METALDEHYDE PREDICTION BY INTEGRATING EXISTING WATER INDUSTRY DATASETS WITH THE SOIL AND WATER ASSESSMENT TOOL

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Abstract

Metaldehyde (a synthetic aldehyde pesticide used globally in agriculture) has been internationally identified as an emerging contaminant of concern. This study aimed to integrate existing water industry, publicly available and purchased licensed datasets with the open-access Soil and Water Assessment Tool (SWAT), to establish if these datasets could be used to effectively model metaldehyde in river catchments. To achieve the study aim, a SWAT model was developed and calibrated for the River Medway catchment (UK). The results of calibration (1994-2004) and validation (2005-2016) of average daily streamflow (m^3/s) showed that the SWAT model could simulate water balance well (P-factor 0.73-0.81 and R-factor 0.64- 0.82, NSE 0.42-0.59). Calibration (P-factor 0.72 and R-factor 1.35, NSE 0.31) and validation (P-factor 0.49 and R-factor 1.37, NSE 0.16) for daily soluble metaldehyde (mg active ingredient) load was also satisfactory. The most sensitive pesticide parameters for metaldehyde simulation included the timing and amount of pesticide (kg/ha) applied to the hydrological response units, the pesticide percolation coefficient and pesticide application efficiency. Outputs from this research demonstrate the potential application of SWAT in large complex catchments where routine monitoring is in place, but isn't designed explicitly for the purpose of predictive modelling. The implications of this, are significant, because they suggest that SWAT could be applied universally to catchments using existing water industry datasets. This would allow more efficient use of historical datasets and would be applicable in situations where resources are not available for additional targeted monitoring programmes.

Keywords

SWAT, metaldehyde, pesticide, management, Water Framework Directive

1. Introduction

Metaldehyde is a synthetic aldehyde pesticide used globally in agriculture, commonly in slug pellet form. The World Health Organisation (WHO) classifies metaldehyde as a 'moderately hazardous' pesticide (class II) (WHO, 2010) and the United States Environmental Protection Agency has designated it a 'restricted use pesticide' (US.EPA, 2006). The European Union Drinking Water Directive (Council Directive 98/83/EC) has set regulatory standards for individual and total pesticides at 0.1 μg/l and 0.5 μg/l respectively (European Commission, 1998). Metaldehyde is an emerging contaminant of concern because it is a highly stable chemical compound in water, can be very mobile in the environment, and is ineffectively removed by current drinking water treatment processes (Kay and Grayson, 2014). Specifically, metaldehyde is not effectively removed by normal pesticide treatments, such as adsorption onto activated carbon and cannot be broken down by using chlorine or ozone (Water UK, 2013). As a result, the consensus is that the best option for reducing transport of this pesticide to surface waters is to control the sources through catchment management approaches. Transport of metaldehyde to surface waters by surface water runoff is more significant than via soil erosion, because metaldehyde has a low K_{OC} value (low sorption coefficient of active ingredient to organic carbon), resulting in less potential for metaldehyde to adsorb to suspended sediments (Asfaw et al., 2018). Consequently, an accurate understanding of surface water runoff generated from agricultural land is important when determining catchment management approaches. Water companies in the UK have legal programmes of work (undertakings) approved by the Drinking Water Inspectorate (DWI), which aim to prevent breaches in pesticide standards (EU pesticide standard of 0.1 μg/l). Programmes of work are largely aimed towards catchment management measures that reduce metaldehyde load at source. Common catchment management initiatives have included catchment sensitive farming schemes (including training and advice for farmers), managed abstraction (avoiding abstraction of water containing metaldehyde concentrations above 0.1 μg/L), promotion of alternative products (especially in high-risk areas) and funding of research into potential treatment options (Water UK, 2013). The Metaldehyde Stewardship Group (an industry led voluntary group with the aim of promoting and encouraging best practice with metaldehyde slug pellets) published guidelines, promoting a maximum individual dose application of 210g of metaldehyde/ha, with a reduced rate of 160g for additional water protection (Metaldehyde Stewardship Group, 2018). The guidelines also included that no pellets should be allowed to fall within a minimum of 10 metres of any field boundary or watercourse and that farmers should not apply when heavy rainfall is forecast. A number of water companies, have led collaborative catchment initiatives with nongovernmental organisations and rivers trusts to reduce metaldehyde loads in source waters. The project 'Slug It Out' funded by Anglian Water (UK) trialled the substitution of metaldehyde with ferric phosphate (facilitated through incentive payments) and demonstrated success in improving source water quality and increasing metaldehyde compliance (Mohamad et al., 2019). However, modelling of the catchments, within the 'Slug It Out' project indicated that over 80% of the natural catchments would require product substitution to achieve complete regulatory compliance (Nineham et al., 2015). Castle et al. (2017) provide a review of catchment management strategies for metaldehyde and note that recent decreases in the number of metaldehyde standard exceedances (0.1 μg/l) in the UK, in part, can be attributed to the increase in take up of ferric phosphate by the agricultural sector.

Since the adoption of the Water Framework Directive (WFD) in 2000, European river basin management has gone through a process of transformation. Hydrological models are increasingly used to predict river flow and water contaminant transport to meet the Directive's need for holistic River Basin Management Plans (RBMP). The WFD seeks to prevent the deterioration of ground and surface water bodies and achieve good ecological and chemical status in water courses (EC, 2000). Therefore, chemical contaminants, including pesticides and their supply into water courses need to be managed. Studies from across the EU have found metaldehyde concentrations regularly exceeding EU standards of 0.1 μg/L (Gillman et al., 2012; Lazartigues et al., 2012; Bloodworth et al., 2015). Kay and Grayson (2014) analysed metaldehyde concentration data collected by a regional water company (in the UK) between 2008 and 2011. The aim was to quantify the presence of metaldehyde in a range of surface and drinking waters. They found that metaldehyde levels exceeded the EU pesticide standard of 0.1 µg/L frequently during the autumn-winter slug pellet application season. Peak concentrations were observed to be in the 0.4-0.6 µg/l range, although sometimes they were an order of magnitude higher. A lack of correlation between metaldehyde concentrations and crop type, soil type and slope, suggested that driving factors are complicated and may include a wide set of variables. Lu et al. (2017) simulated metaldehyde dynamics in the River Thames catchment, UK. They proposed that metaldehyde application rates were the key driver of metaldehyde concentrations in rivers. Their research also demonstrated how more complex models can be effective decision support tools when considering the complex management options required to control land to river transfer of metaldehyde. Asfaw et al. (2018), developed a model focused on prediction of arrival times for metaldehyde concentration peaks in surface runoff at abstraction sites. The model was developed to describe short term dynamics and transport (by precipitation driven runoff rather than longer term processes). The results of this study emphasised the variability of metaldehyde peaks and the significance of runoff generation from high risk areas. In addition, it was noted that metaldehyde dynamics were highly sensitive to temporal and spatial distributions of precipitation and land use.

The Soil and Water and Assessment Tool (SWAT) model is the product of the USDA-Agricultural Research Service, USDA- Natural Resources Conservation Service, and Texas A & M University (Arnold et al., 1998; Arnold and Fohrer, 2005). SWAT is an open-access river basin-scale model that has been used to assess water resource and non-point (diffuse) source pollution issues worldwide, gaining considerable recognition internationally. The model has been the focus of over 3000 peer-reviewed research articles. The purpose of the model is to predict the impact of land management practices on water, sediment, and agricultural chemical yields (e.g., nitrates, phosphates and pesticides) and it can operate at a range of scales, in complex catchments with different soils, land-use and management practices (Arnold et al., 2012; Mehan et al., 2019). SWAT is a semi-distributed and computationally efficient model that is physically-based. The physically-based equations used by the model are provided in the SWAT theoretical documentation (Neitsch et al., 2011) and by Arnold et al. (1998). SWAT is a continuous- time model that operates on a daily time step. There are numerous examples of successful applications of the SWAT model in pesticide fate modelling (Kannan et al., 2006; Luo and Zhang, 2009; Chen et al., 2017; Winchell et al., 2017). Quilbé et al. (2006) reviewed 36 commonly used pesticide models and concluded that for pesticide modelling SWAT was the best model under a wide variety of conditions. As SWAT is a public domain model, it has the potential to be a low-cost tool for aiding metaldehyde management in river catchments. To the authors knowledge, internationally there is only one example of SWAT application to model metaldehyde reported by Anglian Water Services and Mott MacDonald (Nineham et al., 2015). The investigators concluded that SWAT was able to produce robust and technically defensible simulations of metaldehyde concentrations under current and predicted future conditions, but in this instance statistical evaluation criteria for metaldehyde are not available. A recent study that investigated the fate of metaldehyde, using an alternative model (the INCA-contaminants model) expressed a view that, whilst successful at modelling the fate of pesticides, the SWAT model may have data requirements that are too high for use in these scenarios, with many parameters requiring estimation (Lu et al., 2017). Therefore, whilst the SWAT model has potential to be an important and useful tool for the water industry globally, there is still doubt that existing available datasets are currently appropriate for this modelling option. Conversely, SWAT has significant potential to aid catchment management for the reduction of metaldehyde transfer into water bodies and it is important to determine if existing routine monitoring programmes and datasets enable the water industry to effectively apply models such as SWAT. Importantly, this research could also help inform future industry-based monitoring strategies, so that they support modelling of metaldehyde and emerging contaminants, such as the pesticide cypermethrin, which is thought to be a concern in the future.

Therefore, this research aimed to determine whether existing water industry datasets, along with publicly available and purchased licensed datasets could be used to effectively model and predict instream metaldehyde loads in river catchments. To achieve this aim, the following objectives were designed to; 1) Develop a model and forecast instream metaldehyde loads within a large and complex catchment (River Medway catchment, UK) using existing water industry, publicly available and purchased licensed datasets with SWAT, 2) evaluate the quality of these simulations, 3) evaluate and make recommendations on data requirements for satisfactory simulation of metaldehyde and future emerging contaminants.

2. Material and methods

2.1 The River Medway Catchment

The River Medway catchment, UK, was chosen for this study. As one of the largest catchments in South East England (2409 km2), it offered the opportunity to challenge the model with the complexities associated with a river that has varied topography, soils and geology, and runs through a diverse range of land uses (Environment Agency, 2018). The catchment is also subject to frequent discharges and abstractions along its reach and metaldehyde standard EU exceedances (>0.1 µg/L) are of concern. The River Medway catchment has a number of large tributaries including the Eden, Teise and Beult. There are many landscape designations in the catchment (accounting for 75% of the landscape area), including Sites of Special Scientific Interest and important wetland habitats (Environment Agency, 2018).

2.2 Model input data

The fundamental mechanisms of SWAT pesticide modelling are detailed in Wang et al. (2019). To model metaldehyde in the River Medway catchment using SWAT, datasets were obtained. The data collection period was from 2009 to 2016. The digital elevation model (DEM) used in watershed delineation was an OS Terrain 5 map with a 5 m by 5 m grid size resolution and a 1:10,000 scale (Digimap, Edina, UK). The total study area was 1036.4 km^2. Land-use was determined from the Land Cover Map 2007 (LCM2007), which is derived from satellite images and digital cartography. For use of this map, a licence was purchased from the Centre for Ecology and Hydrology (part of the Natural Environment Research Council). The National Soil Map and attributed soil data were obtained from the National Soil Resources Institute, Cranfield University, also through a purchased licence. Meteorological station data (coordinates), along with daily meteorological data (precipitation, relative humidity, solar, temperature, and wind) were obtained from the Meteorological Office Integrated Data Archive System (MIDAS).

Water abstraction locations and quantities were provided by the Environment Agency (EA), UK, under an agreed licence. Daily discharge locations and quantities for point sources and reservoirs, along with all observed streamflow and water quality data (for calibration and validation of the model) were obtained from water industry datasets. Southern Water Services (SWS) Ltd. was the primary supplier of these data (water quality from SWS catchment data), with streamflow and water quality data provided by Sutton and East Surrey Water PLC for the Eden tributary of the River Medway. Crop management data were abstracted from

EDINA Agcensus data (Edinburgh University Data Library and the Department of Environment, Food and Rural Affairs) through a paid subscription. Finally, additional land management information, pesticide application time and quantities were obtained from the Department of Environment, Food and Rural Affairs (DEFRA) and the Food and Environment Research Agency (FERA), respectively. Suspended sediment data was not available for use in this study, consequently an inability to calibrate sediment yield was a limitation of the research.

2.3 Model setup

The Medway catchment was delineated using a digital elevation model (DEM) with a selected sub-basin maximum size of 1000 Ha (10km2), resulting in 110 sub-basins in total (Figure 1). The purpose of delineation was to divide the catchment into hydrologically connected sub-basins. Three streamflow gauge outlets (three points where appropriate average daily streamflow (m3/s) data and one water quality outlet where appropriate daily soluble metaldehyde (mg active ingredient) data existed were selected and imported into the model for calibration and validation purposes. The locations of 137 different wastewater point sources and three reservoirs (Weirwood, Bough Beech and Bewl) were also built into the watershed delineation stage of the model set up (Figure 1). The model outlet was set at the point where the River Medway meets the Thames Estuary, Kent, allowing delineation of the entire River Medway catchment.

Sub-basins were then split into unique combinations of slope class, land-use class and soil class, which resulted in a total of 823 Hydrologic Response Units (HRU). Dividing the sub-basins into HRU allows the model to reflect the differences in evapotranspiration for different crops and soils, as well as predicting run-off for each independent HRU, leading to more accurate prediction of water balance (Neitsch et al., 2011). HRU minimum thresholds for unique combinations were set for land-use (20%), soil class (20%) and slope class (20%) to limit the numbers of HRU to fewer than 10 per sub-basin. Before HRU definition could be performed, land-use, soils and slope required further definition.

As previously mentioned, SWAT was developed in the United States (US), and as a result, the default soil and land-use databases used by the model required alteration before definition in the model. The Land Cover Map (2007) was reclassified according to existing SWAT land-use classifications. The original land-use classifications from the Land Cover Map (2007) included 16 different land-use types. These were subsequently divided into 10 broader SWAT land-use classifications (Table 1). Before HRU definition, using the land use refinement option, land-use classifications were further refined by division of the agricultural land – generic (AGRL) classification into crop types according to percentages of crop type in the survey data from the agricultural census of 2010 (Table 2) (Edina, Agcensus).

To apply UK soil types to the SWAT model, a database of soils present in the River Medway catchment was constructed from soil datasets provided by the National Soil Resources Institute, Cranfield University. These datasets display soil associations, containing the most frequently occurring soil series (which are used to identify the association) and combinations of secondary series. Soil associations were explored to determine if more hydrologically-active soils (not the most commonly identified) were present, which could impact model performance. Within the soil associations, soil sub-groups demonstrated similar drainage characteristics, therefore for database construction, the characteristics of the most commonly occurring soil series were used. As an additional consideration, soil characteristics vary depending on land-use. Therefore, soil series were additionally divided according to the following four land-use categories; PG – Permanent grassland, AR – Arable, LE – Ley grassland and OT – Other. Soils were assigned land-use classifications based on the dominant land use. Once constructed, the completed database of soils was then imported into the SWAT2012 operating database used by the model. Three slope classes were selected for slope definition (>5%, 5-10%, and >10%).

Eight meteorological stations were used for model setup, spanning up to 27 years of observed historical data (for temperature, precipitation, solar radiation and wind). Only stations where missing data did not account for more than 10% of the total were used. No infilling or correction of meteorological data was required. Meteorological station statistics were calculated and input into a 'user weather generator database' (which was imported into the SWAT2012 operational database) for calculation of relative humidity.

Point source daily discharges (obtained from water industry datasets) were input into the model via the 'edit point source input' option in SWAT. Water abstraction from the river was added to the model by editing water use in each sub-basin for each separate month. Abstractions were calculated from daily returns data provided by the Environment Agency. Abstractions, inputs and discharges were also edited for the three reservoirs in the catchment (Bewl, Boughbeech and Weirwood) separately using observed data. Basin transfers were included to account for river abstractions into reservoirs.

Land management was edited for each separate sub-basin using the SWAT 'management edit' option. This feature enabled crop rotations that were indicative of agricultural practises in the South East of England to be implemented for agricultural land row crops, which represented 54.57% of the refined agricultural land (AGRL) classification. Crop rotations presented in Table 3 (including cultivation, tillage, harvest, fertiliser and pesticide application operations) were formulated from survey data from the agricultural census of 2010, with guidance from data presented by Glavan et al. (2012) and Taylor et al. (2016) Application of metaldehyde was also added to the management options, with application quantities and application dates derived from data provided by the Food and Environment Research Agency (FERA). Metaldehyde is not initially included in the pesticide database built into SWAT. However, data relating to the characteristics of metaldehyde were obtained from the SCS/ARS/CES pesticide properties database and were imported (Augustijn-Beckers et al., 1994). The simulation period for the model was 1990 to 2016 with four years of model warm-up (1990-1993). For average daily streamflow (m3/s), the model was calibrated from 1994 to 2004, and validated from 2005 to 2016. Three streamflow gauge outlets were used for calibration and validation, as shown in Figure 1. For daily soluble metaldehyde (mg active ingredient) loads, the longest and most complete data set was recorded at water quality outlet 1. Therefore, this location was selected for model calibration for metaldehyde data (2009-2013) and for subsequent validation (2014-2016). All other sites were deemed to have insufficient data for useful calibration and validation of daily soluble metaldehyde (mg active ingredient) loads.

2.4 Calibration and validation

Abbaspour et al. (2015a) advise that models should be transparently described, including calibration, validation, sensitivity and uncertainty analysis. SWAT-CUP is a stand-alone program developed to aid users in these steps. Therefore sensitivity, calibration and validation analysis were performed in SWAT-CUP using the Sequential Uncertainty Fitting Program (SUFI-2) (Abbaspour, 2015b). Sensitivity, calibration and validation analysis was conducted according to the approach outlined in Figure 2. The Nash–Sutcliffe efficiency

(NSE) performance criterion (Nash and Sutcliffe, 1970) was used in calibration and evaluation of the model performance in SUFI-2. The NSE was chosen because it is robust and can be used to evaluate model performance for a number of temporal scales and output responses including streamflow and pesticides. In addition, NSE can incorporate measurement uncertainty and is commonly used in SWAT model calibration and evaluation, enabling comparison with an extensive range of reported values (Harmel and Smith, 2007; Harmel et al., 2010; Moriasi et al., 2015). In SUFI-2, uncertainty in driving variables (e.g. precipitation), the conceptual model, parameters and measured data is accounted for in the model by expressing input parameters in ranges (uniform distributions). Propagation of these uncertainties results in uncertainties in model output. These are represented by 95% probability distributions (95PPU) that are calculated at the 2.5% and the 97.5% levels of the cumulative distribution of an output variable, generated by Latin hypercube sampling of the propagated parameter uncertainties (Abbaspour, 2015b). In addition to the NSE, to quantify the fit between simulated and observed results, P-factors and R-factors are used. The P-factor is the percentage of observed data enveloped by the modelling result (95% prediction uncertainty), whilst the R-factor is the thickness of the 95% prediction uncertainty envelope. Global sensitivity analysis was performed to reduce the number of parameters used to calibrate the model. The parameters considered important for streamflow and metaldehyde load calibration are displayed in Table 4, along with the results of global sensitivity analysis. Tables 5 and 6 display the calibrated ranges and fitted values for sensitive average daily streamflow (m^3/s) and daily soluble metaldehyde (mg active ingredient) load parameters (p-value <0.05). The most sensitive parameter for streamflow (m^3/s) calibration (t-statistic -20.29, p-value 0.00) was the Soil Conservation Service (SCS) runoff curve number (CN2). The most sensitive pesticide parameters for daily soluble metaldehyde load (mg active ingredient) simulation included the timing and amount of pesticide applied to the HRU (kg/ha), the pesticide percolation coefficient and pesticide application efficiency. The Soil Conservation Service (SCS) runoff curve number (CN2), which was left unaltered after streamflow calibration was also a sensitive parameter for daily soluble metaldehyde (mg active ingredient) calibration.

3. Results and discussion

3.1 Calibration and validation

Sensitivity analysis showed that daily soluble metaldehyde (mg active ingredient) loads were most sensitive to the amount and timing of pesticide application to land, the pesticide percolation coefficient, pesticide application efficiency and the SCS runoff curve number. Metaldehyde has a low K_{OC} value, resulting in less potential to adsorb to suspended sediments and therefore adjustments to parameters that change the filtration/ run-off potential, such as the pesticide percolation coefficient and the SCS runoff curve number could have significant impacts on metaldehyde outputs (Asfaw et al., 2018). Pesticide application efficiency was also a highly sensitive parameter for the calibration of metaldehyde, suggesting that increasing the accuracy of pellet targeting to land and product substitution in high risk areas (steeper slopes with connectivity to water courses), could be an important management option. Sensitivity analysis results highlighted that the slope length for lateral subsurface flow (m) was also a sensitive model parameter for metaldehyde load prediction. Tang et al. (2012) suggest that in regions where soil is underlain by impervious subsoil, these flows can make a considerable contribution to rapid pesticide discharge from agricultural land. Pesticides with a smaller tendency toward sorption, such as metaldehyde also commonly have a greater potential to enter surface waters through subsurface lateral transport (Kookana et al., 1998).

Calibration and validation of the Medway catchment SWAT model was conducted for average daily streamflow (m3/s) out of the reach (calibration; 1994-2004, validation; 2005-2016) and daily soluble metaldehyde (mg active ingredient) load transported out of the reach (calibration 2009-2013, validation; 2014-2016) with a four-year model warm up period from 1990-1993. All three streamflow gauge outlets (Figure 1) were used to calibrate streamflow. It should be noted that not all value ranges refer to replacement values. Parameters, such as the SCS runoff curve number, are different in each HRU and to keep representation of the differences in the HRU, these values were calibrated relative to their original values from model set-up. Water quality outlet 1 was used for metaldehyde load calibration and validation (Figure 1). The calibrated parameter ranges are presented in Tables 5 and 6.

Standards for the success of SWAT model performance have been proposed by Moriasi et al. (2015) who suggest that performance can be judged “satisfactory” for daily streamflow simulations if the NSE is > 0.50 for watershed-scale models. Additionally, they suggest that model performance can be judged “satisfactory” for daily sediment and nitrogen simulations if NSE is > 0.35. To determine the success of pesticide simulation, Chen et al. (2017) adopted the NSE performance criteria threshold used for nitrogen (NSE >0.35) introduced by Moriasi et al. (2015). In addition, Chen et al. (2017) use the 95PPU to determine prediction uncertainty for flow, with results >0.60 P-factor (>60% of data bracketed by the PPU) and less than 1 R-factor (thickness of the PPU envelope) indicating satisfactory flow uncertainty. No values are presented for satisfactory prediction uncertainty for pesticide simulation. Recent SWAT simulation of other pesticides including atrazine, chlorothalonil and endosulfan amongst others has resulted in a wide range of performance results (NSE 0.13-0.92) (Ahmadi et al., 2014; Bannwarth et al., 2015; Fohrer et al., 2014; Baffuat et al., 2015). Comparison of calibration and validation results from this study (Table 7) to these model performance criteria and previous studies indicated that the SWAT model could simulate average daily streamflow (m3/s) out of the reach well (P-factor 0.68-0.85 and R-factor 0.54-0.82, NSE 0.42-0.60), with simulated flow matching closely to observed data (Figure 3). Calibration (P-factor 0.72 and R-factor 1.35, NSE 0.31) and validation (P-factor 0.49 and R-factor 1.37, NSE 0.16) for daily soluble metaldehyde (mg active ingredient) load transported out of the reach was also satisfactory (Table 7 and Figure 4) but results for validation did show a reduced fit of simulated vs observed daily data that may require further investigation. Seventy two percent of measured daily soluble metaldehyde (mg active ingredient) load values were bracketed by the 95PPU (R-factor 1.95) after calibration. Limited studies have reported the 95PPU, however a study conducted by Chen et al. (2017) reported that 31% of the pesticide (diuron) measured data were bracketed by the 95PPU (R-factor 0.85). Observation of plots (Figure 3 and 4) supported the statistical performance results shown in Table 7. The timing of metaldehyde peaks was often accurate, but under-prediction (e.g., 2012 and 2015 peaks) and over-prediction (e.g., 2011 and 2013 peaks) was evident. Over-prediction or under-prediction of daily soluble metaldehyde (mg active ingredient) load in observation plots could be the result of the quality of metaldehyde application data. Metaldehyde application quantities were estimated using census and land use data (from 2007) and the most common crop rotations for the region according to census data and literature (Glavan et al., 2012 and Taylor et al., 2016). Hence it is likely that these assumptions have implications on the accuracy of the model outputs. Since analysis suggested that model simulations were very sensitive to changes in the amount of pesticide applied to the HRU (kg/ha), the authors postulate that more specific and recent land use, management and metaldehyde application data would improve the predictive capabilities of other predictive models with a focus on metaldehyde and other pesticides. In agreement with these findings Parker et al. (2007) suggest that the accuracy of pesticide application timing input data is particularly important for pesticide simulation accuracy, especially when intensive planting is followed by large storm events. They also suggest that the amount of pesticide applied to land, as well as the amount and timing of rainfall are of upmost importance when simulating pesticide runoff. In addition, Fohrer et al. (2014) assessed the environmental fate of the herbicides Flufenacet and Metazachlor with the SWAT model and found that the simulation results were improved considerably with better quality survey information. From Figure 4, it is also apparent that the model under-predicts metaldehyde loads in the 2013 and 2015 peaks, but this under-prediction is not predominant in 2014, when this peak coincides with the largest rainfall event across the calibration and validation period. Results from Holvoet et al. (2005) suggest that direct losses from the clean-up of application equipment, could also represent a significant pesticide contribution to streams. In addition, they conclude that errors in application date, could lead to significant errors in the prediction of direct losses, because randomly assigned application dates can coincide with heavy precipitation, but in reality, the farmer would not apply pesticide in these conditions. Holvoet et al. (2005), recommend adjustments in the SWAT code, to improve modelling of direct loss processes. Whilst, the SWAT code was not adjusted for development of this model, it is possible that these adjustments could improve modelling of direct losses of metaldehyde in future studies.

The authors had theorised that one limiting factor from the use of existing water quality datasets would be the availability of appropriate long-term datasets. However, successful calibration and validation were achieved in this study. One recognised limitation of the model development in this study was the HRU minimum thresholds, that were set for unique combinations at 20% for land-use, soil class and slope class. Whilst these thresholds were set to ensure the number of HRU's were manageable, larger thresholds result in elimination of smaller regions that may still be important in terms of pesticide contributions. In particular, larger land cover thresholds tend to eliminate small land use categories, that could be important for pesticide application (Her et al., 2015). Future studies might explore the use of lower thresholds. However, these results indicate that whilst improvements could be made with greater availability of data and smaller thresholds, the SWAT model was still applicable in a large complicated catchment where data collection wasn't targeted towards modelling studies and where points for calibration were limited. The implications of this, are significant, because this suggests that SWAT could potentially be applied universally to existing water industry datasets without the need for additional, expensive and labour-intensive monitoring programmes. This would also allow for a more efficient use of historical datasets.

Figure 5 displays the spatial distribution of slope class (%), soil hydrologic group, agricultural land cover and average precipitation (mm/year) per sq km. In addition, it also presents simulated median and maximum daily soluble metaldehyde transported out of the reach per sq km of agricultural land cover for the main tributaries of the Medway catchment, Kent, UK. The soil drainage characteristics appear largely uniform with the majority of soils, exhibiting a slow infiltration rate (soil hydrologic group C). Soil classifications with higher infiltration rates are more prevalent in the Bourne tributary and in the lower Medway catchment, approaching the estuary. Unsurprisingly, when maximum and median daily soluble metaldehyde (mg active ingredient) load from the tributaries are compared without context, the tributaries with the largest land areas and agricultural land classification (Beult and the Lower Medway) appear to contribute the highest metaldehyde load to the reaches. The Teise and Upper Medway tributaries, are characterised by slow infiltrating soils and steeper slopes, but the percentage of area covered by agricultural land is low (27% and 18%, respectively) relative to the Beult and Bourne tributaries, with 38% and 33%, respectively.

Emphasising the complexity of predicting metaldehyde contribution risk, the SWAT model output suggests that per km^2 of agricultural land area, the Bourne tributary contributes the greatest soluble metaldehyde (mg active ingredient) load to the River Medway, despite lower average precipitation (mm/year) and a larger proportion of higher infiltration rate soils. In addition to the Bourne tributary, the Beult is also observed to contribute relatively high daily soluble metaldehyde (mg active ingredient) loads from the reach per km^2 of agricultural land, suggesting that preferentially targeting management in this catchment would also be useful. These results, exemplify the potential for SWAT to help water managers to target management options. In this instance, the Bourne tributary is highlighted as an area where product substitution could have the largest impact on reducing metaldehyde (mg active ingredient) loads. Whilst improvement of calibration and validation could be explored in future studies, the results obtained do indicate that the SWAT model could be an important predictive tool for metaldehyde management and future emerging contaminants within the water industry.

4. Conclusions

In this study, existing publicly available, purchased licensed datasets and water industry datasets were integrated with the SWAT model to determine if this modelling approach could be useful for tackling the emerging problem of metaldehyde and other related pesticides in catchments. The results of this investigation may also be of use when selecting modelling tools to assess emerging contaminants, particularly pesticides such as cypermethrin in the future. The following conclusions can be drawn from this research.

- Most importantly for the prospect of modelling emerging contaminants in the future, SWAT was able to model average daily streamflow (m3/s) to a good standard (P-factor 0.68-0.85 and R-factor 0.54- 0.82, NSE 0.42-0.60).

- The accuracy of simulated daily soluble metaldehyde (mg active ingredient) load transported out of the reach was satisfactory for the calibration (P-factor 0.72 and R-factor 1.35, NSE 0.31) and validation (P-factor 0.49 and R-factor 1.37, NSE 0.16) periods, but reduced fit during the validation period, suggests that further investigation may be required into the reasons for a less accurate prediction of metaldehyde during this period.
- Sensitivity analysis suggested that one of the most important parameters for the prediction of peaks in metaldehyde is the amount and timing of pesticide application. Therefore, the inclusion of recent land use and crop rotation data and or survey data from individual farmers could increase the accuracy of simulations.
- These results indicate that whilst improvements could be made with greater availability of data, the SWAT model was still applicable in a large complicated catchment where data collection wasn't targeted towards modelling studies and points for calibration were limited.
- SWAT model output was used to successfully identify tributaries contributing the greatest daily soluble metaldehyde loads to the River Medway (per km^2 of agricultural land), highlighting the potential of this model to help the water industry target management.
- Future work might usefully use SWAT modelling to determine the most important combinations of predictor variables for metaldehyde, highlighting the variables that could be used as real time early warning predictors to peak concentrations.

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Table 1. Area (Ha) and percentage cover (%) of land use classifications for the Medway catchment, Kent, UK

SWAT land use designation	SWAT land-use code	Area (Ha)	Percentage (%)
Agricultural land-generic	AGRL	49423	29.80
Barren Land	BARR	337	0.20
Forest deciduous	FRSD	28684	17.30
Forest evergreen	FRSE	2425	1.46
Pasture	PAST	65910	39.74
Brush	RNGB	716	0.43
Urban industrial	UIDU	2910	1.75
Urban low-medium density	URML	13823	8.33
Water	WATR	1319	0.80
Wetlands non-forested	WETN	306	0.18

Table 2. Land-use refinement of agricultural land- generic (AGRL) classification

SWAT crop designation	SWAT crop code	Percentage (%)
Spring wheat	SWHT	22.08
Corn	CORN	2.16
Spring canola (polish variety)	CANP	1.11
Flax	FLAX	1.31
Agricultural land row crops	AGRR	54.57
Barren	BARR	2.53
Barley	BARL	2.16
Agricultural close grown crops	AGRC	2.37
Orchard	ORCD	4.96
Barley	BARL	1.03
Oats	OATS	1.40
Beans	FDBN	3.40

Table 3. The seven-year crop-rotation and management operations applied within the SWAT model of the Medway catchment for the agricultural land row crops land use designation

Year	Month	Day	Management operation	Description
1	3	15	Tillage	Generic spring ploughing operation
1	4	1	Cultivation	Plant sugar beet
1	4	1	Fertilizer application	Application of 40 kg/ha elemental nitrogen
1	5	1	Fertilizer application	Application of 40 kg/ha elemental nitrogen
1	6	1	Pesticide application	Application of 0.14 kg/ha metaldehyde
1	7	1	Pesticide application	Application of 0.14 kg/ha metaldehyde
1	8	1	Pesticide application	Application of 0.14 kg/ha metaldehyde
1	10	1	Harvest	Harvest sugar beet
2	2	15	Tillage	Generic spring ploughing operation
2	3	1	Cultivation	Plant spring barley
2	4	1	Pesticide application	Application of 0.10 kg/ha metaldehyde
2	4	1	Pesticide application	Application of 0.10 kg/ha metaldehyde
2	5	1	Fertilizer application	Application of 70 kg/ha phosphate
2	5	1	Fertilizer application	Application of 45 kg/ha elemental nitrogen
2	8	3	Harvest	Harvest spring barley
3	1	1	Tillage	Generic spring ploughing operation
3	2	1	Fertilizer application	Application of 40 kg/ha phosphate
3	2	28	Cultivation	Plant field beans
3	5	1	Pesticide application	Application of 0.10 kg/ha metaldehyde
3	8	31	Harvest	Harvest field beans
4	9	15	Tillage	Generic autumn ploughing operation
4	9	30	Pesticide application	Application of 0.13 kg/ha metaldehyde
4	10	1	Pesticide application	Application of 0.15 kg/ha metaldehyde
4	10	5	Cultivation	Plant winter wheat
4	11	1	Pesticide application	Application of 0.10 kg/ha metaldehyde
4	12	1	Pesticide application	Application of 0.21 kg/ha metaldehyde
5	3	1	Fertilizer application	Application of 60 kg/ha phosphate
5	3	1	Fertilizer application	Application of 40 kg/ha elemental nitrogen
5	4	1	Pesticide application	Application of 0.18 kg/ha metaldehyde
5	5	1	Fertilizer application	Application of 120 kg/ha elemental nitrogen
5	8	24	Harvest	Harvest winter wheat

5	9	15	Tillage	Generic autumn ploughing operation
5	10	1	Cultivation	Plant winter barley
5	10	1	Pesticide application	Application of 0.09 kg/ha metaldehyde
6	3	1	Fertilizer application	Application of 40 kg/ha phosphate
6	3	1	Fertilizer application	Application of 60 kg/ha elemental nitrogen
6	4	1	Fertilizer application	Application of 70 kg/ha elemental nitrogen
6	7	15	Harvest	Harvest winter wheat
6	7	16	Tillage	Generic autumn ploughing operation
6	8	1	Pesticide application	Application of 0.17 kg/ha metaldehyde
6	8	31	Cultivation	Plant oilseed rape
6	9	1	Pesticide application	Application of 0.14 kg/ha metaldehyde
6	10	1	Pesticide application	Application of 0.12 kg/ha metaldehyde
6	11	1	Pesticide application	Application of 0.12 kg/ha metaldehyde
6	12	1	Pesticide application	Application of 0.14 kg/ha metaldehyde
7	3	1	Fertilizer application	Application of 60 kg/ha elemental nitrogen
7	3	3	Fertilizer application	Application of 50 kg/ha phosphate
7	4	1	Fertilizer application	Application of 60 kg/ha elemental nitrogen
7	7	30	Harvest	Harvest oilseed rape
7	8	15	Tillage	Generic autumn ploughing operation
7	9	1	Pesticide application	Application of 0.13 kg/ha metaldehyde
7	10	1	Pesticide application	Application of 0.15 kg/ha metaldehyde
7	10	5	Cultivation	Plant winter wheat
7	11	1	Pesticide application	Application of 0.10 kg/ha metaldehyde
7	12	1	Pesticide application	Application of 0.21 kg/ha metaldehyde
8	3	1	Fertilizer application	Application of 40 kg/ha elemental nitrogen
8	3	1	Fertilizer application	Application of 60 kg/ha phosphate
8	4	1	Pesticide application	Application of 0.18 kg/ha metaldehyde
8	5	1	Fertilizer application	Application of 120 kg/ha elemental nitrogen
8	8	24	Harvest	Harvest winter wheat

Table 4. Results of global sensitivity analysis for parameters considered for streamflow and metaldehyde load calibration, with their sensitivity and sensitivity ranking (parameters used in calibration are presented in *italics*).

Parameter Name	Definition	P-Value	Sensitivity ranking
Average daily streamflow in reach (m^3/S)			
CN2	SCS runoff curve number	0.00	1
CH_K2	Effective hydraulic conductivity in main channel alluvium	0.00	2
CH_N2	Manning's "n" value for the main channel	0.00	3
CANMX	Maximum canopy storage	0.01	4
ESCO	Soil evaporation compensation factor	0.01	5
SLSUBBSN	Average slope length.	0.03	6
GWQMN	Threshold depth of water in the shallow aquifer required for return flow to occur (mm)	0.06	7
SOL_AWC	Available water capacity of the soil layer	0.07	8
ALPHA_BNK	Baseflow alpha factor for bank storage	0.08	9
SMFMX	Maximum melt rate for snow during year	0.14	10
GW_DELAY	Groundwater delay (days)	0.14	11
SLSOIL	Slope length for lateral subsurface flow	0.19	12
TIMP	Snow pack temperature lag factor	0.19	13
OV_N	Manning's "n" value for overland flow	0.19	14

SURLAG	Surface runoff lag time	0.27	15
ALPHA_BF	Baseflow alpha factor (days)	0.32	16
SMFMN	Minimum melt rate for snow during the year	0.34	17
EPCO	Plant uptake compensation factor	0.38	18
GW_REVAP	Groundwater "revap" coefficient	0.40	19
CNCOEF	Plant ET curve number coefficient.	0.43	20
HRU_SLP	Average slope steepness	0.56	21
DEEPST	Initial depth of water in the deep aquifer (mm)	0.69	22
SHALLST	Initial depth of water in the shallow aquifer (mm).	0.71	23
SOL_BD	Moist bulk density	0.76	24
REVAPMN	Threshold depth of water in the shallow aquifer for "revap"	0.77	25
SOL_ALB	Moist soil albedo	0.81	26
SFTMP	Snowfall temperature	0.86	27
RCHRG_DP	Deep aquifer percolation fraction	0.90	28
SOL_K	Saturated hydraulic conductivity	0.94	29
Metaldehyde soluble daily load out of the reach (mg active ingredient)			
CN2	SCS runoff curve number	0.00	1
PST_KG	Amount of pesticide applied to HRU (kg/ha)	0.00	2
PERCOP	Pesticide percolation coefficient	0.00	3
AP_EF	Application efficiency	0.00	4
CH_K2	Effective hydraulic conductivity in main channel alluvium	0.01	5
SLSOIL	Slope length for lateral subsurface flow	0.02	6
HRU_SLP	Average slope steepness	0.07	7
SURLAG	Surface runoff lag time	0.11	8
HLIFE_S	Degradation half-life of the chemical on the soil	0.17	9
WOF	Wash-off fraction	0.22	10
HLIFE_F	Degradation half-life of the chemical on the foliage	0.32	11

Table 5. Sensitive average daily streamflow (m^3/s) parameters with calibrated ranges and the fitted value

Parameter	SWAT parameter code	Min	Max	Fitted Value
SCS runoff curve number	r__CN2.mgt	-0.43	0.09	-0.30
Effective hydraulic conductivity in main channel alluvium (mm/hr)	v__CH_K2.rte	-0.01	43.42	3.70
Manning's "n" value for the main channel	v__CH_N2.rte	-0.01	0.18	0.03
Maximum canopy storage	V__CANMX.hru	26.92	80.78	55.92
Soil evaporation compensation factor	V__ESCO.hru	0.42	1.00	0.90
Average slope length	R__SLSUBBSN.hru	-0.06	0.61	0.50

Table 6. Sensitive pesticide parameters with calibrated ranges and the fitted value

Parameter	SWAT parameter code	Min	Max	Fitted Value
Amount of pesticide applied to HRU (kg/ha)	V__PST_KG{..}.mgt	0.28	0.33	0.28
Pesticide percolation coefficient	V__PERCOP.bsn	0.92	1.00	0.98
Pesticide application efficiency	V__AP_EF{..}.pest.dat	0.00	0.22	0.20

Table 7. Calibration and validation performance results from outlets 1-3 for average daily streamflow (m3/s) and daily soluble metaldehyde (mg active ingredient) loads transported out of the reach

Calibration	**Variable**	**Site**	**Sub-basin**	**P-factor**	**R-factor**	**NSE**
	Flow	Outlet 1	24	0.81	0.81	0.57
	Flow	Outlet 2	54	0.74	0.64	0.59
	Flow	Outlet 3	89	0.73	0.82	0.42
	Metaldehyde	Outlet 1	24	0.72	1.35	0.31
Validation	**Variable**	**Site**	**Sub-basin**	**P-factor**	**R-factor**	**NSE**
	Flow	Outlet 1	24	0.85	0.78	0.60
	Flow	Outlet 2	54	0.71	0.54	0.59
	Flow	Outlet 3	89	0.68	0.77	0.54
	Metaldehyde	Outlet 1	24	0.49	1.37	0.16

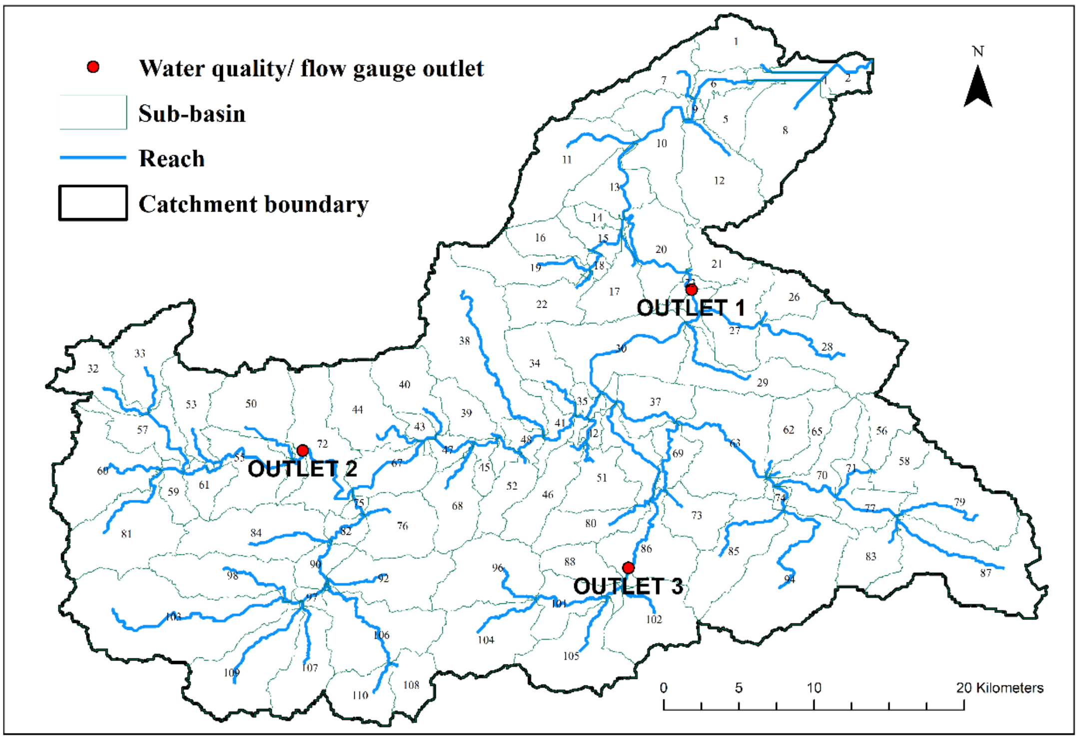

Figure 1: The River Medway (Kent, UK), SWAT delimited catchment, displaying sub-basins, metaldehyde water quality (outlet 1) and streamflow gauge outlets (outlets 1, 2 and 3).

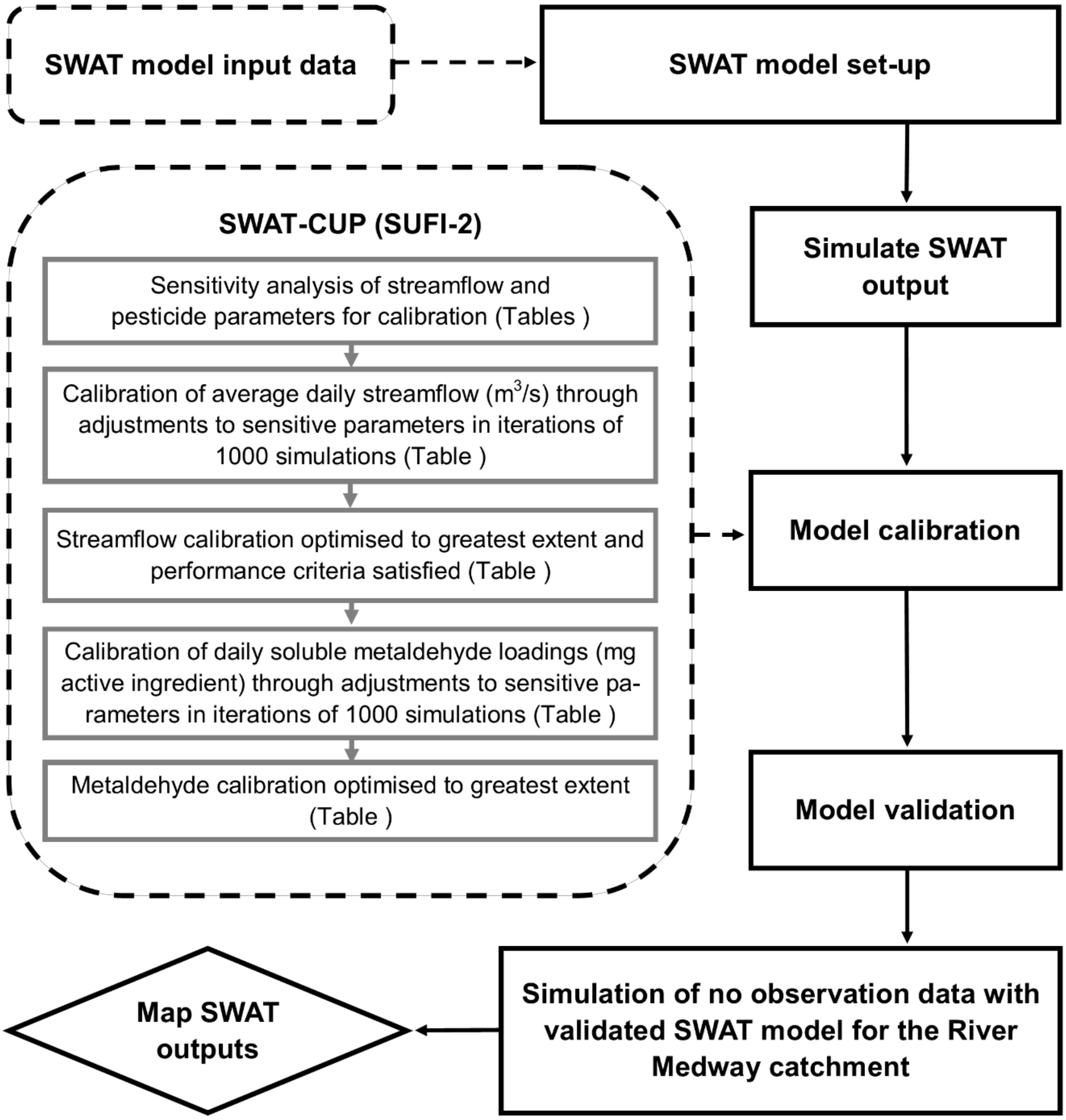

Figure 2. Sensitivity analysis and calibration approach flowchart

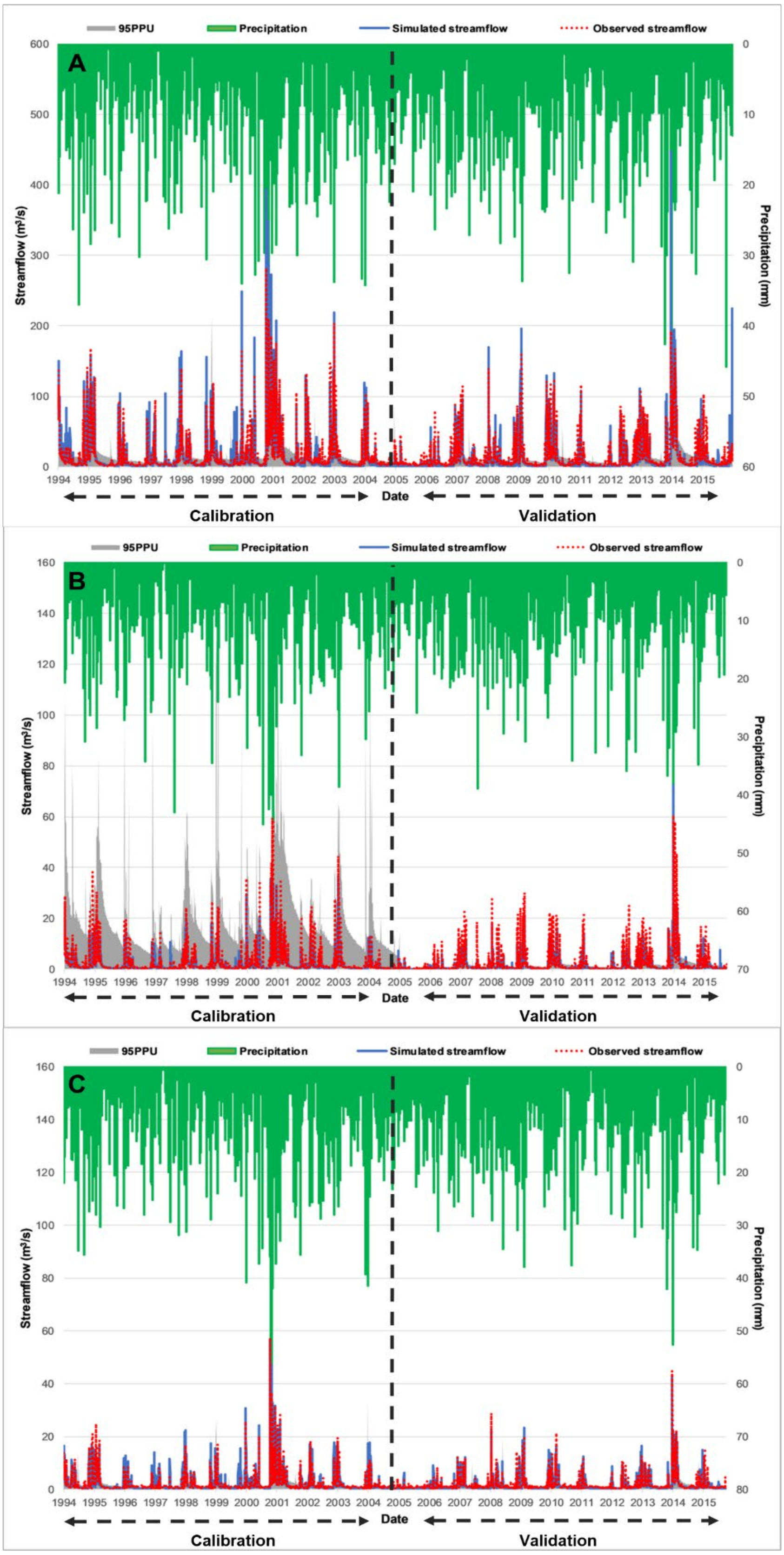

Figure 3: Performance evaluation of streamflow (m^3/s) simulation from outlet 1 (A), outlet 2 (B) and outlet 3 (C) of the calibrated SWAT model with observed data for the calibration period (1994-2004) and validation period (2005-2016).

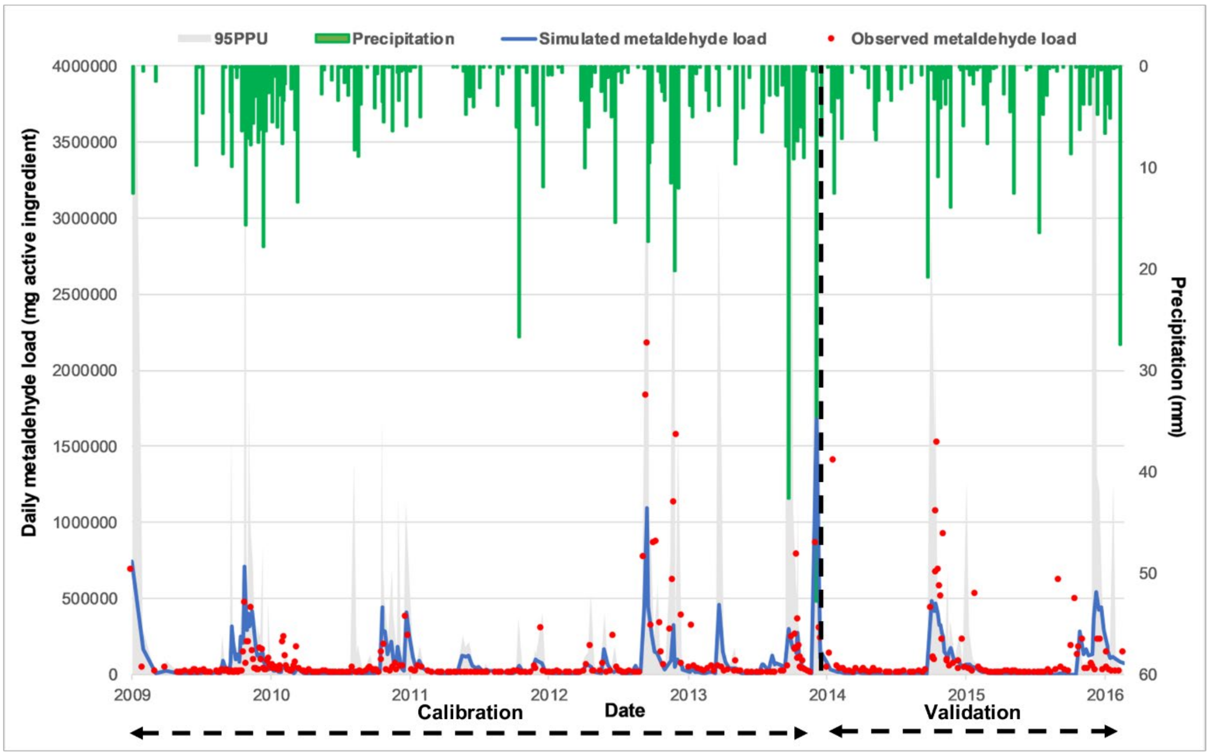

Figure 4: Performance evaluation of daily metaldehyde load (mg active ingredient) simulation from outlet 1 of the calibrated SWAT model with observed data for the calibration period (2009-2013) and validation period (2014-2016).

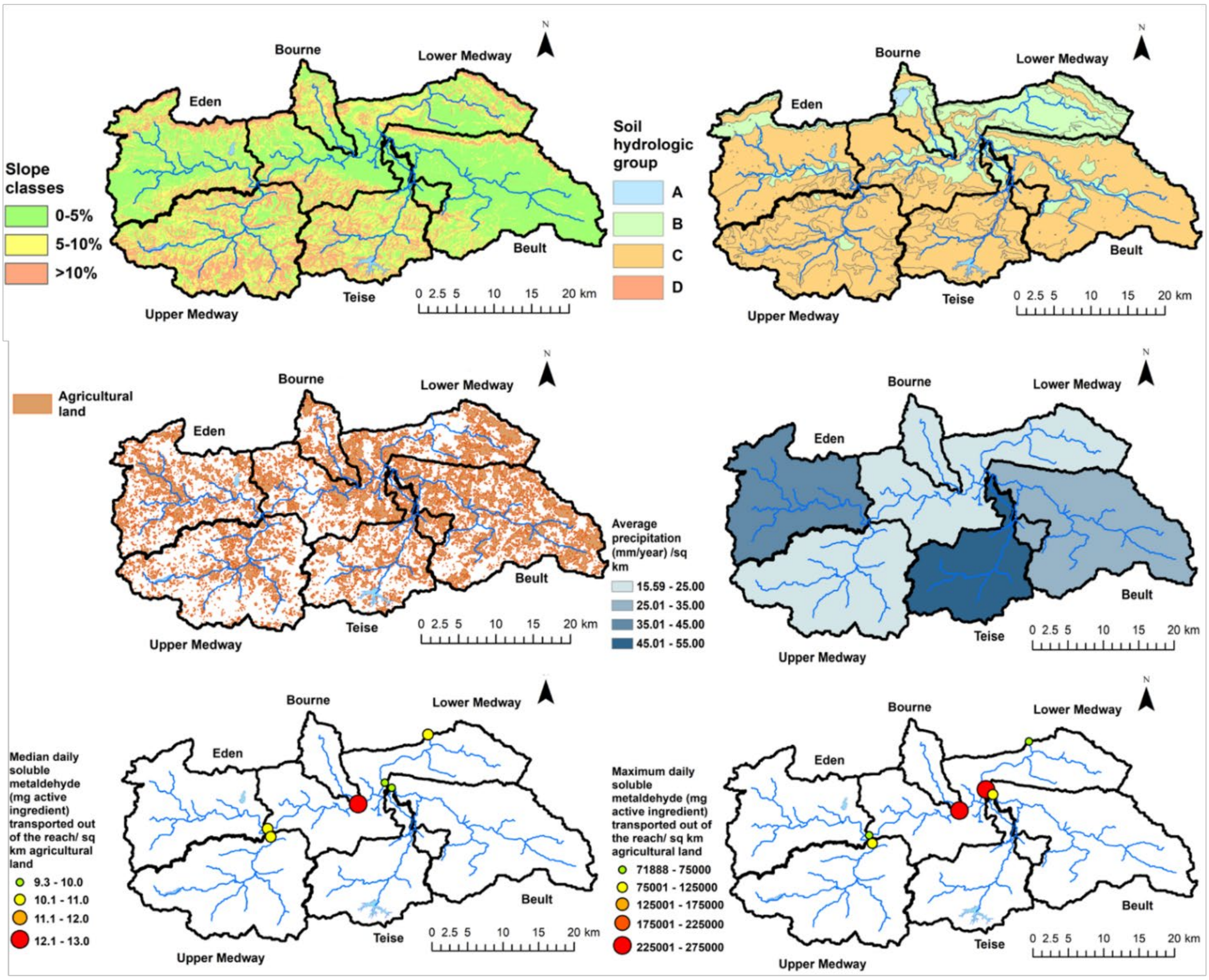

Figure 5: Spatial distribution of slope class (%), soil hydrologic group (A= high infiltration rate, B= moderate infiltration rate, C= slow infiltration rate, D= very slow infiltration rate), agricultural land cover, average precipitation (mm/year) per sq km, and simulated median and maximum daily soluble metaldehyde transported out of the reach per sq km of agricultural land cover for the main tributaries of the Medway catchment, Kent, UK.