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Modelling of metaldehyde concentrations in surface waters: A travel time based approach

A. Asfaw\textsuperscript{a,b,⁎}, K. Maher\textsuperscript{b}, J.D. Shucksmith\textsuperscript{a}

\textsuperscript{a} Department of Civil and Structural Engineering, Sheffield Water Centre, University of Sheffield, Sheffield S1 3JD, United Kingdom
\textsuperscript{b} Severn Trent Water Ltd., Severn Trent Centre, PO Box 5309, Coventry CV3 9FH, West Midlands, United Kingdom

\textbf{A R T I C L E  I N F O}

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\textbf{A B S T R A C T}

Diffuse agricultural pollution is widely recognized as a significant threat to the quality of water resources. Metaldehyde is a soluble synthetic aldehyde pesticide used globally in agriculture which has caused recent concern due to high observed levels (exceeding the European and UK standards for pesticides in drinking water value of 0.1 \text{\textmu}g/l) in surface waters utilized for potable water supply. This paper describes the development of a new travel time based physically distributed metaldehyde prediction model which aims to describe the short term fluctuations of metaldehyde concentrations in surface waters caused by rainfall runoff events. This will enable water infrastructure operators to consider informed control decisions in order to improve the quality of abstracted surface water. The methodology is developed and trailed within a case study catchment in the UK. The new approach integrates spatially and temporally disaggregated surface runoff generation, routing and build-up/wash-off concepts using a simple structure in a GIS environment to build a metaldehyde concentration prediction model. The use of 1 km\textsuperscript{2} resolution radar rainfall data and identification of high risk areas in the catchment provide an approach which considers the spatio-temporal variations of pollutant generation and transport in the catchment. The model is calibrated and validated using available catchment flow and new metaldehyde concentration dataset acquired using automatic samplers over four rainfall events. An average coefficient of determination and model efficiency of 0.75 and 0.46 respectively have been obtained for the rainfall events used to validate the model. This shows the capability of the model for the intended purpose of predicting the arrival of peak metaldehyde concentrations at surface water abstraction sites and informing abstraction decisions.

1. Introduction

Diffuse pollution is a significant threat to the quality of surface water systems, with agricultural runoff commonly recognised as posing the greatest risk (Grayson et al., 2008). Observed levels of diffuse agricultural pollutants in surface water have increased as pesticide application rates have intensified, detection methods have improved and new products emerge onto the market (Losacks et al., 2005). The characteristic behavior of some of these pollutants (e.g. pesticides such as metaldehyde) mean that existing drinking water treatment processes are inadequate to reduce levels to within drinking water regulation limits and thus have recently become a recognized problem to water infrastructure operators (Lu et al., 2017). D’Arcy et al. (1998) recommends that efforts to tackle diffuse pollution problems are best taken at catchment scale (as promoted by the Water Framework Directive) to help avoid the need for energy and cost intensive engineered treatment solutions. However, the complex nature of the processes involved in diffuse pollutant generation and transport in rainfall runoff, along with high temporal and spatial variations in pesticide application and rainfall/runoff events pose challenges for the development and establishment of accurate and reliable modelling and mitigation strategies (Ouyang et al., 2017). Current understanding of short term pollutant dynamics in catchments caused by rainfall/runoff processes is limited due to the scarce availability of water quality data at suitable temporal resolutions (Bach et al., 2001).

The aims of this work are to: 1. Develop a new model to describe the fluctuation of a diffuse agricultural pollutant (metaldehyde) in surface waters caused by rainfall driven runoff; 2. Validate the model against new high resolution datasets of metaldehyde concentration within the catchment following rainfall and surface runoff events. It is anticipated that the new model can be used to forecast metaldehyde concentrations in surface waters and inform short term water abstraction decisions such that high levels of metaldehyde can be avoided.

Metaldehyde is an organic compound with the formula (CH\textsubscript{2}CHO)\textsubscript{4}.

⁎ Corresponding author at: Department of Civil and Structural Engineering, Sheffield Water Centre, University of Sheffield, Sheffield S1 3JD, United Kingdom.
E-mail address: asafawi@sheffield.ac.uk (A. Asfaw).
and has low sorption coefficient of active ingredient to organic carbon ($K_{OC}$) value that ranges between 34 and 240 L kg$^{-1}$ (Kay and Grayson, 2014). It is a soluble molluscicide that is used heavily in a range of agricultural products to control slugs and snails (Li et al., 2010) and has a relatively long half-life in soil that ranges between 3.17 and 223 days. In recent years high levels of metaldehyde exceeding the European and UK standards for pesticides in drinking water value of 0.1 μg/L have been observed in surface waters during the application season (NFU, 2013). Peak concentrations in surface waters are observed particularly following rainfall events (Kay and Grayson, 2014). Water quality assessments carried out by the UK water industry on more than 2300 raw following rainfall events (Kay and Grayson, 2014). Metaldehyde is not effectively removed using conventional drinking water treatment options such as granular activated carbon and ozone due to its high inherent stability resulting from a unique molecular structure (Webber, 2014), and is hence a particular concern for water infrastructure operators.

Diffuse pollutants such as metaldehyde present on farmlands can enter river systems via a number of pathways including surface runo, drains and groundwater flow. The dominant pathway for any particular pollutant is mainly dependent on its properties, weather conditions, soil type, land slope and network of drains in the area (Bach et al., 2001). However a number of studies have showed that surface runo is the dominant pathway for most diffuse agricultural pollutants (Huber et al., 2000; Heathwaite et al., 2005; Huber et al., 1998; Bach et al., 2001). Migration of pollutants through erosion is considered significant only for highly adsorbing substances with $K_{OC}$ values greater than 1000 L kg$^{-1}$ (Kenaga, 1980). Hence metaldehyde tends not to be adsorbed by suspended solids and sediments due to its low $K_{OC}$ Value. This suggests that the transport of metaldehyde through surface runo in dissolved form is more significant than transport via soil erosion. Hence, the amount and rate of surface runo generated from specific farmlands in the catchment where metaldehyde is applied combined with surface runo travel time along flow paths are likely to be critically important in determining metaldehyde concentrations and dynamics in surface waters. Several studies have emphasized the significant impacts of rainfall induced surface runo in mobilizing pesticides into streams (e.g., Vryzas et al., 2009; Taghavi et al., 2011; Du Preez et al., 2005; Ng and Clegg, 1997). However, studies quantifying peak pollutant loads in surface runo and potential exposure to downstream receivers resulting from individual rainfall events are lacking due to the need for high resolution water quality datasets, which are rarely available. Most available water quality data are in daily or coarser time resolutions that fail to capture short term fluctuations in diffuse pollution concentrations caused by individual rainfall driven runoff events. Lack of high resolution validation data has also limited the development of stormwater quality models that are capable of predicting pollutant concentrations in surface runo at smaller time intervals, and hence be utilised in abstraction management systems. The use of automatic water samplers has been identified as a step forward towards addressing this problem (Berenzen et al., 2005; Rabiet et al., 2010).

In this study, automatic samplers were used to collect hourly surface water samples following rainfall events within a UK catchment known to be vulnerable to high metaldehyde concentrations. This enabled the validation of a new operationally suitable stormwater quality prediction model within the catchment. The new model aims to enable the prediction of short term fluctuations in metaldehyde concentrations arriving at a surface water abstraction site which is used for drinking water supply. Whilst a complete understanding of the transport and fate of pesticide in catchments requires consideration of numerous processes such as groundwater transport and reaction/degradation processes, the nature of the organic compound (metaldehyde) as well as the focus on forecasting short term fluctuations in response to rainfall events lead us to propose a modelling approach based on the aggregation of overland surface flow travel times over the catchment, allowing a simpler and more practical model structure than a model incorporating numerous longer term processes such as groundwater transport or erosion. The model is therefore based on the identification and routing of spatially distributed metaldehyde loads in surface runo using build-up, wash-off and surface runo travel time techniques. The approach proposed here provides an improvement to existing stormwater quality models by using high resolution radar rainfall data and identifying application risk areas in the catchment, which enables the consideration of spatio-temporal variations of pollutant generation and transport in the catchment. A raster based data structure is employed in the model and thus various spatially distributed catchment characteristics such as elevation, soil type, land use and rainfall are described in the model using grids. The use of the developed model in water supply catchments can help to quantify potential exposures to peak metaldehyde concentrations at surface water abstraction sites with the aim of enabling better surface water abstraction management. Given the inadequacy of existing water treatment processes in removing metaldehyde, smarter abstraction management informed by predicted arrival of peak pollutant levels at abstraction sites proposed in this study provides a cost-effective and sustainable solution to tackle problems caused by diffuse pollutants.

2. Methodology

This section describes the study catchment as well as the development of a new process based metaldehyde transport model to forecast short term fluxes of metaldehyde in surface waters in response to individual rainfall events. The catchment is divided into five square metre grid cells and surface runo generation, routing and pollutant wash-off is calculated within each cell in response to time series rainfall data collected using radar. The model is calibrated and validated using monitored flow data as well as new high resolution datasets of metaldehyde concentrations collected following rainfall events using automatic samplers.

2.1. Study area

The study area, River Leam catchment, is located in the sub basin of River Severn in central England and drains an area of 300 km$^2$ (Fig. 1). Elevation within the catchment ranges from 46 m to 232 m above sea level with mean annual rainfall of 649 mm. A UK Environment Agency flow gauging station is situated at the outlet of the catchment to monitor abstraction license restrictions. The normal flow depth of the River Leam at the gauging station ranges between 0.24 m and 1.16 m with an average flow of 1.55 m$^3$/s. The most dominant land cover type within the catchment is arable farmland consisting of horticultural plants and cereals. Managed grassland is the second most common land use type with few urban, suburban and rural developments in the catchment. Hence, agriculture is an important land use in the catchment and is likely to have a significant influence on river water quality. The predominant soil types in the catchment are clayey and loamy soils, which make up approximately 65.5% of the total area. Clay soils are vulnerable to compaction and they remain wet for longer periods and have slow natural drainage, leading to sheet runoff as opposed to channel erosion. The remainder of the catchment consists of freely draining slightly acid loamy soils or loamy and clayey soils which are not seasonally wet but suffer from impeded drainage.

The largest use of surface water in the catchment is for public water supply. A surface water abstraction site, located at the outlet of the study catchment, is used by a water utility operator to pump water to impounding reservoirs for water supply purposes (Fig. 1). The main water quality issues in the catchment are nutrients and pesticides from diffuse sources. Metaldehyde is typically applied in the catchment on arable farmlands that grow winter crops such as winter wheat, potatoes and oilseed rape, which usually cover about one third of the catchment
area rotated on a seasonal basis. Favorable conditions for slugs during the usually wet autumn and winter seasons mean that metaldehyde applications are typically made during September to December period. Routine monitoring conducted by the local water infrastructure operator shows that high levels of metaldehyde are present in the river during the application season (Fig. 2). The analyses in the current study focus on data collected in the catchment during the metaldehyde application season over the period of 2014–2017.

2.2. Development of metaldehyde prediction model

The model presented in this paper is comprised of three components: surface runoff generation, surface runoff routing and pollutant build-up/wash-off. Surface runoff is calculated based on overland flow generated from each 5 m² grid cell in the catchment during monitored rainfall events. The travel time based surface runoff routing method estimates storm runoff transport from catchment grid cells to the outlet of the catchment based on Geographic Information System (GIS) tools. The spatially distributed time variant direct runoff travel time technique employed in the model accounts for spatial and temporal variability of runoff generation and flow routing through overland flows and stream networks (Melesse and Graham, 2004; Du et al., 2009) following rainfall events at a 1 hr resolution. The pollutant model estimates metaldehyde build-up through pesticide applications on identified metaldehyde high risk areas and its wash-off to water courses during surface runoff processes. The travel time based surface runoff routing

![Fig. 1. River Leam catchment.](image1)

![Fig. 2. Historic seasonal variation of metaldehyde concentration in the River Leam near the catchment outlet from routine monitoring.](image2)
and build-up wash-off models are integrated to enable rainfall event based prediction of metaldehyde concentrations at the catchment outlet.

2.2.1. Runoff generation

The differential form of the Soil Conservation Service (SCS) curve number (CN) method (Mancini and Rosso, 1989) is used to compute spatially distributed excess rainfall in each grid cell within the study catchment. The SCS-CN surface runoff volume prediction method was originally developed by the United States Department of Agriculture (USDA) Soil Conservation Service (Hjelmfelt, 1991). Detailed procedures of the method were originally documented in the National Engineering Handbook, Sect. 4: Hydrology (NEH-4) in 1956 and subsequently revised in 1964, 1971, 1985, 1993 and 2004 (Li et al., 2015). It is a widely used, well established technique owing to its computational simplicity and use of accessible catchment data. The differential form of the SCS-CN method to calculate cumulative excess rainfall depth \( I_i \) (mm) at timestep \( t \) from each grid cell is given by:

\[
I_i = \frac{(B - 0.2S)^2}{(9.8 + 0.8S)} \quad \text{for } B > 0.2S 
\]

where \( B \) (mm) is the cumulative depth of rainfall at timestep \( t \), calculated as

\[
B = \sum_{i=1}^{t} \rho_i \Delta t \quad \text{(2)}
\]

where \( \rho_i \) is the rainfall intensity at the timestep \( i \) (mm/s), \( \Delta t \) is time step length (s), \( S \) is the maximum soil retention potential (mm), given by \( S = 25400/\text{CN} = 254 \). where CN is curve number ranging between 1 & 100.

When \( B \leq 0.2S \), rainfall is completely absorbed by soils with no overland flow generation and hence resulting in zero runoff depth. Initial CN values for each study year were first determined based on hydrologic soil group (HSG), land use and hydrologic conditions data (Mishra and Singh, 1999). In addition to the soil type, which mainly identifies the soil water retention capacity, antecedent moisture condition plays an important role in runoff generation (Crespo et al., 2011).

In the SCS-CN method, the effect of soil moisture on runoff generation is incorporated by adjusting CN values based on antecedent moisture condition (AMC) categories. No exclusive relations or formulas are available to calculate soil moisture from antecedent rainfall of certain preceding days, but in general the term antecedent for soil moisture calculation purpose is taken to vary from preceding 5–30 days (USDA, 1986). AMC categories in this study were determined for each rainfall event based on cumulative rainfall volumes of the preceding 5 days. The three AMC categories are: AMC-I for dry, AMC-II for normal, and AMC-III for wet conditions. Initially assigned CN values are adjusted for each rainfall event based on their AMC categories to account for the effect of soil moisture on runoff generation. Fig. 3 shows CN values based on normal antecedent moisture condition (AMC – II) for the 2014 application season. The spatially distributed CN values combined with the use of radar rainfall data (see section 2.3.2) enable the computation of spatially distributed runoff depths.

The surface runoff rate \( Q_i \) (mm/s) from each grid cell at time step \( t \) can be calculated using

\[
Q_i = \frac{(I_i - I_{i-1})}{\Delta t} 
\]

2.2.2. Runoff routing

In natural conditions, over land and channel travel times vary based on availability of runoff and rainfall variation in time. This is accounted in the model by employing a time variant travel time computation technique. To determine flow pathways, a GIS flow direction tool was used to determine the steepest descent from every cell in the catchment Digital Elevation Model (DEM). This created unique connections between cells that defined flow paths to the catchment outlet and identified storm runoff flow networks in the catchment. A threshold number was set to identify cells with high flow contributing areas that form concentrated flow and these were used to delineate channel networks in the catchment (Du et al., 2009). The delineated channel network density and extents were compared with stream networks from topographic maps to adjust threshold number of cells. Any cell with less upstream flow contributing cells than the threshold was considered as overland flow cell and others with more flow contributing upstream cells were classified as channel cells. Travel time computation techniques were then employed to determine travel time for each overland and channel flow cells based on available runoff in the cells and other hydraulic parameters.

Cumulative travel times through each pathway computed from topographic data were used to route excess rainfall from each grid cell along flow paths to determine surface runoff hydrographs at the outlet of the catchment. First, kinematic wave theories suggested by Wong (1995, 2003) were used to derive travel time expressions for each grid cell depending on its classification i.e. overland flow cell or channel cell. For an overland flow grid cell with negligible flow backwater effect, the wave celerity (c) travelling down the grid cell was derived using kinematic wave equation given by Eagleson (1970):

\[
c = \frac{dx}{dt} = \alpha \beta \gamma^{\beta-1} \quad \text{(4)}
\]

where, \( \alpha \) and \( \beta \) are parameters used in \( q = \alpha y^\beta \) to relate discharge per unit width (q) to flow depth (y) and (x) is distance along the direction of flow.

Re-writing Eq. (4) in terms of discharge per unit width (q) gives

\[
c = \frac{dx}{dt} = \alpha^{1/\beta} y^{(1-1/\beta)} \quad \text{(5)}
\]

For small period of time, it can be assumed that overland grid cells receive constant and uniform excess rainfall intensity, \( \dot{r} \) and constant upstream inflow, \( q_u \). Thus, the unit discharge at the downstream end of the grid cell over that period can be calculated as

\[
q = q_u + \dot{r} \quad \text{(6)}
\]

Assuming \( \alpha \) is independent of \( x \), substituting Eq. (6) in Eq. (5) and solving the derivatives in Eq. (5) for \( t \) gives an expression for time of concentration for overland grid cells as:

\[
t_c = \frac{1}{\alpha^{1/\beta} \left[ (q_u + \dot{r})L^{1/\beta} - q_u^{1/\beta} \right] \left[ (\lambda + 1)^{1/\beta} \right]} \quad \text{(7)}
\]

where \( t_c \) the time of concentration and \( L \) is the length of the grid cell in the direction of flow. In general, overland flow concentration time for small grid cell areas such as used in this study are shorter than duration of excess rainfalls and Eq. (7) can thus be used to calculate travel time.

The time of concentration formula can be written as:

\[
t_c = \left[ \frac{\dot{r}^\beta - \alpha}{\lambda} \right] \left( \lambda + 1 \right)^{1/\beta} \quad \text{(8)}
\]

where \( \lambda \) relates upstream inflow and influx from excess rainfall as follows:

\[
\lambda = q_u/L \quad \text{(9)}
\]

Values of friction parameters \( \alpha \) and \( \beta \) can be obtained using Manning’s equation as \( \alpha = \sqrt{S/n} \) and \( \beta = 5/3 \) respectively. Thus, the expression for overland flow time of concentration from Eq. (8) can be written as:

\[
t_c = \left( \frac{mL}{S^{0.5}} \right)^{0.6} i^{-0.4} \left[ (\lambda + 1)^{0.6} - \lambda^{0.6} \right] \quad \text{(10)}
\]

where, the units of parameters in Eqs. (9) and (10) above are given as minutes for \( t_c \), m/m for \( S \), m³/s for \( q_u \), mm/h for \( i \), and m for \( L \).
Manning’s $n$ values vary depending on the types of surface and can be selected from values recommended by Engman (1986).

The equivalent of Eq. (8) for channel flow grid cells with negligible backwater effect, a constant upstream inflow, and a uniform lateral inflow is given as

$$t_c = \left( \frac{L_c}{\alpha_c q_L^{1/3}} \right)^{1/\beta_c} \left[ (\lambda_c + 1)^{1/\beta_c} - \lambda_c^{1/\beta_c} \right]$$

(11)

where $t_c$ is time of concentration, $L_c$ is the length of the channel cell in flow direction, $q_L$ is the uniform lateral inflow, $\alpha_c$ and $\beta_c$ are parameters relating the discharge ($Q$) in the channel to the flow area ($A$); and $\lambda_c$ relates the upstream inflow ($Q_u$) to the lateral inflow ($q_L$) as follows:

$$Q = \alpha_c A_c^\beta_c$$

(12)

$$\lambda_c = \frac{Q_u}{q_L L_c}$$

(13)

Replacing $\alpha_c = \sqrt{S/n}$ and $\beta_c = 5/3$ friction parameter values determined from Manning’s equation and uniform lateral inflow ($q_L = q_L$) in Eq. (11) above gives the channel flow time of concentration as:

$$t_c = 7K_c \left( \frac{nL_c}{S^{0.5}} \right)^{0.6} \left[ (\lambda + 1)^{0.6} - \lambda^{0.6} \right]$$

(15)

$$t_u = 7K_c \left( \frac{nL_c}{S^{0.5}} \right)^{0.6} \left[ (\lambda + 1)^{0.6} - \lambda^{0.6} \right]$$

(16)

The value of $K_c$ and $K_u$ parameters are determined by calibration. Finally, travel times calculated for each grid cells using Eqs. (15) and (16) above are summed along flow paths at each model timestep to determine cumulative travel time of surface runoff from each grid cell to the catchment outlet.

### 2.2.3. Pollutant model

The pollutant model estimates metaldehyde build-up on high risk areas during dry days and wash-off to water courses during surface runoff following rainfall events. Metaldehyde risk areas in the catchment have been identified based on available land use data, which provides information on the likelihood of metaldehyde being applied to the land based on crop type during each growing season. Land growing winter crops such as winter wheat, potatoes and oilseed rape, where metaldehyde is commonly applied are identified as high risk areas. Data on land use derived from satellite imagery was acquired from the Centre for Ecology and Hydrology for each growing season used in the analysis (2014–2017). Fig. 4 shows the identified high risk areas for the...
Metaldehyde application doses on these high risk areas and frequency of applications over pesticide application periods determine the accumulation of metaldehyde in the active zone at soil surfaces (Müller et al., 2003). Moreover, the time interval between metaldehyde application and a rainfall event directly affects the amount of metaldehyde transported to water bodies through surface runoff. These processes are represented using build-up and wash-off components in the model.

Pollutant build-up: Metaldehyde build-up on high risk areas occurs through application of pesticides that contain metaldehyde as an active ingredient. Wet conditions during winter provide an ideal environment for slugs to thrive and most metaldehyde applications are made during this period to protect winter crops. Typical single slug pellet application based on guidelines from manufacturers is 5 kg/ha. This is equivalent to 75 g/ hectare (0.19 g per 5 m\(^2\) grid size used in this study) of metaldehyde based on a commonly used 1.5% slug pellet. The statutory legal requirement in the UK on metaldehyde application states that total application in a calendar year should not exceed a maximum of 700 g/ha. Routine monitoring data collected by the local water infrastructure operator shows that almost all high levels of metaldehyde in the river have occurred during the September to December application season (Fig. 2). Thus, it can be assumed that most of the 700 g/ha statutory annual legal limit of metaldehyde is applied during the September to December application period. Based on this assumption and the typical single metaldehyde application value of 75 g/ha, a total of not more than nine applications are expected during the winter crop growing season on any particular high risk farmland. This combined with the relatively long half-life of metaldehyde in soil suggest that metaldehyde presence on farmlands during this period is likely to be consistently high (Castle et al. 2017). In this study, it was initially assumed that metaldehyde was applied on all high risk areas 5 days before rainfall events, which was later adjusted using a calibration parameter.

Pollutant wash-off: Metaldehyde wash-off is dependent on a number of rainfall, catchment and substance characteristics. In this study, pesticide loss equation based on the “simplified formula for indirect loadings caused by runoff” (SFIL) (Berenzen et al. 2005; Reus et al. 1999) is used to calculate percentage loss of metaldehyde at each timestep from high risk areas through runoff.

\[
L_t = \frac{Q_t f c e^{-K_d \frac{\ln l}{100}}}{1 + K_d} \tag{17}
\]

where: 
- \(L_t\) – Percentage of application dose that is washed by runoff water as a dissolved substance at timestep \(t\), 
- \(Q_t\) – Runoff depth generated at timestep \(t\) (mm), 
- \(R\) – Total precipitation depth (mm), 
- \(f\) – Correction factor, with \(f = f_1 f_2 f_3\), 
- \(f_1\) – Slope factor: \(f_1 = 0.02153 \times \text{slope} + 0.001423 \times \text{slope}^2\) if slope < 20\% or \(f_1 = 1\) if slope > 20\%, 
- \(f_2\) – Plant interception factor: \(f_2 = P I/100\), 
- \(f_3\) – Buffer zone

Fig. 4. Identified Metaldehyde high risk areas in the catchment for the year 2014.
factor: $f_i = 0.83W$ with $W$ – width of the buffer zone (m), $t_0$ – Number of days between application and a rainfall event, $D_{\text{fl}}$ – Half-life of active ingredient in soil (days), $K_d$ – Ratio of dissolved to sorbed pesticide concentrations; with $K_{oc} = K_{oc}\%\text{SOC}^1/100$, $K_{oc}$ – Sorption coefficient of active ingredient to organic carbon, $\%\text{SOC}$ – Mass fraction of soil organic carbon content in percent. Runoff rate ($Q_r$) at each model timestep and total precipitation depth ($P_i$) for each high risk cell are obtained from Eqs. (2) and (3) and from rainfall data. The use of parameter $K_{oc}$ in equation (17) above has some limitations as it generally refers to sorption coefficient into soil organic matrix and doesn’t take into account adsorptions to clay particles, which is present in the study area. However, metaldehydes’ low $K_{oc}$ value and solubility mean that this limitation is likely to have an insignificant impact on model outputs as peak metaldehyde concentrations are likely to be mainly due to metaldehyde transport in dissolved form.

The amount of metaldehyde available at soil surfaces during a rainfall event, which is determined by applications and the number of days between applications and a rainfall event, has significant impact on the overall wash-off load that dissolves in surface runoff. However, lack of data on the specific timing of metaldehyde application makes this difficult to determine. Consequently, build-up and wash-off rate parameters are difficult to be inferred from direct measurements in the catchment and are known to commonly introduce uncertainties in pollutant prediction models (Wijesiri et al., 2016). To account for these uncertainties in the estimation of metaldehyde build-up and wash-off, an additional parameter ($K_o$), which depends on initial metaldehyde concentrations $C_i$ in the river at the outlet of the catchment prior to rainfall events, was used in the model. The metaldehyde concentration trend in the river prior to a rainfall event provides a general indication of the level of metaldehyde application in the catchment during a particular pesticide application period (Ryberg and Gillingham 2015). Consequently, it is therefore used in this study to adjust computations of metaldehyde load in surface runoff based on measured metaldehyde presence in the catchment.

Hence, metaldehyde load in surface runoff from each high risk cell at each timestep is determined by

$$M_t = KL_iB$$

(18)

Where: $M_t$ – metaldehyde load in surface runoff at timestep $t$, $K = C_i*K_o$, $C_i$ is metaldehyde concentration in the river prior to each rainfall event ($\mu g/l$), $K_o$ is a calibration parameter ($\mu g$), $B$ – metaldehyde build-up on soil surface through applications (taken as 0.19 g per 5 square meter based on typical application of 5 kg/ha using 1.5% slug pellet).

2.2.4. Model integration

For a given rainfall event over the catchment, rate of surface runoff generation and travel times are computed using Eqs. (3), (15) and (16) (Sections 2.2.1 and 2.2.2) at each model timestep. The calculated travel time from each high risk cell is then used to route metaldehyde load to the outlet of the catchment. Time series of surface runoff and metaldehyde load in surface runoff can then be used to determine metaldehyde concentrations in runoff water arriving at the outlet of the catchment. Metaldehyde transport in ground water is not included in the modelling structure and thus, a measured metaldehyde concentration in the river prior to a rainfall event is used to indicate base flow concentration. Metaldehyde concentrations in base flow are measured at the storm runoff period is assumed to be constant whereas a constant slope method is used to increase the amount of base flow ($Q_b$) over the runoff period (Blume et al., 2007). These are then combined with time series of simulated concentrations in runoff and quantity of runoff water to determine total metaldehyde concentrations in the river. Accurate estimation of the arrival time of peak metaldehyde concentration at the abstraction site is important in terms of enabling smarter surface water abstraction management to avoid peak metaldehyde concentrations. Thus, time to peak ($\Delta T$), prediction error of peak flow ($\Delta PF$) and concentration ($\Delta PC$) are used to evaluate the model performance along with other commonly used criteria as shown in Section 3.1 and 3.2.

Farmland in the study catchment that have high likelihood of metaldehyde being applied (metaldehyde high risk areas) are spread-out in the catchment with some parts of the catchment containing more high risk areas than others. The metaldehyde concentration at the catchment outlet over a specific period is heavily dependent on the density of high risk areas within the relevant travel time isochrones. Fig. 5 shows surface runoff travel time from 2015 high risk areas computed based on a constant and uniform rainfall intensity of 1 mm/hr applied for 1 h over the whole catchment. The sum of histograms in Fig. 5 is found to be 74.7 km$^2$, which is in good agreement with the sum of the total high risk areas in the catchment (74.5 km$^2$). High rates of runoff generation from high risk areas increases metaldehyde levels in the river, whereas high rate of runoff generation from low risk areas have a dilution effect and can lower concentration of metaldehyde in the river. Thus, metaldehyde concentration at the outlet of the catchment significantly depends on spatial variability of a rainfall event in relation to the distribution of high risk areas.
2.3. Model input, calibration and verification data

2.3.1. Land use, soil type and DEM

Land use, soil type and DEM of the catchment were pre-processed to derive various spatial input datasets to the model. Direct model inputs derived from these data are land slope, flow direction, flow accumulation, length of flow pathways, Manning’s coefficients (n), curve numbers (CN) and high risk areas. A vector layer of land use, which was derived from satellite imagery, was obtained from the Centre for Ecology and Hydrology, UK for each study year. The land use map classifies crop types and grassland at field level and was used to assign metaldehyde high risk areas (Section 2.2.3) as well as Manning’s roughness coefficient (n) values for each grid cell based on values published in the literature (Montes 1998; Brater and King 1976). Manning’s roughness values assigned for overland surfaces varied between 0.06 and 0.15 whereas roughness values assigned for channel surfaces (based on the nature of the channels) varied between 0.035 and 0.04. The spatially distributed Manning’s coefficient values and high risk areas were changed for each study year based on changes in land use in the catchment. The soil map for the study catchment was obtained from the UK National Soil Resources Institute (NSRI) database (NSRI, 2009) for the calculation of curve numbers (see Section 2.2.1). Soils in the catchment were categorized into four hydrologic soil groups (A–D) based on the soil’s runoff generating potential (USDA, 1986). Hydrologic soil group A generally has the lowest runoff potential and group D has the highest potential. Hydrologic parameters for the calculation of runoff such as slope, flow direction, flow accumulation, drainage basin and stream network delineation were derived in ArcGIS using OS Terrain 5 digital elevation model, which was obtained from Ordnance Survey, UK.

2.3.2. Rainfall

Radar rainfall data was acquired from the UK met-office’s NIMROD system with spatial and temporal resolution of 1 km2 and 5 min respectively (Met Office 2003). The radar rainfall data was resampled to a 5 m2 grid and aggregated to one hour resolution to match with the model grid and time resolution. This was used as input data for the calculation of runoff generation and pollutant wash-off (see Sections 2.2.1 and 2.2.3). Initially four rainfall events in the catchment were selected to calibrate and validate the travel time based surface runoff model developed in this study. Summary statistics and temporally averaged spatial variation of each rainfall event are provided in Table 1 and Fig. 6 below. The temporal variations of each rainfall event are presented in Fig. 8. Significant rainfall events with a range of rainfall intensity and durations were selected to represent rainfall conditions that are likely to cause metaldehyde spikes at the outlet of the catchment. Historical radar rainfall data was used to compute antecedent soil moisture conditions for each grid cell and this were used to adjust grid cell curve number values. Following the validation of the runoff model, radar rainfall data observed during the four metaldehyde data collection events were used to drive the metaldehyde prediction model simulations. Summary statistics and temporally averaged spatial variation of each rainfall event used for calibration and validation of the metaldehyde prediction model are provided in Table 2 and Fig. 7 below. The temporal variations of each rainfall event are presented in Fig. 9.

2.3.3. Flow

Historical hourly flow data from a flow gauging station situated at the outlet of the catchment was obtained from the UK Environment Agency. The flow hydrographs for each rainfall event were separated into base flow and direct runoff using straight line method (Reddy, 2006). A straight line is drawn from the point where the sharp rise in hydrograph occurs to the end of recession limb, which is used to separate the hydrograph into two distinct components: a fast intermittent runoff response and a slow continuous base flow response of the catchment. The fast response runoff hydrographs resulting from the selected rainfall events (Table 1) were used to calibrate and validate the surface runoff model.

2.3.4. Water sampling and metaldehyde data

Water samples were collected from river Leam using auto-samplers installed at surface water abstraction site used for drinking water supply. The use of auto-samplers enabled the continuous collection of hourly water samples during storm runoff events, which successfully captured the short term fluctuations of metaldehyde concentrations at the abstraction site. The auto-samplers were manually triggered before the arrival of forecasted rainfall events, which were judged likely to cause metaldehyde peaks due to surface runoff. For each event sampling was carried out for a period of 3–5 days, which enabled the acquisition of water samples during the full surface runoff period following the rainfall events. The data collection campaign was carried out over a period of three metaldehyde application seasons between September 2014 and February 2017. Collected water samples were analysed in laboratory to determine metaldehyde concentrations. Details on the metaldehyde detection method used are provided by Li et al. (2010).

3. Results and discussion

This section presents the calibration and verification results of surface runoff and metaldehyde concentration prediction models for the rainfall events presented in Tables 1 and 2. Comparison of simulated model results with measured flow data at the catchment outlet and metaldehyde concentration data from four water quality sampling events are discussed using various error statistics.

3.1. Surface runoff model

The performance of metaldehyde prediction model is dependent on surface runoff travel times from high risk areas to the outlet of the catchment. Thus, the surface runoff model, which consists of surface runoff generation and runoff routing components, needs to be calibrated and validated before it is integrated to the pollutant build-up/wash-off model. Flow data recorded by a gauging station located at the outlet of the catchment is acquired from Environment Agency and is used to calibrate and validate the travel time computation technique used in the surface runoff model. Runoff generation and transport from the entire catchment is considered for the calibration and verification of the surface runoff computation approach. Observed flow data from rainfall event A1 was used to calibrate parameters Ks and Kf (Eqs. (15) and (16)), used in the computation of travel times in over land and channel flow cells respectively. Simulation of the runoff prediction model was carried out using eleven different combinations of $K_s$ and $K_f$.

Table 1

Summary statistics of rainfall events used for surface runoff model calibration and validation.

<table>
<thead>
<tr>
<th>Rainfall event No.</th>
<th>Rainfall event Date</th>
<th>Duration (hr)</th>
<th>Temporal and spatial average rainfall intensity (mm/hr)</th>
<th>Temporal and spatial peak rainfall intensity (mm/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>October 28, 2013</td>
<td>21</td>
<td>1.1</td>
<td>4.5</td>
</tr>
<tr>
<td>A2</td>
<td>November 3, 2012</td>
<td>30</td>
<td>0.6</td>
<td>4.3</td>
</tr>
<tr>
<td>A3</td>
<td>September 24, 2012</td>
<td>10</td>
<td>1.5</td>
<td>5.4</td>
</tr>
<tr>
<td>A4</td>
<td>November 22, 2014</td>
<td>23</td>
<td>0.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Fig. 6. Spatial distribution of temporally averaged rainfall for the rainfall events used in surface runoff model calibration and validation.

Table 2
Summary statistics of rainfall events used for metaldehyde model calibration and validation.

<table>
<thead>
<tr>
<th>Event No.</th>
<th>Event Start Date</th>
<th>Duration (hr)</th>
<th>Temporal and spatial average rainfall intensity (mm/hr)</th>
<th>Temporal and spatial peak rainfall intensity (mm/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>October 8–9, 2014</td>
<td>34</td>
<td>0.2</td>
<td>2.21</td>
</tr>
<tr>
<td>B2</td>
<td>December 12–13, 2015</td>
<td>35</td>
<td>0.38</td>
<td>1.21</td>
</tr>
<tr>
<td>B3</td>
<td>February 6, 2017</td>
<td>9</td>
<td>0.81</td>
<td>1.73</td>
</tr>
<tr>
<td>B4</td>
<td>November 21–22, 2016</td>
<td>35</td>
<td>0.55</td>
<td>3.3</td>
</tr>
</tbody>
</table>
values (Table 3). The performance of the surface runoff model was evaluated using the prediction error of peak flow rate ($\Delta PF$), prediction error of time to peak ($\Delta T$) and volume conservation index (VCI), which was calculated using equation (19). In addition, the overall model prediction efficiency over the entire hydrograph was evaluated using model efficiency coefficient ($E$) as shown in Eq. (20).

$$VCI = \frac{\sum_{t=1}^{T} Q_{m}^t / \sum_{t=1}^{T} Q_{o}^t}{\sum_{t} \frac{(Q_{m}^t - Q_{o}^t)}{(Q_{o}^t)}}$$  \hspace{1cm} (19)

$$E = \frac{\sum_{t=1}^{T} (Q_{m}^t - Q_{o}^t)^2}{\sum_{t=1}^{T} (Q_{o}^t - \bar{Q}_{o})^2}$$  \hspace{1cm} (20)

where $Q_{m}^t$ is predicted flow at discrete times $t$ (m$^3$/s), $Q_{o}^t$ is observed flow at discrete times $t$ (m$^3$/s) and $\bar{Q}_{o}$ is mean of observed flow values over the entire period (m$^3$/s).

The runoff model prediction results and error statistics for rainfall event A1, which was used for model calibration, are summarized in Table 3. The volume conservation index (VCI) for rainfall event A1 is
found to be 0.87. The results indicated that $K_c = 1$ and $K_o = 0.8$ provide the optimum solution considering all the four evaluation criteria. The calibrated parameter value of $K_c = 1$ shows that the Manning’s roughness coefficient values assigned to channels based on values from literature and other parameters used to compute channel travel time required no adjustment. Overall, the calibration results showed that model performance in predicting surface runoff is more sensitive to the computation of channel travel time than overland travel time.

These calibrated parameter values were used to make surface runoff model simulations for the three remaining rainfall events. Table 4 summarizes the results of model simulation and error statistics for the three rainfall events used for surface runoff model validation. It was observed that model simulations of all three rainfall events have efficiencies greater than 0.80 and prediction error of peak flow rate less than 10%. In addition, volume conservation index of more than 80% and time to peak error of less than 6 h have been observed for all rainfall events. With an average efficiency of 0.87 for the rainfall events used for validation, the overall performance of the calibrated travel time based surface runoff model can be considered reasonable. The surface runoff model performed better for rainfall events with higher AMC as compared to rainfall events with low AMC. Comparison of observed and simulated surface runoff hydrographs for all four rainfall events are shown in Fig. 8. Fig. 8 also shows the spatially averaged rainfall over the catchment. In general, the levels of error statistics observed are practically acceptable and predicted surface runoff hydrographs agree well with the simulated hydrographs. Consequently, the calibrated travel time approach can be used for estimation of metaldehyde transport from high risk areas in the catchment.

Table 3
Error statistics for rainfall event A1 with different values of $K_c$ and $K_o$.

<table>
<thead>
<tr>
<th>$K_c$</th>
<th>$K_o$</th>
<th>$\DeltaPF$ (m$^3$/s)</th>
<th>$\DeltaT$ (h)</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0.8</td>
<td>1.16</td>
<td>-7</td>
<td>0.67</td>
</tr>
<tr>
<td>0.9</td>
<td>0.8</td>
<td>1.07</td>
<td>-3</td>
<td>0.86</td>
</tr>
<tr>
<td>1</td>
<td>0.8</td>
<td>0.98</td>
<td>1</td>
<td>0.85</td>
</tr>
<tr>
<td>1.1</td>
<td>0.8</td>
<td>0.91</td>
<td>4</td>
<td>0.69</td>
</tr>
<tr>
<td>1.2</td>
<td>0.8</td>
<td>0.85</td>
<td>8</td>
<td>0.47</td>
</tr>
<tr>
<td>0.8</td>
<td>1</td>
<td>1.14</td>
<td>-6</td>
<td>0.72</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.96</td>
<td>1</td>
<td>0.83</td>
</tr>
<tr>
<td>1.2</td>
<td>1</td>
<td>0.83</td>
<td>8</td>
<td>0.43</td>
</tr>
<tr>
<td>0.8</td>
<td>1.2</td>
<td>1.11</td>
<td>-6</td>
<td>0.77</td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
<td>0.94</td>
<td>1</td>
<td>0.82</td>
</tr>
<tr>
<td>1.2</td>
<td>1.2</td>
<td>0.82</td>
<td>8</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Table 4
Surface runoff model simulation results for flow validation events.

<table>
<thead>
<tr>
<th>Rainfall event No.</th>
<th>VCI</th>
<th>Peak flow (m$^3$/s)</th>
<th>$\DeltaPF$ (m$^3$/s)</th>
<th>Time to peak (h)</th>
<th>$\DeltaT$ (h)</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>0.98</td>
<td>24.5</td>
<td>-2.07</td>
<td>45</td>
<td>5</td>
<td>0.91</td>
</tr>
<tr>
<td>A3</td>
<td>0.99</td>
<td>8.0</td>
<td>-0.15</td>
<td>38</td>
<td>4</td>
<td>0.83</td>
</tr>
<tr>
<td>A4</td>
<td>0.82</td>
<td>7.3</td>
<td>0.5</td>
<td>63</td>
<td>5</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Fig. 8. Comparison of observed and simulated surface runoff hydrographs and spatially averaged rainfall over the catchment ($T = 0$ at start of recorded rainfall).
3.2. Metaldehyde prediction model

The rainfall event based operation of the automatic samplers to collect hourly water samples enabled the capture of high resolution metaldehyde concentrations arriving at the outlet of the catchment following rainfall events. Results of the analysis of metaldehyde concentrations from the collected water quality samples for each event are presented in Fig. 9. The analysis shows that relatively short lived metaldehyde peaks with event durations ranging from 12–48 h occur following rainfall events (Fig. 9). The size and nature of these short lived metaldehyde spikes are highly variable between events. For example, recorded metaldehyde concentrations rise by approximately 500% during event B2, but only by 150% during event B3, however averaged rainfall is of the same order of magnitude for both events. The datasets therefore emphasise that runoff generation from high risk areas has a significant impact on metaldehyde concentrations in the catchment surface waters, and that pollutant dynamics is highly sensitive to temporal and spatial distributions of rainfall and land use. Moreover, soil type on the land where metaldehyde is applied combined with chemical characteristics of metaldehyde such as solubility and sorption coefficient play an important role in the process of mobilizing metaldehyde into water courses.

The metaldehyde concentration prediction model represents metaldehyde transport in surface runoff from high risk areas in the catchment by coupling the travel time technique calibrated in Section 3.1 with build-up/wash-off component. This enabled forecasting of metaldehyde concentration levels following rainfall events at the outlet of the catchment, where the surface water abstraction site is located. Metaldehyde concentration data collected over data collection event B1 was used to calibrate the value of parameter $K_b$, which was used to account for uncertainties associated with the estimation of metaldehyde build-up and wash-off rate. Different values of parameter $K_b$ ranging from 1 to 3.5 were set in the metaldehyde prediction model to simulate metaldehyde concentrations during data collection event B1. The model performance was evaluated using four criteria i.e. prediction error of time to peak concentration ($\Delta T_c$), prediction error of peak metaldehyde concentration ($\Delta PC$), coefficient of determination ($R$) of observed and simulated metaldehyde concentrations and model prediction efficiency ($E$). However, due to the assumption of uniform application of metaldehyde on all high risk areas (Section 2.2.3), changes in parameter $K_b$ result in an overall proportional increase or decrease of predicted metaldehyde concentrations across the prediction period, hence calibration has no impact on the proportion of the variances between predicted and observed concentrations. As a result, coefficient of determination ($R$) values between predicted and observed concentrations are found to be insensitive to changes in parameter $K_b$. The metaldehyde prediction model results for data collection event B1 and associated error statistics are summarized in Table 5. The results indicated that optimum solution is attained with $K_b = 1.6$ considering the remaining criteria for data collection event B1. An initial measured river concentration ($C_0$) value of 0.067 µg/l is used for the calibration event B1. Measured $C_0$ values for each event used for metaldehyde model validation events are presented in Table 6.

### Table 5

<table>
<thead>
<tr>
<th>$K_b$</th>
<th>$\Delta T_c$ (h)</th>
<th>Peak metaldehyde concentration (µg/l)</th>
<th>$\Delta PC$ (µg/l)</th>
<th>$R$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0.11</td>
<td>0.04</td>
<td>0.77</td>
<td>0.10</td>
</tr>
<tr>
<td>1.3</td>
<td>2</td>
<td>0.12</td>
<td>0.03</td>
<td>0.77</td>
<td>0.42</td>
</tr>
<tr>
<td>1.5</td>
<td>2</td>
<td>0.13</td>
<td>0.01</td>
<td>0.77</td>
<td>0.55</td>
</tr>
<tr>
<td>1.6</td>
<td>2</td>
<td>0.14</td>
<td>0.01</td>
<td>0.77</td>
<td>0.60</td>
</tr>
<tr>
<td>1.7</td>
<td>2</td>
<td>0.14</td>
<td>0.01</td>
<td>0.77</td>
<td>0.54</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.15</td>
<td>0.01</td>
<td>0.77</td>
<td>0.47</td>
</tr>
<tr>
<td>2.5</td>
<td>2</td>
<td>0.16</td>
<td>0.01</td>
<td>0.77</td>
<td>0.42</td>
</tr>
<tr>
<td>3.5</td>
<td>2</td>
<td>0.20</td>
<td>0.05</td>
<td>0.77</td>
<td>−0.77</td>
</tr>
</tbody>
</table>

### Table 6

<table>
<thead>
<tr>
<th>Data Collection Event No.</th>
<th>$C_0$ (µg/l)</th>
<th>$\Delta T_c$ (h)</th>
<th>Peak Metaldehyde Concentration (µg/l)</th>
<th>$\Delta PC$ (µg/l)</th>
<th>$R$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>0.05</td>
<td>−3</td>
<td>0.32</td>
<td>0.01</td>
<td>0.81</td>
<td>0.45</td>
</tr>
<tr>
<td>B3</td>
<td>0.03</td>
<td>2</td>
<td>0.07</td>
<td>−0.003</td>
<td>0.7</td>
<td>0.48</td>
</tr>
<tr>
<td>B4</td>
<td>0.4</td>
<td>6</td>
<td>1.7</td>
<td>−0.06</td>
<td>0.74</td>
<td>0.45</td>
</tr>
</tbody>
</table>

3.2.1. Verification

Metaldehyde model simulations were carried out for other three metaldehyde data collection events using calibrated parameter values. Table 6 summarizes model simulation results and error statistics for all three data collection events. It was observed that simulations for all three events have correlation coefficients of 0.70 or more, prediction error of peak metaldehyde concentration less than 5% and time to peak concentration error of 6 or less hours. Observed and predicted metaldehyde concentrations along with spatially averaged rainfall data are shown in Fig. 9 for all four data collection events. In general, metaldehyde concentrations are predicted well for all events with practically acceptable levels of errors in terms of both concentration levels and prediction of peak arrival times. The results showed the capability of the model developed in this study for the intended practical purpose of predicting the arrival of peak metaldehyde concentrations and informing surface water abstractions. Discrepancies in the prediction of the peak arrival time are likely to be caused mainly by uncertainties associated with estimation of channel travel time, antecedent conditions and the assumption of uniform metaldehyde application throughout the high risk areas in the catchment. Some of these errors may be reduced in future via the use of more calibration data and a more detailed consideration of metaldehyde applications informed by data from farmers (i.e. real time application data).
4. Conclusions

Diffuse agricultural pollution is known to be a significant concern to the quality of surface water, with implications for drinking water supply. Smarter management of water resources including forecasting and prediction of pollutant spikes is a possible means to avoid contamination of drinking water supplies and reduce the cost of water treatment. This requires a detailed understanding of pollutant processes in the catchment in response to rainfall events. The occurrence, sources, transport and fate of organic compounds in the environment involve a variety of processes that determine how the compounds are initially distributed, move and react. Consequently, assessing fate and transport of contaminants in the environment is a complex issue. This study focuses on predicting the arrival of peak metaldehyde concentrations in surface runoff at abstraction sites with a view to inform surface water abstraction decisions, hence a model has been developed to describe short term dynamics and transport, primarily driven by rainfall driven runoff, rather than longer term reactions/degradation or groundwater processes. Runoff generation and routing is spatially and temporally variable and hence surface water quality responses are dependent on the spatial distribution of pesticide within the catchment (a function of land use) and the dynamics of individual rainfall events. To date the quantification and understanding of the pollutant dynamics that drive short term fluctuations has been hindered by a paucity of high resolution water quality sampling data. The physically-based distributed metaldehyde prediction approach developed in this study combines surface runoff and build-up wash-off concepts in a GIS environment, enabling the full consideration of spatially and temporally variable rainfall and land use patterns. Model parameters and input data are extracted from radar rainfall data, soil type, land use and DEMs. To address the paucity of current data we attempt to utilize automatic samplers which were triggered during rainfall events to capture the impact of forecasted rainfall events on the concentrations in surface waters. The variation in the metaldehyde concentration response between the rainfall events demonstrates the importance of a full consideration of spatio-temporal rainfall and metaldehyde application data.

In terms of practical application, it is noted that the accurate forecasting of arrival time of peaks is of more value than forecasting of the peak concentration value, as this enables surface water abstraction decision makings such as suspending abstractions temporarily in order to avoid the entrance of high metaldehyde levels into water supply systems. Given the inability of existing treatment techniques to remove high metaldehyde levels from water and the absence of direct metaldehyde detection methods, the model developed in this study provides a cost-effective and sustainable solution. When applied to the trial catchment the model was able to predict peak concentrations to within 6 h in all tested cases, given the availability of water storage infrastructure in the catchment this would enable the operator to suspend abstraction for this period to allow likely periods of high concentration to pass. Given the effective utilisation of storage, such a suspension would not have a significant negative impact on water resources, especially if abstraction was increased at other times to compensate.

The increasing availability of catchment scale spatial datasets combined with the relatively simple GIS based application of the model makes it suitable for use in various catchments where prediction of metaldehyde exposures are required. Moreover, in the presence of reliable spatially distributed datasets, the developed approach can potentially be extended to predict exposures to other pollutants of interest at catchment scale, as well as inform catchment management options.
Future work will investigate the quantification of modelling input and parameter uncertainty on both predicted concentration levels and peak arrival times.

Acknowledgements

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References


