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Metaldehyde Transport Processes in a Water Abstraction Catchment in Essex, Southeast England

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Abstract This paper addresses the issue of pesticide loss from agriculture and its impact on the aquatic environment. Specifically, this study assesses the transport of the relatively water-soluble polar molluscicide compound metaldehyde in a small (14 km^2) water abstraction catchment in Essex, southeast England during a 14-month period (January 2019–February 2020). A rise in metaldehyde concentrations was observed at all monitoring points, to varying extents, in the months of seasonal metaldehyde applications. The highest increases in metaldehyde concentrations (up to 0.05 μg 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 to the Ardleigh surface storage reservoir in the catchment showed that the highest contribution to the total flux to the reservoir was from water transferred from the adjacent River Colne catchment. Atmospheric deposition of metaldehyde followed a similar seasonal pattern to that observed in metaldehyde levels in surface water and field drain runoff, and in certain months accounted for a higher input than influx from surface runoff (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 reservoir are probably due to the aqueous solubility and decreased degradation rates of metaldehyde in the aquatic environment.

Keywords Metaldehyde · Pesticide transport · Catchment · Surface waters · Monitoring · Flux

1 Introduction

Pesticides are widely used in agriculture to protect crops and maximise yield production. Following application on agricultural land, these chemical substances enter surface waters with runoff, causing diffuse pollution and adversely affecting water quality. Certain pesticides, particularly 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

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(Kolkman et al., 2021). One such chemical is metaldehyde, the most widely used molluscicide in the UK over the last decade (Castle et al., 2017). With average water solubility of 190 µg L^{-1} (PAN (Pesticides Action Network), 2021), metaldehyde is highly soluble in water. Although there are no previous studies on atmospheric transport of metaldehyde, this compound has a potential to volatilise due to a vapour pressure of 6.6 Pa (negligible at room temperature) and a Henry's law constant of 3.5 Pa m^3 mol^{-1} at 25 °C (Kamrin, 1997; European Chemicals Agency (ECHA), 2012; PPDB, 2021). Due to the physical and chemical characteristics of metaldehyde, 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.

Due to the difficulty of this pesticide's removal from drinking water supplies using conventional water treatment methods, such as ozonation, granular activated carbon and chlorination (Kay & Grayson, 2014), water companies have been working continuously with the arable farming sector to encourage the best pesticide management practice.

Despite the efforts of the Metaldehyde Stewardship Group (MSG, 2019), including its metaldehyde guide (MSG, 2020), concentrations of metaldehyde during the typical application season in the UK (August-December months) often exceed the EU Drinking Water Directive (DWD) limit of 0.1 µg L^{-1} (EC, 1998). Recently, a ban on metaldehyde use outdoors has been introduced in the UK (Department for Environment, Food and Rural Affairs (DEFRA), 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. Whilst the outdoor use of metaldehyde is banned in the UK, this pesticide is still approved for use in many countries globally, including the USA, and most EU countries.

Although existing studies on metaldehyde geo-spatial dynamics at various scales (e.g. Castle et al., 2018, 2019; Kay & Grayson, 2014) provide a valuable insight into metaldehyde transport within a watercourse at a catchment scale, limited research of metaldehyde transport, persistence and fate of the pesticide in the environment is available (Castle et al., 2017; Lu et al., 2017). Moreover, no peer-reviewed studies currently exist that consider atmospheric and sub-surface runoff pathways in a source-mobilisation-pathway-delivery continuum (Haygarth et al., 2005). Furthermore, current research on metaldehyde concentration trends in surface water lacks incorporation of metaldehyde data into a mass budget model for a water body at a catchment scale. Such knowledge is essential in understanding metaldehyde sources, scale of impact and the potential of the chemical to degrade in a reservoir.

To bridge the gap in these areas of research, this study includes two aims: to assess metaldehyde transport and the role of source-mobilisation-pathway-delivery mechanisms in metaldehyde export at a sub-catchment scale in surface waters of the Ardleigh catchment in Essex, southeast England; and 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 concentrations in surface waters and field drain runoff; (ii) to evaluate deposition of metaldehyde within the Ardleigh catchment from atmospheric deposition, and surface water and field drain runoff; and (iii) to estimate the impact of individual sources of metaldehyde on the metaldehyde budget of the Ardleigh Reservoir.

Following an analysis of decadal long-term and seasonal spatio-temporal trends in metaldehyde concentrations and fluxes in surface water of the adjacent River Colne (Balashova et al., 2021), a separate study was conducted here to explore further the environmental drivers that govern metaldehyde transport at a sub-catchment scale. This fieldwork-based study investigates metaldehyde concentrations 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 two Salary Brooks that flow into the Ardleigh Reservoir in order to improve understanding of metaldehyde transport at the finer sub-catchment scale. In addition to surface water and field drain runoff of metaldehyde, this study also uniquely considers the contribution to metaldehyde transport from atmospheric deposition of the pesticide.

2 Materials and Methods

2.1 Study Area

The study area comprises the Ardleigh catchment in Essex, southeast England. The Ardleigh catchment is one of seven trial catchments (surrounding reservoirs) of the *Slug it Out* campaign, initiated by Anglian Water Services in 2015. This voluntary catchment management initiative is focused on controlling metaldehyde 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, and to replace metaldehyde use on their land with an alternative method of slug control, such as use of ferric phosphate (Anglian Water, 2020).

The watercourse network includes the Northern and Western Salary Brooks that drain to the Ardleigh Reservoir (Table 1, Fig. 1). The Northern and Western Salary Brooks constitute two natural (gravity flow-fed) sub-catchments areas of 6.5 and 7.5 km^2, respectively, giving a total catchment area 14 km^2. Both the Western and Northern Salary Brooks are shallow (up to 0.5 m deep) and narrow (with widths varying between 0.5 and up to 1.5 m along their tributary lengths). The reservoir is relatively shallow with a depth varying from 3.9 m to a maximum depth of 13 m, and with a maximum volume of 2.19×10^6 m^3 (Redshaw et al., 1988). 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 to 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 1 General characteristics of the Ardleigh Reservoir (Environment Agency Catchment Data Explorer, 2018)

Characteristic	Value
Hydromorphological designation	Artificial
Easting	603,190
Northing	228,294
Mean depth	4.158 m
Altitude	34 m
Catchment area	14 km^2
Surface area	0.57 km^2

The superficial geology of the study area includes deposits of clay, silt and chalk-rich diamicton, as well as sand and gravel deposits of glacial origin that were formed during the Pleistocene epoch of the Quaternary period (2.6 to 0.01 Ma) (British Geological Survey (BGS), 2022). Bedrock material of the catchment is represented by silt, silty and sandy clay deposits that belong to the London Clay Formation of the Thames Group, formed during the Paleogene period

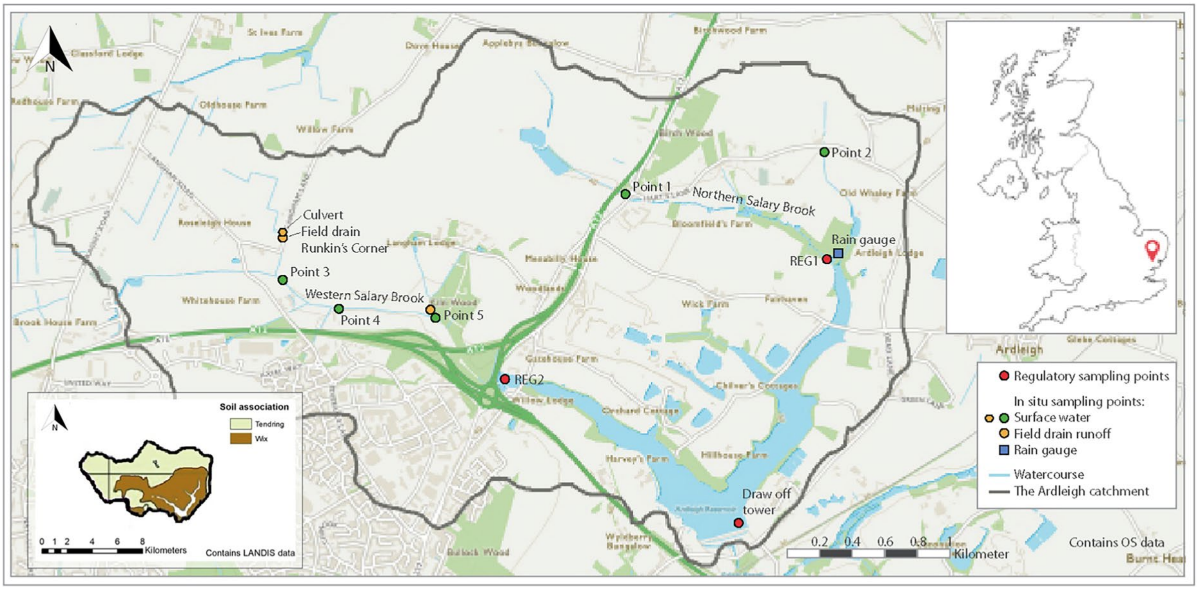

Fig. 1 Geographical location of the study site. The hydrological network of the study area includes the locations of sampling points, including the atmospheric deposition sampling point (rain gauge) (Digimap, 2021)

in the Eocene epoch (56 to 33.9 Ma). The underlying deposits include clay, silt, sand and gravel bedrock material of the Lamberth Group (56 to 66 Ma) followed by chalk deposits of the Sussex White Chalk Formation (Cretaceous period, Late Cretaceous epoch: 100.5 to 66 Ma) (BGS, 2022).

Soils in the Ardleigh catchment are loamy and clayey, slightly acidic with impeded drainage. These include the Tendring and the Wix soil associations (Cranfield University, 2022a, 2022b). Tendring association 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 (Fig. 1). These soil types allow flexible conditions for crops, although they are more suitable for autumn-sown crops (Cranfield Soil and Agrifood Institute Soilscapes(CSAI), 2022).

The area is characterised by a temperate maritime climate with the mean annual temperature ranging between 9.5 and 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, 2022).

The catchment consists of predominantly agricultural/horticultural land and grassland with some woodland. Together, these classes contribute up to 85% of the total catchment area. The urban/suburban land use classes (approximately 15%) are minor in comparison (UK Centre for Ecology and Hydrology (UKCEH), 2017).

The network of monitoring points established for this study included exploratory/in situ and regulatory 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 (Fig. 1) and at an urban area site (8.5 km from the Ardleigh site at 216°, 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, Fig. 1). The regulatory sampling site adjacent to the study area (point REG3) is at the River Colne catchment outlet (TM007255), 8 km south of the Ardleigh catchment, where surface water is abstracted and transferred by pumping to the Ardleigh Reservoir.

2.2 Data Collection and Analysis

2.2.1 *Water Sampling and Analytical Procedure*

Surface water sampling took place during the period January 2019–February 2020, covering two winter seasons. Non-composite samples were collected at the exploratory sampling points 1–5 (Fig. 1) on a monthly basis during March–September 2019 and fortnightly in January–February 2020 and October 2020–February 2020. Weekly sampling was conducted by Anglian Water Services at the REG1–REG3 regulatory sites and from the Ardleigh Reservoir (draw-off tower, Fig. 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, with no field drains 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^{o} C within 24 h of collection.

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 1.8 m above ground level, and the bottle was stored in a stainless-steel container. The amount of rainfall 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 2×2 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.

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

2.3 Hydrological and Climatic Data

Daily stream flow (discharge) data (m^3 s^{-1}) used in this study were obtained from the Environment Agency. Stream flow was recorded at gauging station 37,005 at the bottom of the Colne Catchment (TL962261) with an area 70 km^2. Climatic data were recorded at the Agrii weather station located in the Ardleigh catchment (TM022306). These data included daily records of rainfall, air temperature and humidity, soil temperature and soil moisture. Data sets were collected for the period January 2019–February 2020. The water levels and volume of water in the Ardleigh Reservoir, as well as the volume of water transferred from the River Colne to the reservoir and the volume pumped from the reservoir to the water treatment works were provided by Anglian Water Services.

2.3.1 Calculations and Statistical Data Analyses

Modelled Stream Flow The Northern and Western Salary Brooks are ungauged watercourses and so daily stream flow estimation at these sites was required. Daily stream flow was modelled using the Area-Ratio method, which is based on a regionalization approach and is a common way to address unmonitored catchments by transferring information from a similar donor (in this case, gauging station 37,005 of the adjacent River Colne) to receiver (the Northern and Western Salary Brooks) catchments (Li et al, 2019; Shu & Ouarda, 2012). With this method, an estimate of streamflow in an ungauged catchment is found from:

$$Qy = \frac{Ay}{Ax}Qx \tag{1}$$

where Q_y is estimated stream flow at an ungauged site, Q_x is recorded stream flow at a gauged site and A_y and A_x are the drainage areas of the ungauged and gauged areas, respectively. As a check on the Area-Ratio method, calculation of the effective precipitation for the Northern and Western Salary Brooks using a water balance method, where effective precipitation equals precipitation minus actual evapotranspiration (assuming no abstraction), gave values of flow estimation that were within 5 mm of values calculated using the Area-Ratio method.

Metaldehyde Fluxes in Stream Water The monthly load (ML, flux) of metaldehyde in stream water was calculated using the approach described by Rabiet et al. (2010):

$$ML = QxC_ixt_i \tag{2}$$

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 (µg L^{-1}) and t_i is the time period considered (seconds, i.e. 60×60×24×number of days in the month).

Volume-Weighted Concentrations and Fluxes of Metaldehyde in Rainwater The monthly volume-weighted concentrations of metaldehyde in rainwater were calculated using the following formula:

$$VWC = \frac{CiRi}{Ri} \tag{3}$$

where C_i is metaldehyde concentration in a rainwater sample collected each month (µg L^{-1}) and R_i is the amount of monthly rainfall (mm) (Huang et al., 2010).

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

$$Fi = C_i\mathrm{x}R_i \tag{4}$$

where F_i is the atmospheric deposition flux of metaldehyde 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 rainfall (mm) (Huang et al., 2010). Atmospheric deposition flux was calculated for use in the metaldehyde mass budget for the Ardleigh Reservoir by multiplying the surface area of the reservoir by the monthly atmospheric deposition flux of metaldehyde.

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

$$M_i = \sum Minput - Moutput \qquad (5)$$

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 the Ardleigh Reservoir to the water treatment works 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 the 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).

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.

A Student's *t*-test (statistical test that is used when two independent groups are compared) was applied to compare the degree of difference between the means of metaldehyde concentration in rainwater collected at the urban and rural sites. Significance level in all statistical tests used in this study was set to 0.05.

3 Results

3.1 Hydrological Conditions

Observed daily precipitation records for the period January 2019–February 2020 (Table 2) showed that the lowest mean precipitation values in the range 0.3–1.2 mm were recorded from January to May 2019 with a maximum of 9.0 mm 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 in August. The highest (interquartile range) variability in precipitation and mean/median values were observed between December 2019 and February 2020. Mean daily precipitation values ranged between 1.2 and 3.8 mm during these three months. The maximum daily reprecipitation recorded in the period January 2019–February 2020 was equal to 27 mm in June 2019 (Table 2).

When descriptive statistics of modelled stream flow in the Northern and Western Salary Brooks were analysed (Table 2), mean stream flow 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. The lowest (interquartile range) variability and mean stream flow values were observed between April and October 2019 with mean stream flow 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, the highest variability and mean values of modelled stream flow were registered in December 2020 (0.10 and 0.12 m^3 s^{-1}, NSB and WSB, respectively). Mean stream flow in the Salary Brooks during the period January–February 2020 was also considerably higher than in January and February 2019 (up to 0.07 m^3 s^{-1}

Table 2 Descriptive statistics of daily precipitation and modelled stream flow data, during the period January 2019–February 2020

			Metaldehyde concentration (μg L^{-1}) in rainwater and surface water samples				
	Stream flow at Western Salary Brook (m^3 s^{-1})	Stream flow at Northern Salary Brook (m^3 s^{-1})	Precipitation (mm)	Rainwater	REG1	REG2	REG3
Sample size	425	425	425	22	98	98	98
Mean	0.03	0.03	1.67	0.02	0.01	0.01	0.02
Median	0.02	0.01	0.00	0.02	0.01	0.01	0.01
Std. deviation	0.05	0.04	3.31	0.02	0.00	0.01	0.02
Minimum	0.00	0.00	0.00	0.00	0.01	0.01	0.01
Maximum	0.48	0.41	27.00	0.05	0.02	0.04	0.14
25th percentile	0.01	0.01	0.00	0.01	0.01	0.01	0.01
50th percentile	0.02	0.01	0.00	0.02	0.01	0.01	0.01
75th percentile	0.03	0.03	2.00	0.03	0.01	0.01	0.02

versus 0.03 m^3 s^{-1}). Maximum modelled stream flow 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 2).

3.2 Spatio-temporal Variations in Metaldehyde in surface water at the sub-catchment level

3.2.1 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 (Fig. 2C).

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} (Fig. 2C). 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}) (Fig. 2D). In several instances, peak metaldehyde concentrations (Fig. 2D) were observed only at sampling point REG2, for example in October to the beginning of November 2019 (Fig. 2C, 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 at points 3–5 in the Western Salary Brook (0.01 μg L^{-1}) were not significantly different. In the Northern Salary Brook, 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}) and points 3–5 in the Western Salary Brook (Figs. 2F, 3D, Table 3). 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 (Fig. 2E).

3.2.2 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 (Fig. 3). Lowest measured flux values in the range 0.11–0.26 g $month^{-1}$ were observed in the

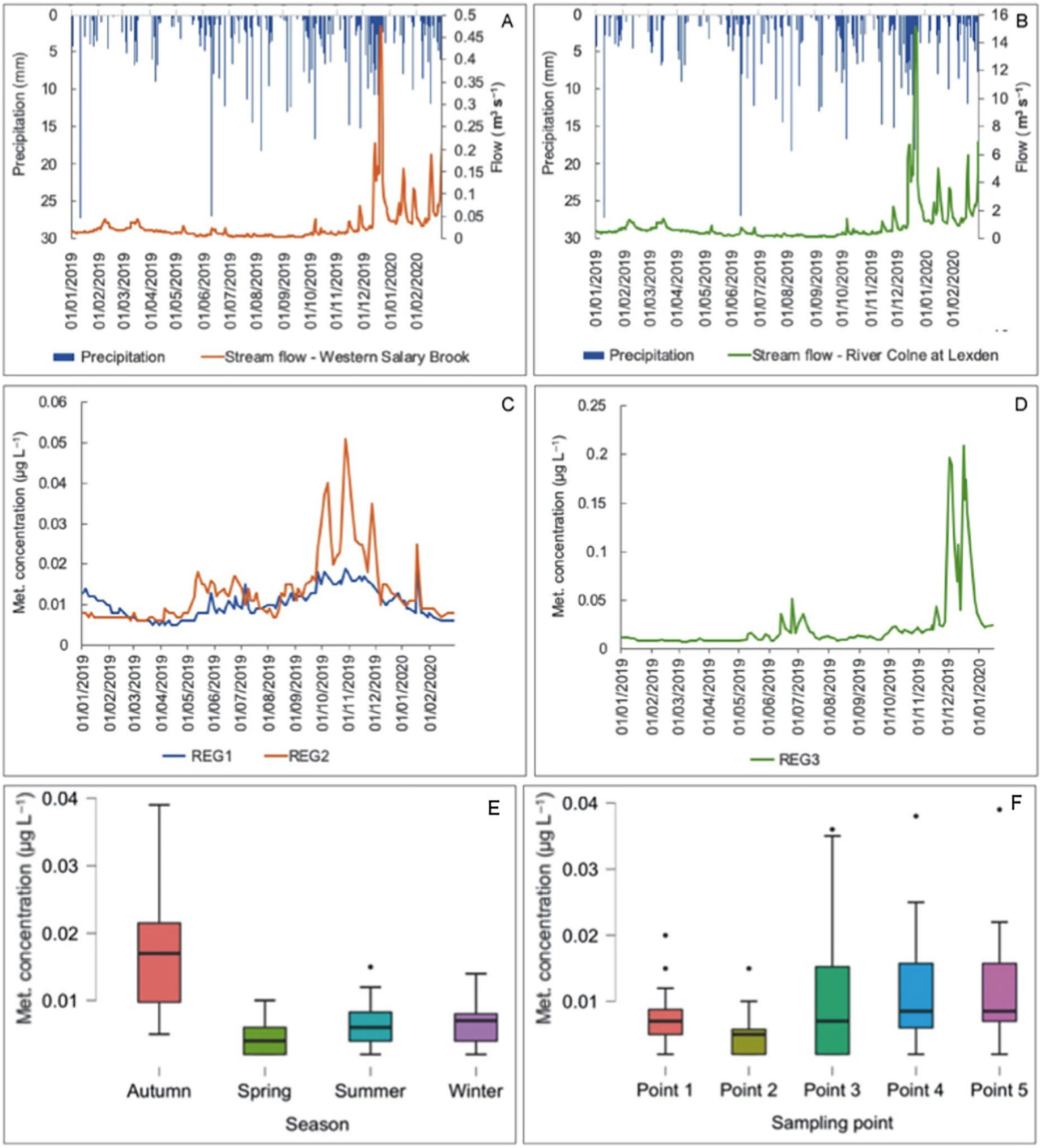

Fig. 2 **A** Precipitation and modelled daily stream flow (m^3 s^{-1}) in the Western Salary Brook (REG2), **B** precipitation (mm day^{-1}) recorded in the Ardleigh catchment and stream flow recorded at gauging station 37,005 (River Colne at Lexden). **C** Metaldehyde concentration (μg L^{-1}) at regulatory sampling sites REG1 and REG2 in the Ardleigh catchment, and **D** at the abstraction site at the River Colne (REG3). **E** Temporal and **F** spatial variability in metaldehyde concentrations in the Ardleigh catchment 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

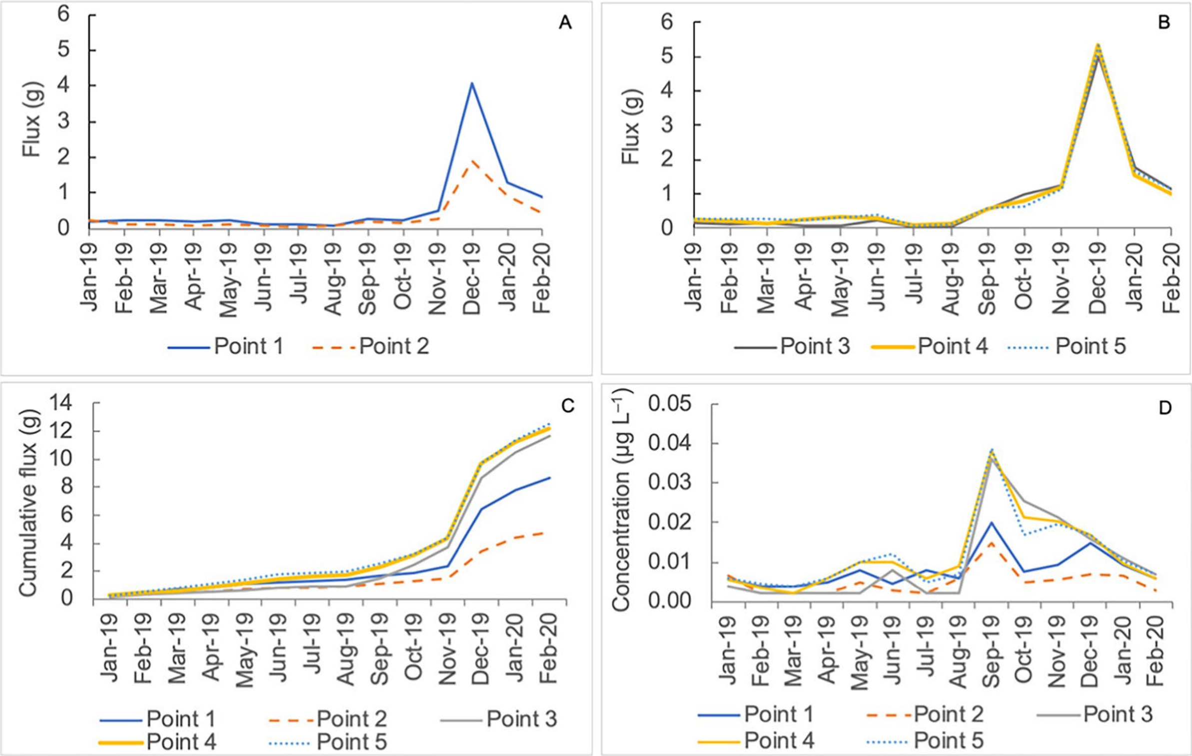

Fig. 3 Monthly flux of metaldehyde (g) in the Northern Salary Brook (**A**) and Western Salary Brook (**B**). Cumulative metaldehyde flux (**C**) and metaldehyde concentration (**D**) in the Northern Salary Brook (points 1, 2) and Western Salary Brooks (points 3–5) during the period January 2019–February 2020

Table 3 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

$^*p < .05$, $^{**}p < .01$, $^{***}p < .001$

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 the period September–November 2019 (Fig. 3).

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) (Fig. 3).

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 only 8–16% of the annual flux values (Table 4).

3.3 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 and 0.05 μg L^{-1} during February 2019-February 2020 (Fig. 4). 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 (Fig. 4).

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 (Figs. 3D, 4A, B). 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, respectively. Average monthly concentrations in rainwater and surface water during the winter months were less than 0.01 μg L^{-1} in March 2019 and in January–February 2020 (Figs. 3D, 4A).

Mean values of metaldehyde concentration in rainwater collected in the vicinity of the Ardleigh Reservoir tended to be lower than the mean concentration in rainwater measured at the nearby Colchester rain gauge site, although the difference between the means 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.

Concentrations in field runoff samples collected upstream (field drain at Runkin's Corner) and downstream (field drain WSB adjacent 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 (Fig. 4C). 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, following which concentrations remained below 0.015 μg L^{-1} (Fig. 4C, D).

3.4 Mass Budget of Metaldehyde in the Ardleigh Reservoir

Metaldehyde fluxes from individual sources displayed a similar temporal pattern with rising levels in May–June and September–December 2019 (Fig. 5). 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 (sampling points REG1, REG2), 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

Table 4 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%

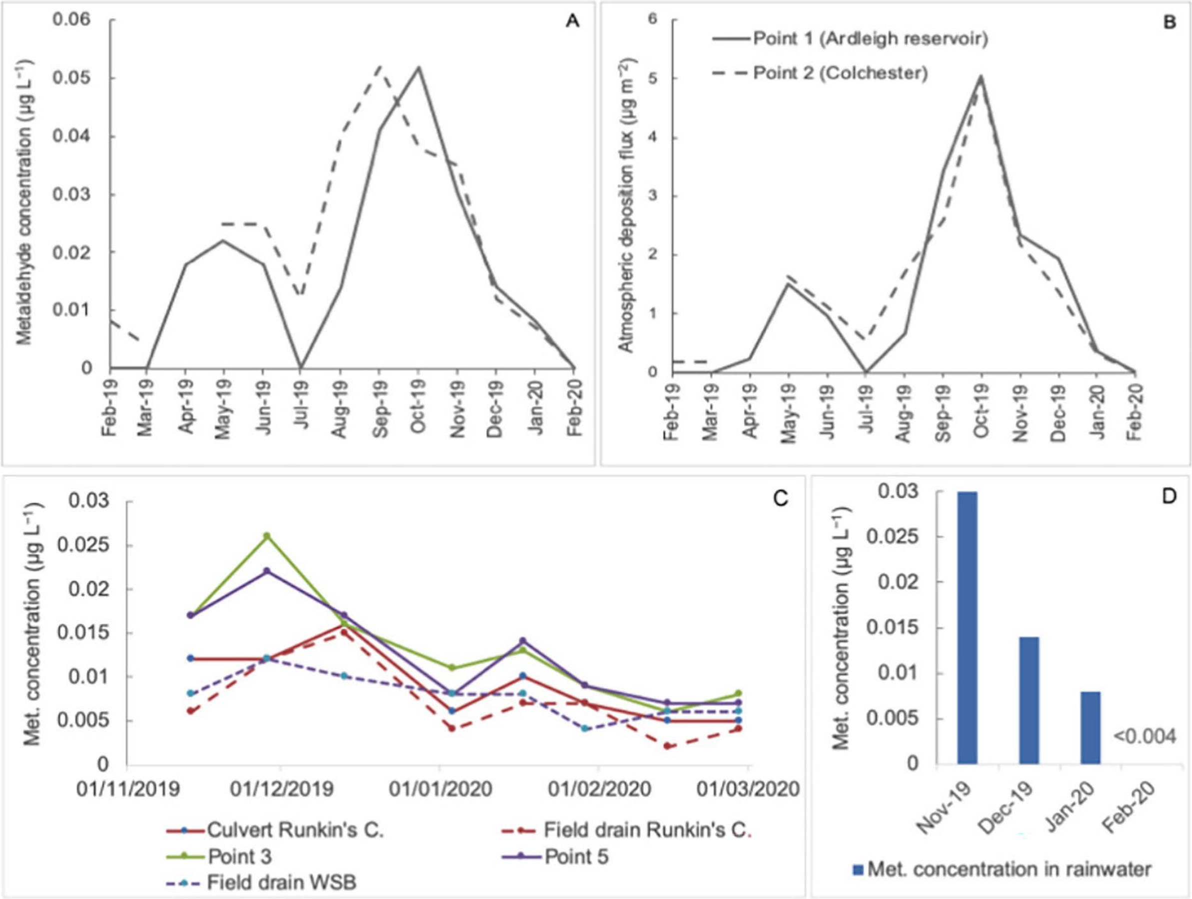

Fig. 4 **A** Monthly metaldehyde concentration (µg L^{-1}) in rainfall and (B) atmospheric deposition flux (µg m^{-2}) recorded during January 2019–February 2020 in the Ardleigh catchment. (C) Metaldehyde concentration (µg $L.^{-1}$) in surface water and field drain runoff in the Western Salary Brook (WSB) sub-catchment in the period November 2019–February 2020. **D** Metaldehyde concentration in rainwater collected at the rain gauge located near Ardleigh Reservoir during the period November 2019–February 2020

Salary Brooks in July 2019 (0.35 g, 4% of the cumulative flux), and maximum values were registered in December 2019 (7.25 g, 40% of the cumulative flux) (Fig. 5A, C). 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 (Fig. 5D, E), 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 (Fig. 5D, E), respectively. No atmospheric input of metaldehyde to the Ardleigh Reservoir and catchment occurred during the periods February–March 2019 and July 2019 (Fig. 5C).

The highest fluxes were measured in surface water abstracted and transferred from the River Colne (REG3). Values varied from 3.99 g in February 2019 to 15.5 g in October 2019. Minimum and maximum percentage 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

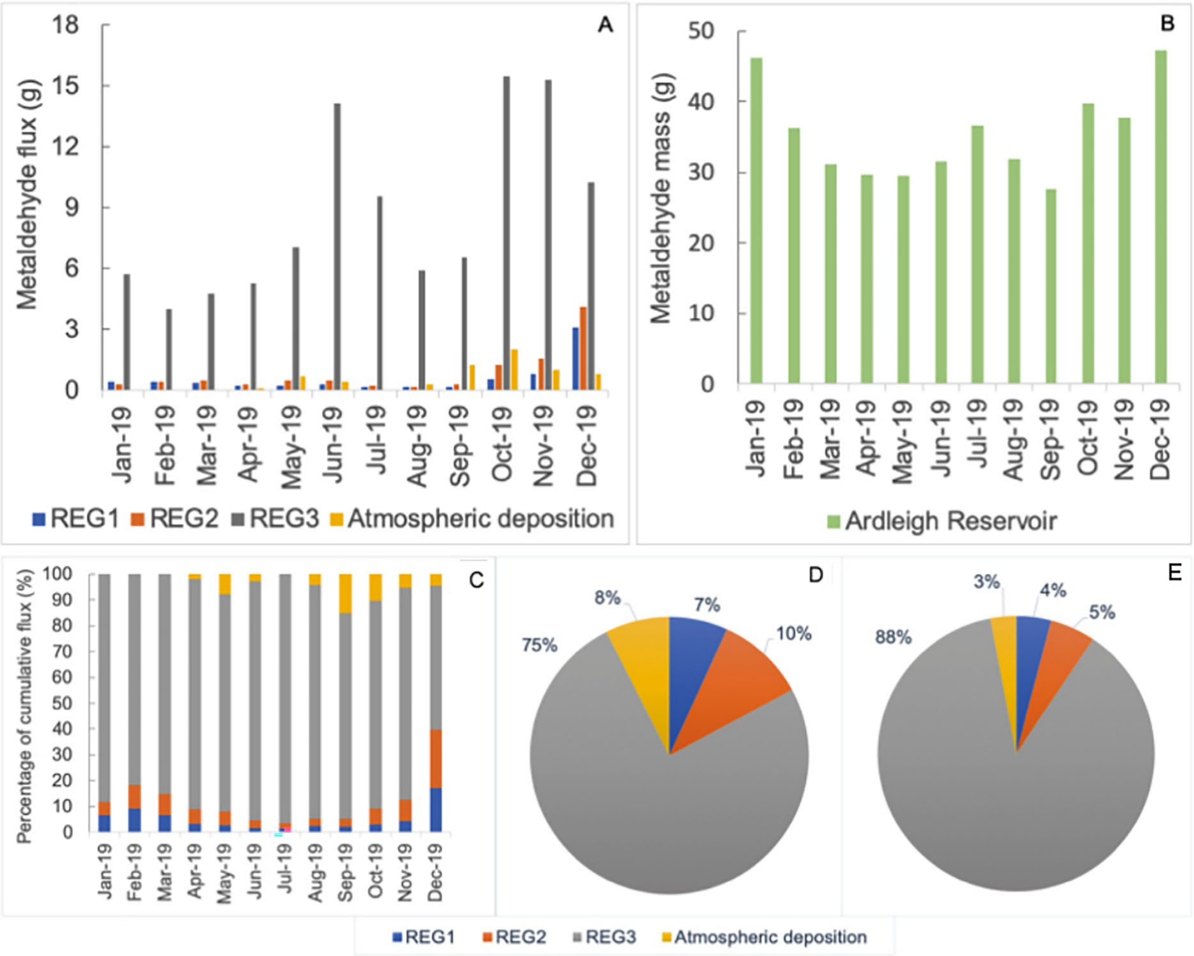

Fig. 5 **A** Monthly metaldehyde flux (g month^{-1}) recorded within the Ardleigh catchment stream network, abstraction point REG3 at the River Colne outlet, and atmospheric deposition of metaldehyde to the Ardleigh Reservoir. **B** Monthly mass content (g month.$^{-1}$) of metaldehyde retained within the Ardleigh Reservoir. **C** Individual loads of metaldehyde expressed as a percentage of monthly total/cumulative metaldehyde load to the Ardleigh Reservoir for the period January 2019–February 2020. **D** Metaldehyde flux from the individual sources expressed as a percentage of the total flux during the autumn–winter application period (August–December 2019) and **E** the spring–summer application period (February–June 2019)

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 (Figs. 5D, 5E), 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. In context it is noted that metaldehyde slug pellets typically contain between 3 and 1.5% of the active ingredient. Thus, the upper load value of 47.4 g can be reconciled with between 1.58 and 3.16 kg of bulk pellet application. Seasonal peaks were observed in January, July and December 2019 (Fig. 5B, Table 5). 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 (Fig. 5A, B).

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

Table 5 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

in the mass of metaldehyde occurred in October and December 2019 (12.2 and 9.64 g, respectively; Table 5). 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).

4 Discussion

4.1 Metaldehyde Transfer Within The Catchment: Source-Mobilisation-Pathway-Delivery Perspective

Overall, trends observed in respect of pathway-delivery mechanisms of metaldehyde transport within the catchment were similar to those observed within the adjacent River Colne catchment in previous years (Balashova et al., 2021). Metaldehyde transport patterns displayed seasonality, with peaks in the pesticide levels from all pathways observed to various extents during the March–June and September–December 2019 application periods. Although concentrations detected in the Northern and Western Salary Brooks remained under the EU 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 recorded at the individual sampling points was generated in the period August–December 2019 (Table 4). These periods coincided with typical metaldehyde application times in the spring/summer (February–June) and autumn/winter (August–December) months to protect winter cereal and oil seed rape crops, the predominant crops within the Ardleigh catchment. Trends in metaldehyde levels are highly comparable with those reported in previous studies (e.g. Castle et al., 2018; Kay & Grayson, 2014; Lu et al., 2017).

In addition to temporal trends in metaldehyde levels across the catchment, their 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 (Figs. 2, 3; Table 3). Significantly lower ($p < 0.05$) concentrations were recorded in the Northern Salary Brook compared to the Western Salary Brook and this is considered to be due to multiple factors, including the 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 creates 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 found in the lower part of the catchment (Fig. 1). 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 in the topsoil that leads to restricted rooting and associated loss of yield (Cranfield University, 2022a).

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, 2022b). These soils are 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 (Western Salary Brook sub-catchment), compared to the upper part (Fig. 6).

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

Peaks in metaldehyde levels in runoff during periods when tile drainage was active are 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 physicochemical 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, 2021; PPDB, 2021). 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 in soil (Balashova et al., 2020; Thomas et al., 2013). 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).

An increase in metaldehyde levels following wet weather conditions in June 2019 also suggests that metaldehyde is mobilised relatively rapidly in the environment. Maximum annual precipitation (27 mm day^{-1}) was observed on 10 June 2019, and a rise in concentration was observed at all regulatory

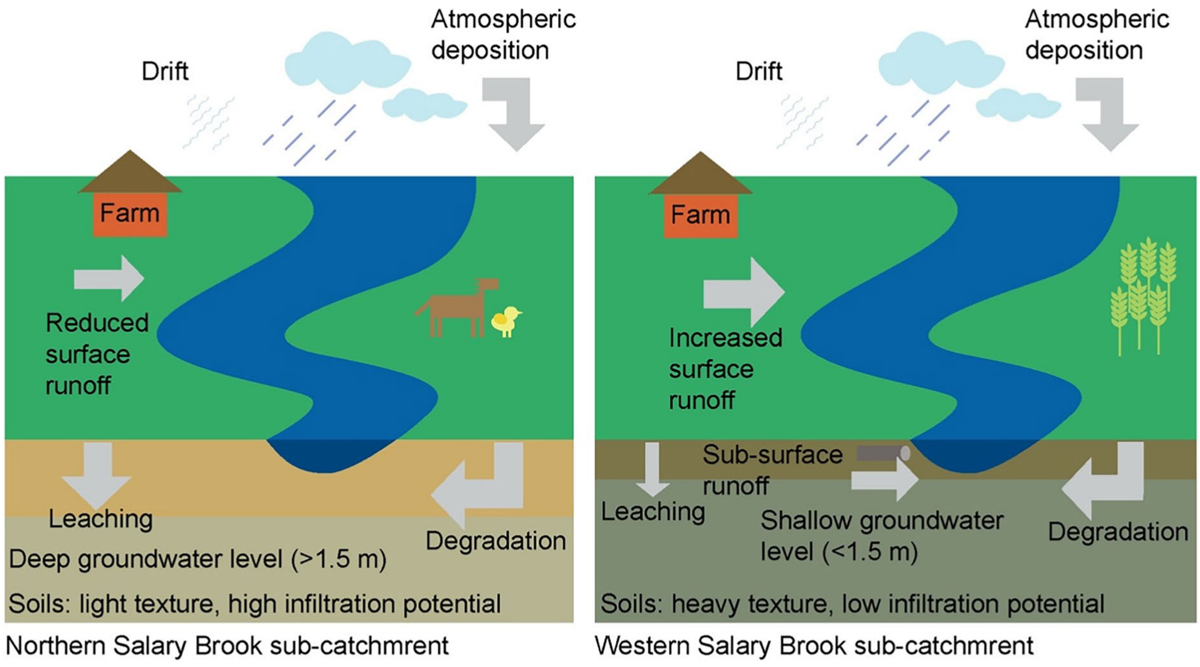

Fig. 6 Schematic representation of metaldehyde transfer in the Ardleigh catchment: the Northern Salary Brook and Western Salary Brook sub-catchments. The arrow size represents the scale of processes within the source-pathway-mobilisation-delivery continuum

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 at 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. In certain months (e.g. March, August 2019), metaldehyde levels detected in rainwater were up to 0.03 μg L^{-1}, these levels being higher than concentrations detected in the River Colne (REG3). This observation indicates that metaldehyde is susceptible to volatilisation and atmospheric transport at times in the year coincidental will metaldehyde applications. This time lag between rainwater and higher surface water metaldehyde concentrations could be due to several factors. For example, (i) amounts of applied metaldehyde are lower due to less "slug" 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 as 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. The high vapour pressure of metaldehyde drives its volatilisation and subsequent wet deposition, assisted by high aqueous solubility of the compound. Although no published peer-reviewed studies on atmospheric transport of metaldehyde are available to date, research on atmospheric transport and deposition of other agrochemicals demonstrates that a wide range of pesticides are subject to being transported at regional-/long-range scales. Elevated levels in rainwater are typically associated with seasonal application times (Asman et al., 2005; De Rossi et al., 2003; Huang et al., 2010; Kreuger et al., 2006; Unsworth et al., 1999; Vogel et al., 2008).

4.2 Mass Budget and Seasonal Dynamics of Metaldehyde in the Ardleigh Reservoir

Metaldehyde was present in the reservoir during all observation months in 2019 (Fig. 5B, Table 5). 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 (Fig. 5C–E). The mass outflow was larger than the total inflow of metaldehyde during the year except in June and the period October–December 2019 that coincide with the application seasons of the pesticide. Increases in mass were comparable with variations in the 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 (Fig. 5B, Table 5)).

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 only in the period May–July 2019. The following peaks were observed in October and December 2019, when metaldehyde loads from individual sources (Northern and Western Salary Brooks, the River Colne and atmospheric deposition) were at their highest levels (Fig. 5A, B). A delay of up to 2 months in peaks of metaldehyde mass in the reservoir could be due to mixing mechanisms and the residence time (the average residence time is 100 days; Table S1) 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 EU DWD standard and to 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 the Ardleigh Reservoir during periods when high concentrations of metaldehyde are detected in surface water at the East Mills abstraction point (REG3). Applying a catchment modelling approach to assess pesticide contaminant risk, 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.

Catchment characteristics such as soil type and land use are lesser 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 considerations as application technique and timing, application rates and type of product (Kay & Grayson, 2014). Farming interventions as well as application timing have a direct impact on pesticide loss to surface waters. Nature-based solutions on farmland, such as swales and buffer zones, help to reduce runoff, which in turn help to reduce the amount of pesticide loss from the terrestrial to the aquatic system (e.g. Simelton et al., 2021). Similarly, sustainable pesticide management practices have a 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 field 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). Farming communities should continue following these principles that are applied in the *Slug it Out* campaign (Anglian Water, 2020) to maintain the positive impacts of catchment sensitive farming on the aquatic environment.

Further, continuous regulatory monitoring of metaldehyde will enable researchers and other stakeholders to assess changes in metaldehyde loss to surface waters in the UK following the withdrawal of metaldehyde for use in March 2022. Such monitoring will allow an evaluation of the legacy effects and metaldehyde transport dynamics in the aquatic environment following cessation of the application of metaldehyde. Moreover, findings of this research can be extrapolated and incorporated into monitoring, catchment management and risk assessment practices with relation to this and other polar pesticides currently approved for use.

5 Conclusions

Spatial trends in metaldehyde concentrations and fluxes at a sub-catchment level are likely to be driven by a combination of factors: land use, soil type and topography. In this research, concentrations 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 more arable Western Salary Brook sub-catchment in the lower part of the Ardleigh catchment. Temporal patterns in metaldehyde concentrations were very similar to those reported by Balashova et al. (2021): peaks in metaldehyde concentrations (up to 0.48 μg L^{-1}) and increased fluxes at all monitoring points (monthly fluxes between 1 and 5 g) 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 μg 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 one to two 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), with an increase in mass during the typical application periods. Due to the limited degradation potential and high solubility of metaldehyde in water, its presence in the reservoir is likely to persist for less than a year following the withdrawal of metaldehyde for outdoor use in March 2022. Reduced levels of metaldehyde are likely to be seen in stream/river water following withdrawal i.e. when the input source is curtailed. In turn, the withdrawal of metaldehyde should 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 most prominent source of metaldehyde influx to the reservoir. With decreasing concentrations of metaldehyde in source waters that replenish the reservoir, a decrease in the metaldehyde load, via dilution, would be expected in subsequent years.

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Data Availability Data used in this research are available upon the request.

Declarations

Conflict of Interest The authors declare no competing interests.

References

Anglian Water. (2020). *Slug it out*. Retrieved on May 13, 2022 from https://www.anglianwater.co.uk/business/help-and-advice/working-with-farmers/slug-it-out/

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

Asman, W. A. T., Jørgensen, A., Bossi, R., Vejrup, K. V., Bügel Mogensen, B., & Glasius, M. (2005). Wet deposition of pesticides and nitrophenols at two sites in Denmark: Measurements and contribution from regional sources. *Chemosphere, 59*, 1023–1031.

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

Balashova, N., Hiscock, K. M., Reid, B. J., & Reynolds, R. (2021). Trends in metaldehyde concentrations and fluxes in a lowland, semi-agricultural catchment in the UK (2008–2018). *Science of the Total Environment, 795*, 148858.

Blessing, A. (Ed.). (1998). *Pesticides and water quality: Principles, policies, and programs.* Purdue University Cooperative Extension Service.

British Geological Survey (BGS). (2022). Geology map of Britain. Retrieved on January 20, 2022, from http://mapapps.bgs.ac.uk/geologyofbritain/home.html

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

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

Castle, G. D., Mills, G. A., Gravell, A., Leggatt, A., Stubbs, J., Davis, R., & Fones, G. R. (2019). Comparison of different monitoring methods for the measurement of metaldehyde in surface waters. *Environmental Monitoring and Assessment, 191*(75), 1–13.

Commission, E. (1998). Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. *Official Journal of the European Communities L, 330*, 32–54.

Cranfield Soil and Agrifood Institute Soilscapes (CSAI). (2022). National Soil map (1:250,000 scale), soil-survey data. Retrieved January 5, 2022, from http://www.landis.org.uk/soilscapes/

Cranfield University. (2022a). *The soils guide.* Retrieved on January 20, 2022a, from https://www.landis.org.uk/services/soilsguide/mapunit.cfm?mu=58205

Cranfield University. (2022b). *The soils guide.* Retrieved on January 20, 2022b, from http://www.landis.org.uk/services/soilsguide/mapunit.cfm?mu=57302

De Rossi, C., Bierl, R., & Riefstahl, J. (2003). Organic pollutants in precipitation: Monitoring of pesticides and polycyclic aromatic hydrocarbons in the region of Trier (Germany). *Physics and Chemistry of the Earth, 28*, 307–314.

Department for Environment, Food and Rural Affairs (DEFRA). (2020). *Outdoor use of metaldehyde to be banned to protect wildlife.* Retrieved on January 20, 2022, from https://www.gov.uk/government/news/outdoor-use-of-metaldehyde-to-be-banned-to-protect-wildlife

Digimap. (2021). [Map of the study area] (Roam, OS Open Map, Scale: 1:10,000). Retrieved on February 14, 2021, from http://digimap.edina.ac.uk

Environment Agency Catchment Data Explorer. (2018). Ardleigh Reservoir. Retrieved on March 8, 2018, from http://environment.data.gov.uk/catchment-planning/WaterBody/GB30539944

European Chemicals Agency (ECHA). (2012). *CLH report for metaldehyde*. Retrieved from https://echa.europa.eu/documents/10162/30efe717-a796-400d-b581-c2b7e197025f

Farmers Guide. (2016). *It's critical to take care using metaldehyde-based slug pellets*. Retrieved on December 4, 2021, from https://www.farmersguide.co.uk/its-critical-to-take-care-using-metaldehyde-based-slug-pellets/

Haygarth, P. M., Condron, L. M., Heathwaite, A. L., Turner, B. L., & Harris, G. P. (2005). The phosphorus transfer continuum: Linking source to impact with an interdisciplinary and multi-scaled approach. *Science of the Total Environment*, *344*(1–3 SPEC. ISS.), 5–14.

Huang, D.-Y., Peng, P., Xu, Y.-G., Sun, C.-X., Deng, H.-M., & Deng, Y.-Y. (2010). Distribution, regional sources and deposition fluxes of organochlorine pesticides in precipitation in Guangzhou, South China. *Atmospheric Research, 97*, 115–123.

Kamrin, M. (1997). *Pesticide profiles: Toxicity, environmental impact, and fate*. CRC Press LLC.

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

Kolkman, A., Vughs, D., Sjerps, R., Kooij, P. J. F., van der Kooi, M., Baken, K., Louisse, J., & de Voogt, P. (2021). Assessment of highly polar chemicals in Dutch and Flemish drinking water and its sources: Presence and potential risks. *ACS ES&T Water, 1*(4), 928–937.

Kreuger, J., Adielsson, S., & Kylin, H. (2006). *Monitoring of pesticides in atmospheric deposition in Sweden 2002–2005. 211* (Technical Report 103 to Swedish Environmental Protection Agency), Swedish University of Agricultural Sciences. Retrieved on July 4, 2021, from https://www.diva-portal.org/smash/get/diva2:716438/FULLTEXT01.pdf

Li, Q., Peng, Y., Wang, G., Wang, H., Xue, B., & Hu, X. (2019). A combined method for estimating continuous runoff by parameter transfer and drainage area ratio method in ungauged catchments. *Water (Switzerland), 11*(5).

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

MSG. (2019). *Enhanced stewardship.* Metaldehyde Stewardship Group. Retrieved on June 19, 2021, from https://www.getpelletwise.co.uk/enhanced-stewardship/

MSG. (2020). *MSG stewardship guidelines*. Metaldehyde Stewardship Group. Retrieved on June 19, 2021, from https://www.getpelletwise.co.uk/home/msg-guidelines/

Nineham, N., Elwell, F., Naicker, J., & Eyre, S. (2015). Catchment modelling of pesticide contamination risk in East Anglia, UK. Retrieved from https://www.iwra.org/member/index.php?page=286&abstract_id=2830

Met Office. (2022). Eastern England: climate. Retrieved January 10, 2022, from https://www.metoffice.gov.uk/climate/uk/regional-climates/ee#temperature

PAN (Pesticides Action Network). (2021). *Metaldehyde–Identification, toxicity, use, water pollution potential, ecological toxicity and regulatory information*. Retrieved on July 28, 2021, from https://www.pesticideinfo.org/chemical/PRI4057

PPDB. (2021). *Metaldehyde*. Pesticide Properties DataBase. Retrieved on July 28, 2021, from http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/446.htm

Rabiet, M., Margoum, C., Gouy, V., Carluer, N., & Coquery, M. (2010). Assessing pesticide concentrations and fluxes in the stream of a small vineyard catchment–Effect of sampling frequency. *Environmental Pollution, 158*, 737–748.

Redshaw, C. J., Mason, C. F., Hayes, C. R., & Roberts, R. D. (1988). Nutrient budget for a hypertrophic reservoir. *Water Research, 22*(4), 413–419. https://doi.org/10.1016/0043-1354(88)90035-8

Shu, C., & Ouarda, B. M. J. T. (2012). Improved methods for daily streamflow estimates at ungauged sites. *Water Resources Research, 48*, W02523. https://doi.org/10.1029/2011WR011501

Simelton, E., Carew-Reid, J., Coulier, M., Damen, B., Howell, J., Pottinger-Glass, C., Tran, H. V., & Van Der Meiren, M. (2021). NBS framework for agricultural landscapes. *Frontiers in Environmental Science, 9*(August), 1–16. https://doi.org/10.3389/fenvs.2021.678367

Thomas, J. C., Moir, J. W. B., Helgason, T., Sinclaire, C., & Thwaites, R. (2013). The biotic degradation of Metaldehyde. Food and Environment Research Agency (FERA), 10, York, UK.

UK Centre for Ecology and Hydrology (UKCEH), Rowland, C. S., Morton, R. D., Carrasco, L., McShane, G., O'Neil, A. W., & Wood, C. M. (2017). Land Cover Map 2015 (25 m raster, GB). NERC Environmental Information Data Centre.

United Kingdom Accreditation Service (UKAS). (2019). *Schedule of accreditation* (Issue No. 058), Staines-upon-Thames, UK.

Unsworth, J. B., Wauchope, R. D., Klein, A. W., Dorn, E., Zeeh, B., Yeh, S. M., Akerblom, M., & Racke, K. D. (1999). Significance of the long range transport. *Pure Applied and Chemistry, 71*(7), 1359–1383.

Vogel, J. R., Majewski, M. S., & Capel, P. D. (2008). Pesticides in rain in four agricultural watersheds in the United States. *Journal of Environmental Quality, 37*(3), 1101–1115. https://doi.org/10.2134/jeq2007.0079