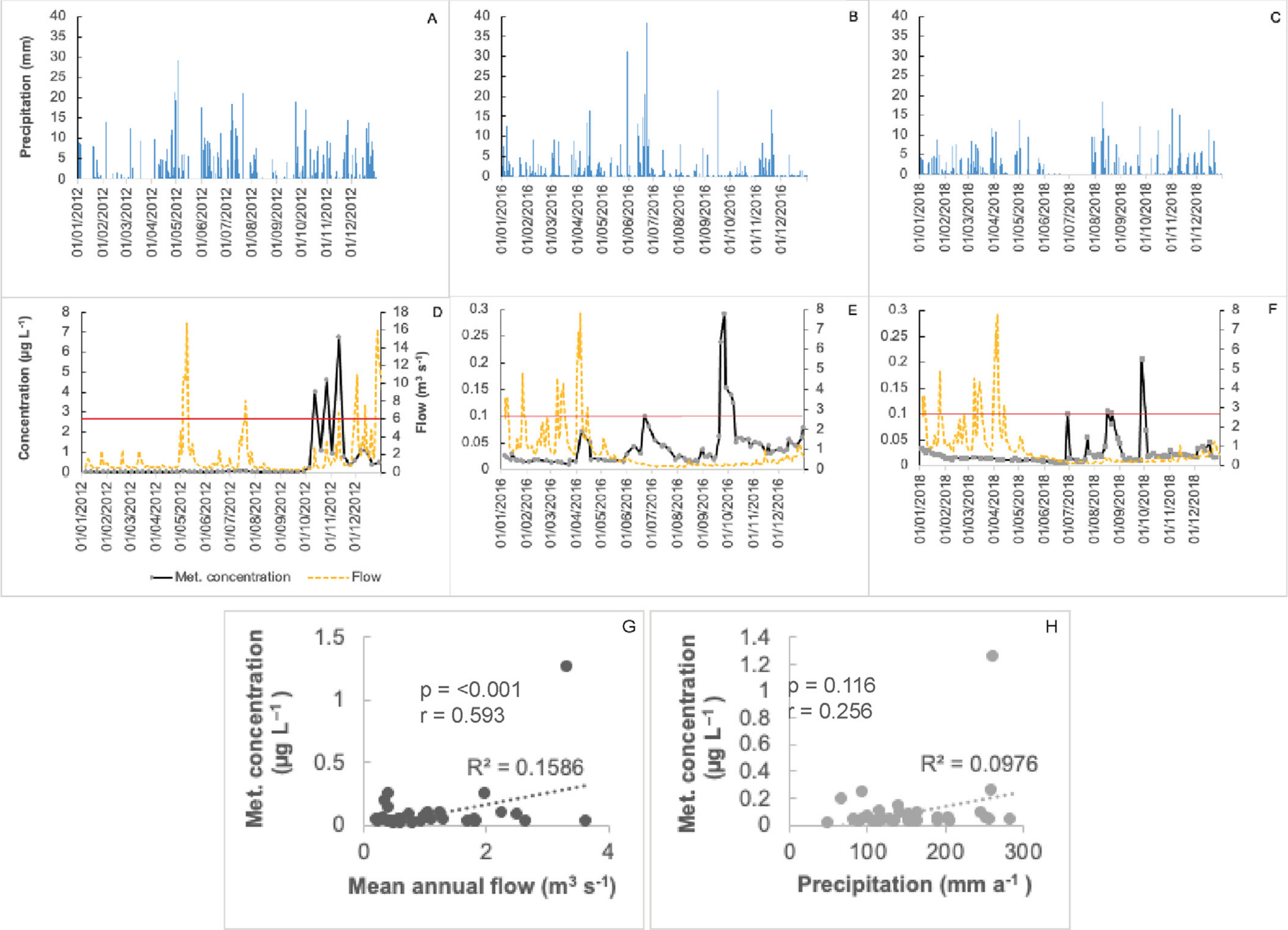

Fig. 4. Panels A–C: Daily rainfall (mm) in 2012, 2016 and 2018. Panels D–F: Metaldehyde concentration (μg L^{-1}) and water flow ($m^3 s^{-1}$) at monitoring point C7 in 2010, 2016 and 2018. Red line represents the EU DWD limit (0.1 μg L^{-1}). Panels G, H: relationship between mean annual metaldehyde concentration with mean annual flow and precipitation, respectively, ($n = 40$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

L^{-1}, with 22% of all samples collected in August–December 2008–2018 (112 out of 511) containing metaldehyde above the EU DWD limit. More than 50% of samples collected in August–December 2008, 2012 and 2014 had metaldehyde concentrations above 0.1 μg L^{-1} (Table 5).

Cumulative fluxes in dry (2010, 2018) and wet years (2016) at the catchment outlet were compared across metaldehyde application seasons (Table S4). In dry years, cumulative flux during January and July (no metaldehyde application) was equal to 0.1 kg (2010, 2018) and up to 0.3 kg during the spring/summer application period (February–June) in 2010. In the autumn/winter period of these dry years metaldehyde flux was 0.5 and 0.1 kg (2010, 2018, respectively). Maximum fluxes across all application seasons were observed in 2016 when 0.2, 0.6 and 1.3 kg (no application, the spring/summer and autumn/winter application periods, respectively) (Table S4) were recorded.

4. Discussion

4.1. Temporal and spatial trends in metaldehyde concentrations and fluxes

Time series analysis of metaldehyde presence in the study area revealed that the molluscicide was consistently present in stream networks at concentrations that generally did not exceed the EU DWD limit (0.1 μg L^{-1}). Peak concentrations, with frequent increases in concentrations by an order of magnitude, regularly occurred during the application periods (September–December) each year. Noticeably smaller increases in metaldehyde levels, when concentrations tended to rise occasionally from 0.01 to 0.03–0.05 μg L^{-1}, and up to 0.09 μg L^{-1} on rare occasions, were observed during the spring-summer application period in February–June. These trends agree with observations of metaldehyde time series in other studies. Peak concentrations of a similar order of magnitude were reported by Kay and Grayson (2014), Lu et al. (2017) and Castle et al. (2018).

The increase in metaldehyde concentrations and frequent exceedance of the regulatory limit during the months September–December are linked to land use in the study area: 51% of all crops in the Colne catchment comprise winter cereals and oilseed rape. Applications of metaldehyde are made to protect these crops during the months August–December. Higher amounts of the metaldehyde are applied in the autumn (up to 210 g ha^{-1} active substance from a permitted maximum total of 700 g ha^{-1} active substance per calendar year) during August–December (MSG, 2020), compared to applications made to protect crops in the spring and summer. However, several exceptions were observed, for example in February–March 2013 and 2017, when metaldehyde applications to protect spring crops commenced and wet antecedent soil moisture conditions caused an increase in surface runoff, metaldehyde concentrations were in the range 0.03–0.1 μg L^{-1}.

Compared to the upper catchment reaches, higher fluxes of metaldehyde were identified in the mid-section and lower part of the Colne catchment due to higher stream discharge, particularly during the application period September–December when flowing field drains provide greater hydrological connectivity. Stream flow at site C7 receives metaldehyde delivered to the river network from upstream, resulting

Table 3
Metaldehyde loss to the watercourse network (g ha^{-1}) from the River Colne sub-catchments C1–C6 and the catchment outlet C7.

	Metaldehyde loss (g ha^{-1})					
	C1	C2	C3	C4	C5	C6
Year	All crops					
2015	0.33	0.09		0.11	0.25	0.07
2016	0.42	0.23	0.23	0.20	0.21	0.10
2017	0.17	0.05	0.11	0.05	0.18	0.03
2018	0.10	0.03	0.09	0.03	0.08	0.02
	C1	C2	C3	C4	C5	C6
Year	Cereals and oilseed rape crops					
2015	0.88	0.14	N/A	0.14	0.40	0.09
2016	1.13	0.35	0.26	0.25	0.34	0.13
2017	0.46	0.08	0.13	0.07	0.30	0.05
2018	0.28	0.05	0.10	0.04	0.13	0.02

Metaldehyde loss (g ha^{-1})		
	C7	
Year	All crops	Cereals and oilseed rape crops
2008	0.58	0.78
2009	0.14	0.18
2010	0.06	0.09
2011	0.03	0.04
2012	1.79	2.39
2013	0.18	0.24
2014	0.30	0.40
2015	0.08	0.11
2016	0.15	0.19
2017	0.07	0.07
2018	0.03	0.04

in an elevated flux of the molluscicide, particularly during wet years such as 2012. The peak concentration of 6.78 μg L^{-1} at site C7 in 2012 was the highest recorded in the Colne catchment in the period 2008–2018 (Fig. S3, Table 2).

This finding compares with Lu et al. (2017) who reported increased metaldehyde concentrations of up to 1.6 μg L^{-1} recorded at several sites along the River Thames under high flow conditions in 2012. Lu et al. (2017) suggested that in years such as 2012, when a warm winter was followed by wet summer and autumn months, farmers tend to apply metaldehyde at maximum allowable rates to control slug populations. In this study, the median and maximum levels of metaldehyde in 2012 (0.04 μg L^{-1} and 6.78 μg L^{-1}, respectively) recorded at monitoring point C7 at the bottom of the Colne catchment were consistently higher in comparison with concentrations recorded at other monitoring points during 2015–2018. The highest percentile of samples above 0.1 μg L^{-1} (33% and 34% in 2012 and 2014, respectively) corresponded with high values of annual precipitation and average discharge recorded in 2012 and 2014 (Figs. S4, S5).

Increased concentrations of metaldehyde were observed in the smaller sub-catchments (e.g. at C1, C3). In these areas, arable land use, the relatively small size of the sub-catchments and the lack of metaldehyde dilution, compared to the River Colne, make these areas especially responsive to changes in metaldehyde applications.

4.2. Relationship between metaldehyde concentrations, hydrological regime and application rates

The results indicate that metaldehyde concentration peaks were detected during metaldehyde application periods in the autumn and winter periods. These months coincide with increased precipitation and stream discharge, and highest peaks in metaldehyde levels were often, but not always, associated with periods of wet weather. Rainfall events following pesticide application play an important role in pesticide transport and loss to the stream network, and peaks in pesticide concentrations, including metaldehyde, are associated with periods of high flow and periods of increased rainfall (Tediosi et al., 2012; Bloodworth et al., 2014). Additionally, duration, frequency and amount of precipitation control runoff generation, amount and rate (Holvoet et al., 2007). Increased frequency and larger, high-intensity rainfall events are likely to cause larger amounts of pesticides being transported to watercourses from land (Banks et al., 2005; Sandin et al., 2018) in the autumn and winter when soils are often at or near field capacity. When soils with low permeability are subject to seasonal waterlogging, such as soils of the Tendring and the Wix soil associations in the lower part of the Colne catchment (CSAI, 2019) that are developed on silt, silty and sandy clay superficial deposits (BGS, 2019), it is more likely that pesticides could be mobilised via sediment runoff and also be transported via runoff in dissolved form. Surface and

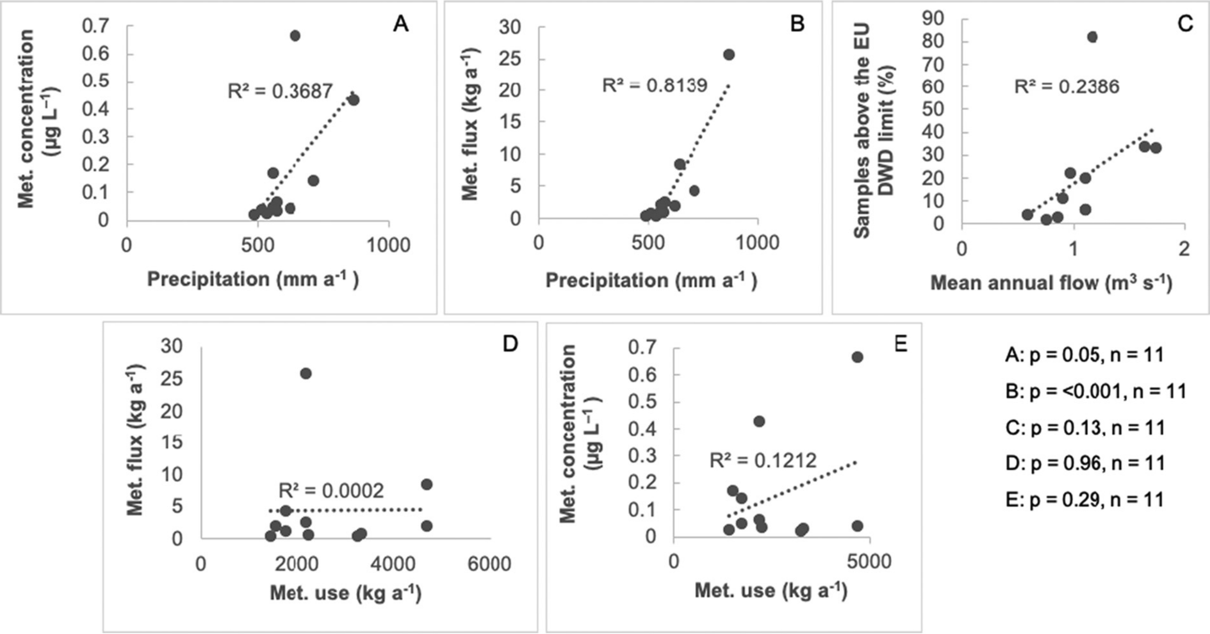

Fig. 5. Panels A, B: correlation plot showing the relationship between mean annual metaldehyde concentrations (μg L^{-1})/flux (kg a^{-1}) and precipitation (mm a^{-1}) in the period 2009–2018. Panel C: Correlation between percentage of samples above the EU DWD limit and mean annual flow in the period 2009–2018. Panels D, E: correlation plot showing the relationship between mean annual metaldehyde concentrations/flux and annual metaldehyde use, active applied (kg a^{-1}) in the period 2009–2018.

Table 4
Multiple forward stepwise linear regression results.

Model summary - Met. flux (kg)	Variable/intercept	R	R^2	Adjusted R^2	RMSE	Standard error	t	p
1	(Intercept)	0	0	0	7.449	2.246	1.977	0.076
2	(Intercept)	0.902	0.814	0.793	3.388	6.038	−5.446	<0.001
	Precipitation (mm a^{-1})					0.01	6.272	<0.001
3	(Intercept)	0.944	0.891	0.864	2.748	6.957	−6.42	<0.001
	Precipitation (mm)					0.022	5.029	0.001
	Average annual flow ($m^3 s^{-1}$)					6.866	−2.383	0.044
Model summary - Met. concentration (μg L^{-1})	(Intercept)					0.063	2.431	0.035
1	(Intercept)	0	0	0	0.208	0.311	−1.768	0.111
2	Precipitation (mm a^{-1})	0.607	0.369	0.299	0.174	5.084e−4	2.293	0.048

Note. The following covariates were considered but not included: i) Flux regression model: Metaldehyde use (active applied, kg a^{-1}), Average metaldehyde concentration (μg L^{-1}), Annual discharge ($m^3 a^{-1}$); ii) Metaldehyde concentration regression model: Average annual flow ($m^3 s^{-1}$), Annual discharge ($m^3 a^{-1}$), Metaldehyde use (active applied, kg a^{-1}).

subsurface runoff in field drainage is likely to be a predominant mode of metaldehyde transport in the Colne catchment due to the physical characteristics of the soil and sub-soil. Similarly, Castle et al. (2018) reported elevated metaldehyde concentrations following intensive rainfall events in early June 2016 in the River Dee catchment, North West England, and suggested that a spike in metaldehyde was caused by a possible use of metaldehyde in the summer growing season or from the washout of residual molluscicide in the soil. A further factor in metaldehyde transport is overspreading due to poor application techniques that can lead to the risk of residual pesticide loss during rainfall events.

In the study by Asfaw et al. (2018), when metaldehyde concentrations were monitored and compared with high-resolution rainfall event data, short-lived metaldehyde peaks occurred with a duration of 12–48 h. In this study, peaks in metaldehyde concentration occurred up to 5–7 days following high rainfall events (daily precipitation ≥10 mm), which indicates a relatively short time period for the pollutant to reach the stream network.

In this study, the regulatory limit exceedances of metaldehyde concentrations were associated with a series of rainfall events and were rarely observed to occur outside of application periods. These results

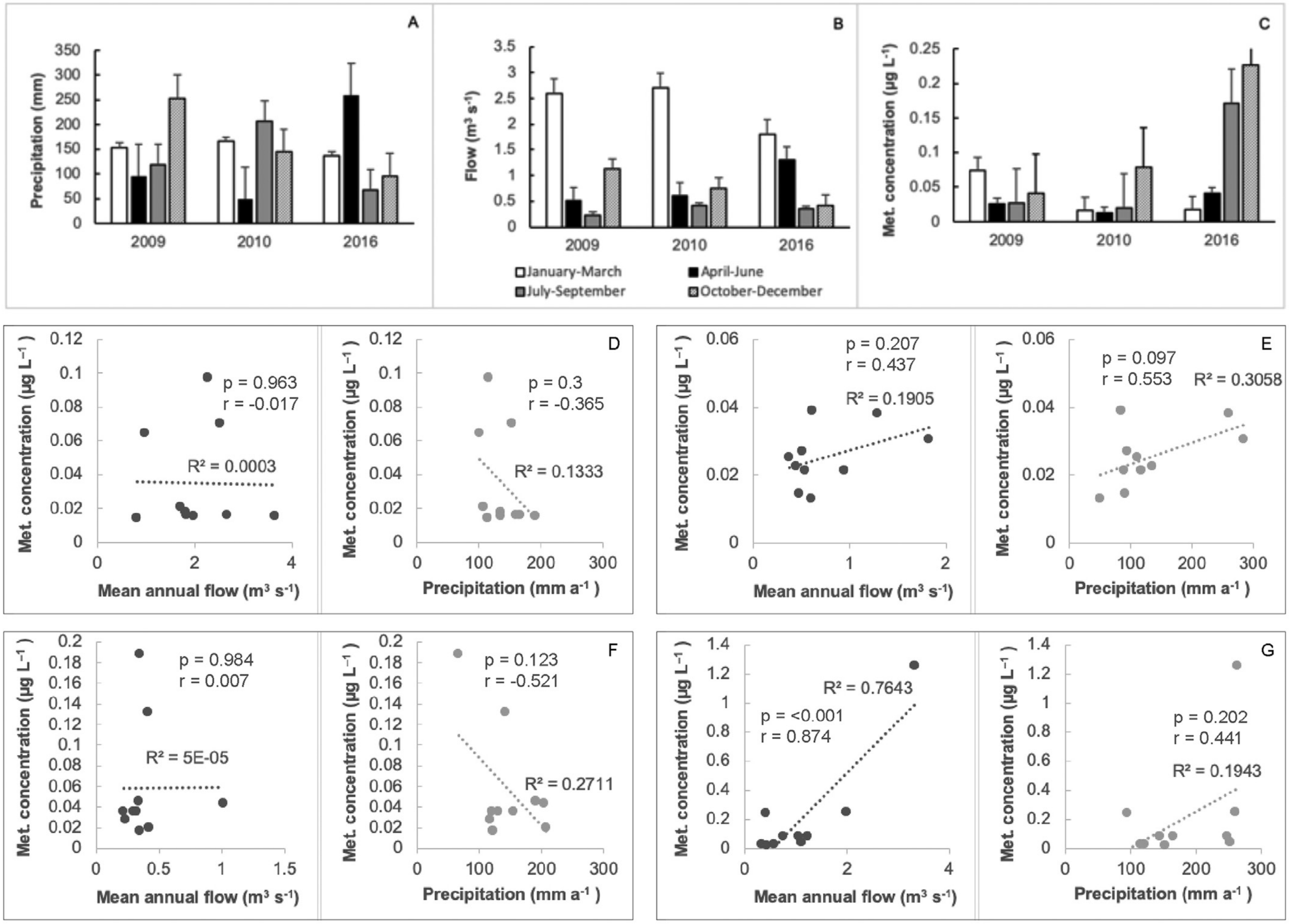

Fig. 6. Panels A–C: Cumulative rainfall (mm) (A), average stream flow ($m^3 s^{-1}$) (B), and average metaldehyde concentration (μg L^{-1}) (C) at monitoring point C7 in the periods 2009, 2010 and 2016. Error bars are standard error of the mean. Panels D-G: relationship between average quarterly metaldehyde concentration and average flow/precipitation during the period 2009–2018 (n = 10; D: January–March, E: April–June, F: July–September, G: October–December).

Table 5
Statistics of metaldehyde concentrations above the EU DWD limit for August–December (the autumn/winter application period), February–June (the spring/summer application period to protect rooted vegetables and other spring/summer crops), and January and July (no application) during the period 2008 to 2018 at the catchment outlet C7.

Site	Year	Total number of samples			Number of samples above the EU DWD limit			Percentile of samples above the EU DWD limit		
		August–December	February–June	January, July	August–December	February–June	January, July	August–December	February–June	January, July
C7	2008[a]	19	2	1	18	0	0	95	0	0
	2009	22	22	8	0	0	3 (January)	0	0	38
	2010	22	22	8	3	0	0	14	0	0
	2011	21	22	8	0	1 (April)	0	0	5	0
	2012[a]	27	21	10	19	0	0	70	0	0
	2013	46	42	18	11	8 (including 1 in February, 6 in March, and 1 in April)	2 (January)	24	19	11
	2014[a]	46	21	10	26	0	0	57	0	0
	2015	49	21	10	9	0	0	18	0	0
	2016[a]	76	24	12	24	1 (June)	0	32	4	0
	2017	90	22	24	1	1 (February)	3 (January)	1	5	13
	2018	93	26	29	1	1 (May)	2 (July)	1	4	7

[a] Year with >30% of samples above the EU DWD limit (0.1 μg L^{-1}) collected in August–December.

suggest that increased precipitation and stream flow outside the typical metaldehyde application periods would not lead to frequent metaldehyde concentration exceedances of the EU DWD limit (0.1 μg L^{-1}). Metaldehyde concentrations above the regulatory standard were more likely to occur when metaldehyde application coincided with rainfall events, as happened in 2012 when maximum concentrations and fluxes of metaldehyde in stream water were observed.

Frequent and prolonged rainfall events in the summer, as well as mild and wet conditions in the autumn and winter in England in 2012 promoted the increased application of metaldehyde under these conditions (Bloodworth et al., 2014; Lu et al., 2017). Metaldehyde concentrations of up to 1.5 μg L^{-1} were recorded in September 2012 in the River Thames catchment, when the maximum application rate should have been reduced to.

33 g ha^{-1} a^{-1} to meet the drinking water standard limit, according to metaldehyde transport modelling conducted by Lu et al. (2017). Lu et al. (2017) concluded that precipitation coupled with application rates and soil hydraulic properties are the key factors controlling metaldehyde presence in streams (Lu et al., 2017). Similarly, Guo et al. (2004) found that pesticide use and precipitation amount were the two main factors controlling pesticide transport to surface water when regression analyses were undertaken for other pesticides.

($R^2 = 0.9$ at the single basin scale). Furthermore, Kreuger and Tornqvist (1998) established that the amount of pesticides applied to land was the most important predictor of pesticide fluxes and concentrations in stream water, explaining up to 85% of pesticide concentration variability in their multiple regression model. In the current study, although precipitation and flow are the main factors controlling metaldehyde concentrations and flux, metaldehyde application amount was not a significant variable predicting metaldehyde levels in surface water. This contrast could be due to several factors, including the sample size, difference in physico-chemical properties of pesticides, and time period considered in the reported studies. For example, Kreuger and Tornqvist (1998) included between 16 and 21 pesticides in the analysis, where a separate regression model was used to evaluate the relationship between variables in individual years during the period May–September. The linear stepwise regression in the Colne catchment included a reduced sample size of variables, considered one pesticide, and compared annual values of variables, including the application rate.

In this study, low metaldehyde concentrations in a similar concentration range (0.01–0.03 μg L^{-1}) were recorded in 2009–2011 and during 2017–2018. A lower intensity hydrological regime was prevalent during these periods, particularly during the metaldehyde application season. Relatively dry weather conditions minimised slug population rates, reducing the inherent need for larger amounts of metaldehyde application to agricultural land. Furthermore, statutory requirements of an application limit of 700 g a^{-1} and a 6-m no-application buffer adjacent to a watercourse (EA, 2016), as well as metaldehyde application guidelines of the Metaldehyde Stewardship Group (for example, a maximum application rate of 210 g active substance ha^{-1} during August–December; MSG, 2020), were beneficial for controlling metaldehyde runoff from agriculture during these dry periods in the Colne catchment.

Spatio-temporal trends of metaldehyde levels in watercourses observed in this and other studies (Kay and Grayson, 2014; Lu et al., 2017; Asfaw et al., 2018; Castle et al., 2018, 2019) suggest that surface and subsurface runoff-driven transport of metaldehyde serves as a major pathway in explaining the presence of metaldehyde in surface water. Hydrological conditions of high intensity during and following metaldehyde application coincide with metaldehyde concentration spikes. At the same time, wet weather conditions during months associated with high flow (up to 18 m^3 s^{-1}) and periods of increased rainfall (≥10 mm day^{-1}) with no application of metaldehyde and metaldehyde application in spring and summer were not connected with an increase in metaldehyde concentrations >0.03 μg L^{-1}. These results suggest that metaldehyde at concentration levels above the EU DWD limit is short-lived in the aquatic environment.

Although elevated levels of metaldehyde have a seasonal nature and tend to occur in the autumn and winter seasons, metaldehyde is continuously present in streams at concentrations that are an order of magnitude lower than the EU DWD limit of 0.1 μg L^{-1}. The presence of metaldehyde in the stream network at background concentrations (0.01–0.03 μg L^{-1}) is likely to be associated with applications of the molluscicide during August–December and February–June, causing the pollutant to be present in the aquatic environment all year around. In addition, due to its physio-chemical properties (including its relative high solubility and low sorption potential) metaldehyde legacy sources (e.g. stream sediment and the soil profiles) and groundwater recharge are potential contributing vectors active during periods of low hydrological intensity and low/no application.

Collectively, the findings of this study suggest that metaldehyde concentrations in aquatic systems are likely to be below the EU DWD standard of 0.1 μg L^{-1} in areas with catchment characteristics and farming practices similar to the study area (East of England) following withdrawal of metaldehyde for outdoor use applied in the UK in March 2022. The remaining pool of metaldehyde residues from historic applications in soil profiles is likely to be degraded by soil microbial communities over time due to the high biodegradation potential of this chemical (Balashova et al., 2020).

5. Conclusions

This study is the first to examine long-term temporal trends of metaldehyde concentrations in surface water in a semi-agricultural catchment at both catchment and sub-catchment scales. Metaldehyde concentration and flux data for a ten-year period (2008–2018) were analysed and compared with hydrological parameters (stream flow and precipitation). Although metaldehyde levels varied on an annual basis, there were seasonal commonalities in metaldehyde presence in surface waters.

In each year, metaldehyde concentration peaks above the EU DWD limit (0.1 μg L^{-1}) occurred during September–December and coincided with periods of metaldehyde application and the onset of autumn rainfall and increased surface/subsurface runoff. An increase in metaldehyde concentrations were ubiquitously associated with metaldehyde application periods. The EU DWD limit exceedances of metaldehyde concentration were considerably lower during the application periods in 2009–2011 and 2017–2018 years, when hydrological conditions of lower intensity were prevalent, particularly in the autumn and winter months. The results of this study indicate the significance of the coincidence of the hydrological regime during periods of metaldehyde application, coupled with the rates of molluscicide applied, on metaldehyde concentrations in stream water. Metaldehyde levels varied spatially, with higher concentrations observed in the small headwater sub-catchments with predominantly agricultural land use, as well as at the regulatory point at the bottom of the Colne catchment.

Metaldehyde concentrations in stream water during months when metaldehyde is not normally applied to agricultural land in the East of England (January and July) and during application times to protect spring and summer crops (February–June) were in general an order of magnitude lower than the EU DWD limit of 0.1 μg L^{-1}. Periods of high intensity hydrological conditions during months with no metaldehyde applications were not associated with an increase in metaldehyde concentrations above 0.1 μg L^{-1}.

It is concluded that the presence of metaldehyde in stream runoff observed in the Colne catchment suggests that metaldehyde at concentrations above the EU DWD limit is short-lived in the aquatic environment, Furthermore, metaldehyde residues in soil and aquatic sediment mobilised during high flow conditions do not pose a long-term concern for meeting the EU DWD water quality standard. Collectively, the results of this study indicate that metaldehyde levels in surface water are likely to be consistently below the EU DWD limit once the withdrawal of metaldehyde for outdoor use is enforced in the UK in March 2022.

CRediT authorship contribution statement

Natalia Balashova: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization, Project administration, Funding acquisition. **Kevin M. Hiscock:** Validation, Supervision, Writing – review & editing, Funding acquisition. **Brian J. Reid:** Supervision, Writing – review & editing. **Richard Reynolds:** Supervision, Resources, Writing – review & editing.

Declaration of competing interest

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.148858.

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