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1 A modelling framework to simulate river flow and pesticide loss via preferential flow  
2 at the catchment scale

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5 **Abstract**

6 A modelling framework with field-scale models including the preferential flow model MACRO was  
7 developed to simulate transport of six contrasting herbicides in a 650 km<sup>2</sup> catchment in eastern  
8 England. The catchment scale model SPIDER was also used for comparison. The catchment system  
9 was successfully simulated as the sum of multiple field-scale processes with little impact of in-  
10 stream processes on simulations. Preferential flow was predicted to be the main driver of pesticide  
11 transport in the catchment. A satisfactory simulation of the flow was achieved (Nash-Sutcliffe model  
12 efficiencies of 0.56 and 0.34 for MACRO and SPIDER, respectively) but differences between  
13 pesticide simulations were observed due to uncertainties in pesticide properties and application  
14 details. Uncertainty analyses were carried out to assess input parameters reported as sensitive  
15 including pesticide sorption, degradation and application dates; their impact on simulations was  
16 chemical-specific. The simulation of pesticide concentrations in the river during low flow periods  
17 was very sensitive to uncertainty from rain gauge measurements and the estimation of  
18 evapotranspiration.

19 **Highlights**

- 20 • The catchment system can be simulated as the sum of multiple field-scale processes  
21 • Pesticide concentrations in stream flow were driven by field-scale processes  
22 • In-stream processes had little effect on simulations  
23 • Uncertainties in rain gauge recording affected the simulation of low-flow periods  
24 • SPIDER simulates important lateral flow losses that can occur when drains are not flowing

25 **Keywords:** Pesticide; preferential flow; MACRO; SPIDER; in-stream; catchment

26 **1 Introduction**

27 Modelling the fate of pesticides at the catchment-scale is an important tool for pesticide management  
28 to gain insight into behaviour at this scale and to evaluate the impact of different management

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29 practices. Pesticide loss through subsurface drainage (when tile drains are present) is a dominant  
30 route for pesticide transport to surface waters with surface runoff also locally important (Harris and  
31 Catt, 1999; Johnson et al., 1996). Heavy clay soils with artificial drainage frequently exhibit  
32 pesticide transport via preferential flow, causing surface water contamination (Brown et al., 1995;  
33 Johnson et al., 1996).

34 The model of water flow and solute transport in macroporous soil, MACRO (Jarvis et al., 1991), is  
35 the most widely used preferential flow model at the field scale in Europe. A few studies have applied  
36 field-scale models in catchment modelling by considering that the fate of pesticides in the catchment  
37 would be the result of the sum of multiple field-scale processes (Lindahl et al., 2005; Tediosi et al.,  
38 2013). Monitoring studies of diffuse water pollution by pesticides at different hydrological scales  
39 have shown that pesticide losses normally occur as pulses of fluctuating concentrations with  
40 similarities in their pattern; thus, patterns (but not magnitude) of concentrations measured in a small  
41 receiving water body adjacent to an arable field are broadly conserved in terms of the timing and  
42 duration of peaks when the same pesticide is monitored further downstream (Brock et al., 2010).  
43 These patterns of peak concentrations are largely dependent on rainfall behaviour, suggesting that  
44 processes occurring within the river network may not be a major influence on the timing and  
45 magnitude of peak pesticide concentrations in surface waters at larger scales.

46 Coupling fate models involves combining more than one model in order to establish a modelling  
47 framework that can simulate a broader system than can any of the component models in isolation  
48 (Zhu et al., 2013). In this paper a modelling framework was developed by combining hydrological  
49 and fate models in an attempt to simulate various pathways of water flow and their associated  
50 pesticide losses in the Wensum catchment in the eastern region of the UK. The Wensum is one of the  
51 six priority catchments in England and Wales targeted under the Catchment Sensitive Farming  
52 programme (CSF), to reduce diffuse water pollution by pesticides. Regular pesticide monitoring has  
53 been undertaken since 2006 to evaluate the effectiveness of the management actions. The modelling  
54 framework using MACRO aimed to test whether the catchment system can be simulated as the sum  
55 of multiple field-scale processes.

56 The catchment scale model SPIDER is a preferential flow model that simulates hydrological flow  
57 and pesticide fate in small catchments (Renaud et al., 2008). In contrast to field-scale models like  
58 MACRO, SPIDER considers spatial variability of soils, crops and pesticide usage in the catchment to  
59 simulate the effect of the transport and sorption of pesticides in the river network. SPIDER was also  
60 applied to the Wensum to compare results from a catchment model to the modelling framework  
61 using a field-scale model.

62 Despite the importance of uncertainty analyses, very few pesticide modelling studies include them in  
63 their results. Physically-based hydrological and pesticide transport models require a large amount of  
64 input data from the study area that are not always known with certainty (Sohrabi et al., 2002).  
65 Depending on the level of accuracy needed and the sensitivity of the model, parameters can be left at  
66 their default values, taken from databases, derived from empirical equations or estimated using  
67 expert judgment; any of these procedures will introduce uncertainty into the model, in addition to the  
68 simplification of the physics and processes by a model conceptualisation (Dubus et al., 2003). These  
69 uncertainties are responsible for reducing the predictive capacity of the simulation, providing results  
70 that differ from reality. In addition, different sources of uncertainty can magnify the overall  
71 uncertainty of the outputs (Zhang et al., 1993). An uncertainty analysis of key sources of uncertainty  
72 in the input parameters was also included to assess their impact on model simulations.

## 73 **2 Methods**

### 74 **2.1 Site description and data acquisition**

75 The Wensum catchment is located in the eastern region of the UK, to the north west of Norwich and  
76 covers an area of approximately 650 km<sup>2</sup>. The River Wensum flows approximately 78 km through  
77 the county of Norfolk from Colkirk Heath to its confluence with the River Yare in Norwich (Figure  
78 1). The monitoring point located at Sweet Briar Road Bridge (National Grid Reference: TG 206 095)  
79 defined the simulated catchment. Slowly permeable soils with tile drainage systems located on the  
80 river valley (Beccles and Burlingham associations) constitute the main soils in the catchment (Hodge  
81 et al., 1984), accounting for 57% of the catchment area. At the top of the catchment, the soils are a  
82 combination of well-drained loamy soils (Barrow) with patches of sandy soils (Newport), whilst the  
83 Newport association predominates at the base of the catchment. The floodplains are dominated by  
84 peaty soils (Adventurers) and loamy and sandy soils with naturally high groundwater and peaty  
85 surface layers (Isleham). Meteorological data from the closest stations to the catchment were used  
86 including Norwich Airport (hourly rainfall), Wattisham (hourly solar radiation and daily maximum  
87 and minimum temperature) and Marham (hourly wind speed and vapour pressure) (Figure A-1).

88 Physicochemical properties of the pesticides used in the models were taken from typical values  
89 reported in the literature (Table A-1). Reported mean values of the soil-water partition coefficient  
90 normalised to soil organic carbon content ( $K_{oc}$ ) were used in the model; the exception was for  
91 propyzamide where the reported  $K_{oc}$  was very large (840 ml g<sup>-1</sup>). Pedersen et al. (1995) reported soil-  
92 water partition coefficient ( $K_d$ ) values for various soils with different organic carbon contents. Based  
93 on the organic carbon content of Beccles (1.7%) and Burlingham (1.4%),  $K_d$  values of 4.96 and 4.09  
94 ml g<sup>-1</sup>, respectively, were estimated by extrapolation of the reported data. These  $K_d$  values

95 correspond to an average  $K_{oc}$  value of  $292 \text{ ml g}^{-1}$  that was then used in the model to improve the  
96 simulation of propyzamide.

97 The simulated crops were winter wheat (WW) and oilseed rape (OSR) as they are the main crops  
98 present in the catchment and all of the pesticides simulated are applied to one or both crops. Generic  
99 crop parameters were taken from FOCUS (2000) Châteaudun scenario, except for dates of growth  
100 stages for WW which were modified to agree with typical growing information for the UK. Crop  
101 areas (Table A–2) and pesticide usage (Table A–3) reported biannually by crop and pesticide type as  
102 the total area treated with pesticide (in ha) and total pesticide weight applied (in kg) for the Eastern  
103 region were used to determine the proportion of crop area treated with pesticides and the application  
104 rates by assuming that the usage in the catchment would match that in the region. Dilution from  
105 untreated areas was implicitly included by calculating average application rates for the whole  
106 catchment for each of the pesticides simulated.

107 Measured data on water flow and pesticide concentrations in the River Wensum used for the model  
108 evaluation were supplied by the Environment Agency of England and Wales. Water flow was  
109 measured at the gauging station at Sweet Briar Bridge with 15-minute resolution and reported as  
110 daily mean flow. The frequency of water samples collected for pesticide analysis varied during the  
111 year but was usually twice a week (CSF, 2012). Grab water samples were also collected at Sweet  
112 Briar Road Bridge and sent for analysis by the UK National Laboratory Service using accredited  
113 methods developed to analyse suites of pesticides in natural waters. Table A–4 shows the limit of  
114 quantification for each pesticide as these changed during the studied period.

## 115 **2.2 MACRO model parameterization**

116 MACRO is a one-dimensional physically-based model of water flow and solute transport that divides  
117 the soil porosity into two flow domains, micropores and macropores. A full description of the  
118 governing equations and the model parameters has been given elsewhere (Jarvis et al., 1991).  
119 MACRO 5.2 was used to simulate water flow and pesticide loss through deep percolation and tile  
120 drainage. A modelling framework using MACRO was developed to simulate river flow in the  
121 Wensum which included a groundwater mixing model to simulate the baseflow behaviour of the  
122 river and to allow leaching water and pesticide in the saturated zone to mix before being routed to the  
123 river.

124 Urban areas are reported to account for approximately 2% of the Wensum catchment (Sear et al.,  
125 2006); however, this information refers to major urban areas, not taking into account roads, farms  
126 and small villages. For modelling purposes it was estimated that the total developed (constructed)  
127 areas would be about 4% of the catchment. In the model, it is considered that 50% of the rainfall

128 from hard surfaces will enter the river network as rapid runoff. Surface runoff was the only source of  
 129 flow considered from the developed areas.

130 Comparison of river flow with modelling using RZWQM (Ma et al., 2004) and PRZM (Carsel et al.,  
 131 1985) suggested that surface runoff from arable land was not a significant process in the catchment,  
 132 so neither model was included in the framework (Villamizar, 2014). Other inflow and outflow  
 133 sources (such as water abstraction, irrigation and sewage discharge) were assumed to have little  
 134 impact on the hydrograph. Modelling results for the different pathways of water flow were scaled-up  
 135 to the entire catchment using an area-weighted average approach based on soil type. The conceptual  
 136 scheme in Figure 2a) summarises this strategy. Travel time was ignored, assuming that there is no  
 137 delay (larger than a day) between flow leaving the field and arriving at the catchment outlet.

138 An important aspect of flow estimation is the calculation and incorporation of the baseflow  
 139 component of the hydrograph. Baseflow is primarily generated from groundwater discharge into the  
 140 river network which depends on regional hydrological conditions. A simple groundwater mixing  
 141 model was developed to simulate the baseflow in the Wensum catchment and the transfer of  
 142 pesticide that could reach the groundwater by leaching. The groundwater mixing model,  
 143 implemented via a spreadsheet calculation, performs a simple mass balance of water flow and  
 144 pesticide mass at a daily time step (Figure 2b and Equation 1). Input data are the simulated inflow  
 145 volume of deep water recharge ( $V_{i,t}$  in  $\text{m}^3$ ) and pesticide leaching mass that reaches the groundwater  
 146 ( $m_{i,t}$  in mg), predicted by MACRO at a daily time-step ( $t \geq 1 \text{ day}$ ). The aquifer is represented as a  
 147 mixing tank ( $T$ ) with the same base area as the catchment. The daily volume of water ( $V_{T,t}$ ), pesticide  
 148 mass ( $m_{T,t}$ ) and concentration ( $C_{T,t}$ ) in the aquifer are also calculated on a daily basis (in  $\text{m}^3$ , mg and  
 149  $\text{mg m}^{-3}$ , respectively). The outputs ( $o$ ) from the model are the volume of water ( $V_{o,t}$ ), pesticide mass  
 150 ( $m_{o,t}$ ) and concentration ( $C_{o,t}$ ) outflow (in  $\text{m}^3$ , mg and  $\text{mg m}^{-3}$ , respectively) moving from the  
 151 groundwater (or tank) to the river at the rate of the outflow factor,  $OF$ , which was set at a constant  
 152 value. The outflow factor and the initial tank volume ( $V_{T,1}$ ) were set by manual trial-and-error  
 153 calibration against Nash-Sutcliffe model efficiency coefficients plus visual comparison to match  
 154 measured flow during periods dominated by baseflow and the flow at the beginning of the  
 155 simulation, respectively. Pesticide degradation and sorption in the saturated groundwater zone are  
 156 assumed to be negligible within the model.

157 *Inflow (i)*  $V_{i,t}; m_{i,t}$

158 *Tank (T)*  $\begin{cases} V_{T,t}; m_{T,t} = m_{i,t}; C_{T,t} = m_{T,t} / V_{T,t}, & \text{if } t = 1 \\ V_{T,t} = V_{T,t-1} - V_{o,t-1} + V_{i,t}; m_{T,t} = m_{T,t-1} - m_{o,t-1} + m_{i,t}; C_{T,t} = m_{T,t} / V_{T,t}, & \text{if } t > 1 \end{cases} \quad (1)$

159  $Outflow (o) V_{o,t} = (V_{T,t} + V_{i,t}) \times OF; m_{o,t} = C_{T,t} \times V_{o,t}$

160 Soil profiles for each simulation were divided into 60 layers. The only soils requiring tile drainage  
161 systems were Beccles and Burlingham. Initial moisture content in the different horizons at the start  
162 of the simulations was set to field capacity. A constant hydraulic gradient was used as the bottom  
163 boundary condition in the model. Input values were established from a combination of guidance on  
164 how to parameterise MACRO (Beulke et al., 2002; FOCUS, 2000) as follows: the boundary water  
165 tension between micropores and macropores (CTEN) for each horizon was selected from suggested  
166 values based on clay content. Then, their respective water content values (XMPOR) were derived  
167 from water release curves measured on intact cores in the laboratory (water content at zero suction)  
168 (Hallett et al., 1995) by interpolation between the two points of the water release curve closest to  
169 CTEN; the boundary conductivity (KSM) was calculated from CTEN and XMPOR using the  
170 equation proposed by Laliberte et al. (1968) and Jarvis et al. (1997) and the pore size distribution  
171 factor for macropores (ZN) was initially established by expert judgement and then adjusted by model  
172 calibration.

173 Only very limited calibration of crop and soil parameters was carried out to improve the simulation  
174 of the flow recovery at the end of low-flow periods. Maximum root length was decreased to reduce  
175 soil water extraction from deeper layers. Soil parameters for Beccles and Burlingham were calibrated  
176 to increase water infiltration capacity by facilitating the movement of water in the soil profile. The  
177 modified parameters were the tortuosity/pore size distribution factor for macropores (ZN) and the  
178 effective diffusion path length (ASCALE). ZN was reduced by 1.0 for all horizons in Beccles and by  
179 0.5 for the first two horizons in Burlingham. For Burlingham, ASCALE was increased to 10 for the  
180 first horizon since the original value of 5 was relatively small (common values range between 10 and  
181 40). ZN is a sensitive parameter that influences preferential flow and cannot be measured directly;  
182 hence, systematic calibration is normally required (Beulke et al., 2002).

### 183 **2.3 SPIDER model parameterization**

184 The preferential flow model SPIDER simulates pesticide loss into surface water from the most  
185 important routes of pesticide entry which are spray drift, drainflow, surface runoff and lateral flow  
186 (lateral transport within the soil profile); a detailed description of the model is presented by Renaud  
187 et al. (2008). The catchment is described in the model as a series of land blocks (with similar soil and  
188 land use) and stream reaches interconnected according to the possible pesticide entry pathways  
189 which may be specified by the user. The model enables representation of the spatial variability of the  
190 catchment. In order to simulate pesticide transport in the soil profile in SPIDER, the soil porosity is

191 divided into two pore domains (macropores and micropores). This is a similar approach to MACRO,  
 192 but simplified to enable a reasonable simulation time at an hourly resolution at the catchment scale,  
 193 and also to simplify the parameterisation process. Then, vertical and lateral movement of water is  
 194 triggered by soil moisture exceeding field capacity. The water balance (mm for  $\theta$ , and mm h<sup>-1</sup> for all  
 195 other terms) at an hourly time step  $t$  is calculated from Equation 2:

$$196 \quad \theta_t = \theta_{t-1} + R_{soil,t} + Ir_t - ETa_t - P_t - LM_t - D_t - Ru_t \quad (2)$$

197 where  $\theta$  is the soil water content,  $R_{soil}$  and  $Ir$  are the amount of rainfall and irrigation, respectively,  
 198  $ETa$  is actual evapotranspiration,  $P$  is percolation through the soil profile,  $LM$  is lateral flow,  $D$  is  
 199 drainage via tile systems, and  $Ru$  is surface runoff (Renaud et al., 2008). Daily reference  
 200 evapotranspiration ( $ETr$ ) is first calculated with the FAO Penman-Monteith equation; then hourly  
 201  $ETr$  values are assumed to be the same for each hourly interval during daylight hours and hourly  $ETa$   
 202 is calculated from the crop and water stress coefficients following Allen (1998). Percolation above  
 203 any drained soil layer is calculated to include preferential flow where soil wetness exceeds a  
 204 threshold water tension at which macropore flow is initiated. Loss of water from the base of the  
 205 profile is controlled by a groundwater recharge value in the deepest layer of the soil profile specified  
 206 by the model user. If soil water content after percolation is greater than soil water at field capacity,  
 207 excess water can be removed as lateral flow for layers above the bottom elevation of a reach. Lateral  
 208 flow is described by the kinematic storage model of Sloan and Moore (1984) using the lateral  
 209 hydraulic conductivity, flow velocity, soil depth, slope angle and field length. Drainage is generated  
 210 in the model when the layer below the drained horizon is saturated and the soil water content is  
 211 greater than the field capacity in the drained horizon, or when the water table reaches the drained  
 212 horizon. Surface runoff is simulated when rainfall intensity exceeds the saturated hydraulic  
 213 conductivity of the soil or when rain falls on an already saturated soil.

214 The general equation of the soil pesticide balance to calculate the pesticide load (mg for  $PestL$  and  
 215 mg h<sup>-1</sup> for all other terms) at an hourly time step  $t$  for each layer is given by Equation 3.

$$216 \quad PestL_t = PestL_{t-1} + IL_t + PL_t - SDL_t - RL_t - DrL_t - LFL_t \quad (3)$$

217 where  $PestL$  is the pesticide load in the layer,  $IL$  is the load from either application or a layer above,  
 218  $PL$  is load from percolation,  $SDL$  is the pesticide degraded in the soil,  $RL$  is the load from runoff,  
 219  $DrL$  is load from drainage, and  $LFL$  is load from lateral flow. Any pesticide transferred from a field  
 220 into a stream reach is then transported with water flow into consecutive segments up to the  
 221 catchment outlet. Water flow is routed using the Muskingum method. Pesticide mass balance in  
 222 stream reaches accounts for pesticide inputs from land blocks, pesticide sorption to stream



223 sediments, degradation, losses by percolation and transport to the next stream reach (Renaud et al.,  
224 2008).

225 The Wensum catchment was described in SPIDER by dividing the river network into 24 stream  
226 reaches and the catchment area into 44 land blocks according to their soil association and their  
227 location relative to the river sections (Figure A–2). The assumption of relatively homogeneous  
228 conditions within these landscape elements is a prerequisite for the approach. Water lost as recharge  
229 was used as input to the groundwater mixing model to include the baseflow component of the  
230 hydrograph. The saturated vertical and lateral hydraulic conductivities of the soil as well as the  
231 hydraulic conductivity at field capacity were set to be calculated by the pedotransfer functions in  
232 SPIDER (Evans et al., 1999). The saturated hydraulic conductivity of the sediment layer was 0.5  
233 mm/h and the sediment bulk density, 0.8 g/cm<sup>3</sup>. Effective sediment thickness for interaction with  
234 pesticide was initially set to 3 mm but then was calibrated to a value of 1 mm to reduce total  
235 pesticide sorption to the sediment. Apart from pesticide degradation in the soil, SPIDER also  
236 simulates degradation in the river network so degradation values in water and sediment must be  
237 supplied to the model (Table A–5).

238 Model calibration was applied to SPIDER in order to improve the simulation of the water flow by  
239 adjusting the water balance to increase the predicted flow in the river network (i.e. increasing  
240 percolation and drainflow volumes and reducing evapotranspiration). Evapotranspiration coefficients  
241 for all crops were reduced taking into account winter conditions in the Wensum which is prone to  
242 freezing during this period. The new values were selected according to ranges reported by Allen  
243 (1998).

#### 244 **2.4 Model evaluation**

245 Modelling results were evaluated using visual comparison against the observed flow and pesticide  
246 concentrations and from calculation of the Nash-Sutcliffe model efficiency coefficients (NSE; (Nash  
247 and Sutcliffe, 1970). NSE values for the simulated flow were calculated on a daily and average daily  
248 time-step ( $t$ ) for MACRO and SPIDER, respectively for each hydrological year (September 1<sup>st</sup> to  
249 August 31<sup>st</sup>) using Equation 4.

$$250 \quad NSE = 1 - \frac{\sum_{t=1}^T (Q_o^t - Q_m^t)^2}{\sum_{t=1}^T (Q_o^t - \bar{Q}_o)^2} \quad (4)$$

251 where  $Q_o^t$  and  $Q_m^t$  are the observed and modelled flow at time  $t$ , respectively; and  $\bar{Q}_o$  is the observed  
252 mean value. NSE values can range from  $-\infty$  to 1. An efficiency of  $NSE = 1$  corresponds to a perfect  
253 match between the model and the observed data. A model efficiency of  $NSE = 0$  indicates that the

254 simulation is as accurate as the mean of the observed data, whereas simulations with NSE <0 occur  
255 when the observed mean is a better predictor than the model. Therefore, the best simulation results  
256 would have positive efficiency values near to one.

257 Comparisons between pesticide results were carried out on the simulated loads and maximum  
258 concentrations for each hydrological year (matching a crop year running September 1 – August 31)  
259 during the simulation period (2007-2011). The observed pesticide load was calculated from the daily  
260 measured pesticide concentration and water flow using Equation 5 when the concentration was  
261 above the LOQ.

$$262 \quad \text{PestL} = Q \cdot \text{PestC} \cdot 10^{-6} \quad (5)$$

263 where *PestL* is the daily pesticide load in kg, *Q* is the daily water flow in m<sup>3</sup> and *PestC* is the  
264 measured daily pesticide concentration in µg l<sup>-1</sup> multiplied by a conversion factor of 10<sup>-6</sup>. Daily  
265 simulated loads were first calculated and then added together to estimate the annual simulated load  
266 from SPIDER and MACRO for each crop year for the period 2007-2011.

267 Additional assumptions were made to calculate pesticide loads on days when the pesticide  
268 concentration was reported to be below the limit of quantification (LOQ). A limit value of 0.001 µg  
269 l<sup>-1</sup> was used to define the minimum pesticide concentration that was taken into account for the  
270 calculations. This value is set as the smallest of the LOQ reported for the studied pesticides (Table  
271 A-4). Then, the assumptions made for calculating the loads for these days were:

- 272 1) For days when the models (SPIDER or MACRO) simulated a pesticide concentration below a  
273 value of 0.001 µg l<sup>-1</sup>, the measured and the simulated concentrations were assumed to be zero. It  
274 was considered that if pesticide was neither detected in the sample nor simulated by the models,  
275 it is very unlikely that pesticide was actually present in the water.
- 276 2) For days when either of the models simulated a concentration above 0.001 µg l<sup>-1</sup>, the measured  
277 concentration was (arbitrarily) assumed to be 25% of the LOQ. This means that if one of the  
278 models predicts a pesticide concentration above the set limit of 0.001 µg l<sup>-1</sup> but it is not  
279 analytically quantified in the samples, there is reasonable probability that the pesticide was  
280 present in the water at a concentration smaller than the LOQ.

## 281 **2.5 Uncertainty analysis**

282 Model performance in the simulation of pesticide concentrations can be affected by several sources  
283 of uncertainty in the input parameters in addition to the simplification of the physical description and  
284 processes inherent to the model (structural error), the spatial scale and the temporal discretisation

285 applied in the simulations. The influence of uncertainties on model results varies depending on the  
286 sensitivity of the parameters; higher uncertainties on the most sensitive parameters would generate a  
287 greater impact on the accuracy of the simulation. Sensitivity analysis of pesticide fate models  
288 including SPIDER and MACRO have shown that simulations are greatly influenced by the quality  
289 and adequacy of precipitation data (Dubus and Brown, 2002; Renaud and Brown, 2008), pesticide  
290 sorption and degradation parameters (Dubus and Brown, 2002) and pesticide usage details,  
291 particularly application dates (Boithias et al., 2014; Holvoet et al., 2005).

292 For many years, the UK Meteorological Office (2010) has used the tipping-bucket rain gauge for the  
293 automatic recording of rainfall. Uncertainties from tipping-bucket gauges depend mainly on  
294 precipitation intensity and timescale (Ciach, 2003; Wang et al., 2008). Ciach (2003) estimated errors  
295 in rainfall data using tipping-bucket rain gauges for different timescales applying non-parametric  
296 regression tools; a standard error of 10% was obtained for hourly recordings and rainfall intensities  
297 similar to those observed at Norwich Airport. The effect of this uncertainty in model input was  
298 investigated by running simulations with consistently  $\pm 10\%$  of the measured hourly rainfall data.

299 Although, there are typical application dates reported for pesticides, actual application can vary  
300 depending on several factors such as the weather, recommendations on pesticide application and  
301 different crop types that the product can be applied to (Gericke et al., 2010). Actual information on  
302 pesticide usage in large catchments is seldom available and is difficult to obtain (Boithias et al.,  
303 2014; Dubus et al., 2003). An uncertainty analysis into the effect of the use of typical application  
304 dates in the model was undertaken for five of the six pesticides; the exception was MCPA since the  
305 observed emissions mainly occurred during summer periods when very little or no drain flow was  
306 simulated by both models. Carbetamide and propyzamide are post-emergence herbicides with  
307 residual action usually applied to OSR between the middle of October and the end of February. The  
308 recommendation is not to apply if heavy rain is expected within 48 hours and if drains are flowing or  
309 are about to flow. Assuming that farmers had followed these recommendations, SPIDER and  
310 MACRO were run varying the application date in intervals of 5 days by analysing the rainfall  
311 patterns during the crop season. Simulations for chlorotoluron and mecoprop, herbicides mostly  
312 applied on cereals during the autumn-winter period, were run between late October and November  
313 with 5-day intervals. Clopyralid is a herbicide with a variety of uses in crops and grassland usually  
314 applied during the spring. Simulations for this pesticide were run with a combination of two  
315 application dates from late February to early March together with an application in May.

316 The effect on pesticide simulations due to uncertainties in the use of average reported pesticide  
317 sorption and degradation values was evaluated by running different simulations for four of the six

318 pesticides and comparing with the original simulation. The selection criteria for inclusion was  
319 availability of average and range in sorption and degradation values from regulatory studies within  
320 the pesticide properties database (PPDB) (Lewis et al., 2015). An evaluation of extreme parameter  
321 combinations was carried out for each compound by running four simulations combining maximum  
322 and minimum  $K_{oc}$  and degradation half-life ( $DT_{50}$ ) values (Table A–1).

### 323 **3 Results**

#### 324 **3.1 Simulation of water flow**

325 The uncalibrated simulations from both models showed under-estimation of the flow for all  
326 hydrological years (Table 1 and Figure A–3). After calibration the flow increased significantly for all  
327 hydrological years and a good match of the flow was obtained for the year 2009/10 using MACRO.  
328 In general, MACRO was closer in the simulation of the observed water flow than SPIDER. For both  
329 models, 2008/09 was the hydrological year with greatest under-estimation of the flow; this year was  
330 the driest of the four simulated (Table 1). The calibrated hydrographs are compared to the observed  
331 flow in Figure 3. Both models showed good simulation of the pattern of water flow. However, both  
332 models over-estimated flow during periods of greatest flow and under-estimated flow during periods  
333 of low flow. The level of under-estimation throughout the simulation was a more significant issue  
334 than over-estimation, particularly during low-flow periods. A better simulation of the recession  
335 periods was achieved for MACRO while the simulated flow from SPIDER was significantly smaller  
336 than the observed flow. In contrast, during periods of flow recovery (i.e. at the end of low-flow  
337 periods) SPIDER matched the timing of increase in flow much better than MACRO.

338 No surface runoff was predicted by the models for the Wensum primarily due to the efficiency of the  
339 tile drainage system. From this result, it was expected that surface runoff generated from arable land  
340 would be small. Both models achieved positive model efficiency values for all hydrological years;  
341 however, best NSE values were generally achieved for MACRO. A comparison of the actual  
342 evapotranspiration calculated by the two models (Figure A–4) showed that for MACRO was 10.1%  
343 larger than that for SPIDER over the simulation period. This difference in evapotranspiration is very  
344 evident particularly during the summer periods for MACRO which reduces soil moisture content and  
345 prevents the soil from wetting up as rapidly as for SPIDER.

#### 346 **3.2 Pesticide concentrations**

347 Comparisons between simulated and measured pesticide concentrations are presented for  
348 chlorotoluron, carbetamide and clopyralid in Figure 4 and for mecoprop, propyzamide and MCPA in  
349 Figure A–5. Most of the pesticide simulations showed that the models were able to simulate the  
350 overall pattern, though not the exact magnitude and timing, of pesticide concentrations at the

351 catchment outlet. The exception was for pesticides applied during spring and summer periods such as  
352 clopyralid (Figure 4c) and MCPA (Figure A-5c) where large disagreement was observed  
353 between simulations and the measured concentrations. Table A-5 compares measured and simulated  
354 values for load and maximum concentration in each hydrological year for all pesticides.

355 Both models achieved a relatively good simulations of the overall pattern of pesticide concentrations  
356 for chlorotoluron (Figure 4a). Some differences were observed between simulations. SPIDER  
357 predicted peaks earlier than MACRO with first presence in water generally simulated from  
358 November and December for SPIDER and MACRO, respectively. MACRO tended to over-estimate  
359 concentrations for most of the years by up to one order of magnitude whereas SPIDER had a better  
360 match in timing and magnitude of the peaks for most of the hydrological years; the exception was for  
361 2008/09 where SPIDER under-estimated pesticide concentrations by up to a factor of six.

362 For carbetamide (Figure 4b), both models under-estimated concentrations by similar amounts.  
363 SPIDER again simulated water contamination earlier in the winter than MACRO. Better simulations  
364 for carbetamide were observed using SPIDER than MACRO, especially in 2010/11 where a good  
365 match in the pattern and timing of the peaks was obtained. For clopyralid (Figure 4c.), SPIDER  
366 achieved a better simulation and was able to simulate most of the observed peaks, while MACRO  
367 only simulated one peak (in March 2010) at a concentration larger than the LOQ.

368 Brown et al. (2002) proposed a semi-quantitative approach to evaluating a catchment model intended  
369 for pesticide management purposes, whereby simulated loads and maximum annual concentrations  
370 were evaluated as being within a factor of 2, 5 or 10 of measured values. Applying this approach to  
371 the data in Table A-6, both models gave good simulations of maximum concentrations of  
372 chlorotoluron and mecoprop (many simulations within a factor of 2 of observed values, all  
373 simulations within a factor of 5). Simulations of loads for these two compounds were also good with  
374 the exception of 2009/10 where MACRO in particular over-estimated the loads significantly. All  
375 simulated maximum concentrations and loads of carbetamide were within a factor of 10 of measured  
376 values, whilst propyzamide was often well simulated (factors of 2-5) except in 2008/09 when  
377 transport was greatly under-estimated by both models. SPIDER gave much better simulations than  
378 MACRO for clopyralid, whereas both models failed to match the observed behaviour for MCPA as  
379 noted above.

380

### 381 **3.3 Uncertainty analysis for SPIDER and MACRO simulations**

#### 382 **3.3.1 Uncertainty in the rainfall data**

383 The observed flow for each hydrological year and for the simulation period 2007-2011 was bounded  
384 for some periods by the simulations from the two rainfall datasets (measured +/-10%) for both  
385 models (Figure A-6). However, the effect of uncertainty in the rainfall was more evident for  
386 MACRO. The exceptions were for hydrological years 2008/09 and 2010/11 when both models and  
387 only SPIDER, respectively, under-estimated the flow even after increasing the rainfall by 10%.  
388 Uncertainty in the rainfall data had a big impact on the simulation of stream flow for the two models  
389 in both high- and low-flow periods but the greatest relative change during storm flow events was  
390 observed when increasing the rainfall by 10%. A large effect on the simulated flow was observed for  
391 the end of low-flow periods using MACRO; a great improvement was observed by increasing the  
392 rainfall data by 10% since the model predicted some of the peaks that were not simulated previously.  
393 A similar behaviour was observed from SPIDER but the impact was smaller than for MACRO  
394 during low-flow periods. In addition, the difference between the simulated and observed flow in the  
395 timing of flow recovery after summer for both rainfall datasets was approximately 15 days for  
396 SPIDER, but almost one month for MACRO.

#### 397 **3.3.2 Uncertainty in the application date**

398 Table 2 and Table A-7 show the variation in simulated pesticide loads over a 4-year period (kg/4  
399 years) on dates when pesticide application is likely to occur for carbetamide and the other pesticides,  
400 respectively. The simulated loads from both models over a 4-year period for carbetamide were  
401 within a factor of two for most of the application dates in November compared to the observed load  
402 and were very similar between models. Application dates in mid- or late November showed better  
403 agreement with the measured load.

404 Uncertainty in the application date had a smaller impact on pesticide loads for some pesticides. For  
405 instance, the resulting loads for propyzamide using SPIDER and for clopyralid using MACRO varied  
406 by less than 0.3 kg across all application dates simulated. Mecroprop was the pesticide that showed  
407 the greatest variation in loads (more than 100 kg using both models); this compound is impersistent  
408 in soil so timing of application relative to timing of storm event is an important influence on  
409 simulations. Across the full dataset, there was a tendency for SPIDER to be more sensitive than  
410 MACRO to changes in application date.

### 411 **3.3.3 Uncertainty in pesticide sorption and degradation**

412 The effect of uncertainty from using average sorption and degradation data was analysed by  
413 comparing pesticide loads for simulations using combinations of extreme input data (maximum and  
414 minimum sorption and degradation values derived from the literature). The results of this bounds  
415 analysis are shown in Table 3 and Table A–8 for carbetamide and the other pesticides, respectively.  
416 This source of uncertainty had a greater impact on the simulated pesticide load than the uncertainty  
417 due to the application date, but the impact was again compound-specific.

418 Simulated loads were greatest for the combination of minimum  $K_{oc}$  and maximum half-life while the  
419 smallest loads were obtained by using maximum  $K_{oc}$  and minimum half-life. Extreme differences in  
420 simulated loads were obtained for MCPA; losses were negligible when using the minimum half-life  
421 value because the pesticide largely degraded in soil before the first flow event after application.  
422 Uncertainty in pesticide sorption had a bigger impact on the simulation of loads than uncertainty in  
423 degradation. The simulated ranges for both models covered the observed loads for most pesticide-  
424 model combinations. For example, the range of simulated loads from both models covered the  
425 observed load of 23.3 kg over 4 years at the catchment outlet for carbetamide (Table 3); this  
426 measured load corresponds to  $0.36 \text{ g ha}^{-1} \text{ yr}^{-1}$  or 0.023% of applied carbetamide.

427

## 428 **4 Discussion**

### 429 **4.1 Simulation of water flow**

430 The hydrograph simulations from MACRO and SPIDER showed a reasonably good match in the  
431 timing and size of peak flow compared to the measured data. However, there was a trend for the  
432 models to over-estimate flow during periods of greatest flow; this may be attributable to structural  
433 errors within the models due to their simplified representation of the environment, but might also  
434 relate to flood control measures within the catchment that were not included in the model. Flood  
435 management in the Wensum includes changes in the course and dimensions of the river channel,  
436 changes in the connectivity between the river and the floodplain, removal of the bed substrate and  
437 deposited fine sediment, control of aquatic and riparian vegetation and alterations to the water levels  
438 within the channel and downstream movement of sediment (mill weirs, sluices) (Sear et al., 2006).  
439 Model efficiency values after calibration showed that the simulation of the water flow from MACRO  
440 (NSE = 0.56) was better than that achieved by SPIDER (NSE = 0.34). Renaud and Brown (2008)  
441 obtained very similar model performance for SPIDER in two field studies in the UK (at Cockle Park,  
442 Northumberland and Maidwell, Northamptonshire) but in both cases SPIDER simulations were not  
443 calibrated. The authors found similar model performance for MACRO (NSE = 0.35) and SPIDER

444 (NSE = 0.32) for the site located at Cockle Park, whilst for the site located at Maidwell, model  
445 performance without calibration was considerably better for SPIDER (NSE = 0.23) than for MACRO  
446 (NSE = -0.61). The water flow simulation from SPIDER was significantly improved for Maidwell  
447 after minimal calibration (NSE = 0.55). Calibration to improve simulation of drainage early in the  
448 period was achieved through small changes to the water content at field capacity and the initial water  
449 content of the soil, a reduction in the rate of recharge and an increase in the fraction of soil in contact  
450 with macropores. Both studies reported by Renaud and Brown (2008) were carried out at field scale  
451 where input parameters are likely to have smaller variability than that observed at catchment level so  
452 that less uncertainty was expected in model results.

453 The GW model significantly improved model efficiency for both models before model calibration  
454 (from NSE = -0.12 to NSE = 0.45 for MACRO and from NSE = -0.19 to NSE = 0.23 for SPIDER).  
455 Tediosi et al. (2013) also reported a coupled model using MACRO and a simple groundwater model  
456 to simulate the water flow in a small (15.5 ha) headwater sub-catchment located in the Upper  
457 Cherwell in central England. This groundwater model was developed based on a variation of the  
458 saturated thickness (Rushton and Youngs, 2010) using typical values of hydraulic conductivity and  
459 specific yield for the study area. According to the authors, this approach showed a good  
460 representation of the recession periods in the hydrographs and the simulation of the water flow which  
461 increased model efficiency from 0.02 to 0.56 and the hydrograph was only affected by under-  
462 estimation of flow during periods of either standing snow or low precipitation.

463 Model calibration was applied to the simulations using MACRO and SPIDER to increase water flow  
464 and to improve the simulation of the low-flow periods. The simulation of recovery flow was slightly  
465 improved in both models; however, no improvements were observed for the recession periods of  
466 flow in the summer (Figure A-3). SPIDER generally simulated peaks in drainflow earlier than  
467 MACRO at the end of the lowest flow periods. One possible reason is an over-estimation of  
468 evapotranspiration by MACRO. Besien et al. (1997) suggested that such an over-estimation caused  
469 the model to miss drainflow events generated by low rainfall in early spring affecting both drainflow  
470 and pesticide simulations for that period. In this study, it was found that over-estimation of  
471 evapotranspiration was also critical for the early autumn period (i.e. at the beginning of the winter  
472 flow period), which caused the model to misrepresent the flow recovery rate. Over-estimation of  
473 evapotranspiration by MACRO during the summer periods delays flow recovery, consequently  
474 causing the water flow simulation to miss drainflow and pesticide losses at those times. When pre-  
475 calculated evapotranspiration from SPIDER was used in MACRO, both drainflow and river flow  
476 showed an improvement in simulation of earlier drainflow events and in the flow rate at the end of



477 the lowest flow periods (Figure A-7). This suggests that the FAO Penman–Monteith equation  
478 (Allen, 1998) used by SPIDER may be a better approach than the original Penman–Monteith  
479 equation (Monteith, 1965) used by MACRO for the calculation of the evapotranspiration under the  
480 study conditions. The FAO Penman–Monteith equation is recommended by Allen (1998) as it  
481 provides more consistent evapotranspiration values in all regions and climates.

482 A common challenge in hydrological modelling is to obtain accurate rainfall data since it is the main  
483 driver controlling the accuracy of hydrological and solute simulations (Bardossy and Das, 2008).  
484 Rainfall gauge measurements are subject to uncertainty, and under-estimation of rainfall from rain  
485 gauge measurements is common during low intensity precipitation and/or high winds (Ciach, 2003;  
486 Wang et al., 2008). As errors in rainfall measurements are variable over time, the impact on water  
487 flow simulation varies during the hydrological year. Owing to the complex nature of rainfall, model  
488 calibration from this source of uncertainty can only be achieved by the use of more accurate  
489 measurements. Other hydrological models such as rainfall-runoff models used for flood forecasting  
490 have also been affected by rainfall uncertainty (Bardossy and Das, 2008; Moulin et al., 2009).  
491 Moulin et al. (2009) suggested that meteorological services should deliver rainfall data along with  
492 information about the confidence intervals generated in real time. This information would be useful  
493 in applying probabilistic approaches that could express uncertainty in hydrological simulations. In  
494 addition, climate data and particularly the precipitation falling over a location vary both spatially and  
495 temporally (Obled et al., 1994; Wood et al., 1988). A limited number of rain gauges may not be able  
496 to capture the spatial variability of rainfall, particularly on large catchments, adding errors to model  
497 results.

#### 498 **4.2 Pesticide simulation**

499 This is the first time that SPIDER has been tested using long-term monitoring data collected for a  
500 relatively large catchment. Both models were able to simulate a large number of the observed peaks  
501 for pesticides at the catchment outlet as well as the overall pattern of behaviour of most of the  
502 pesticides despite the simple nature of the models and not including surface runoff in the simulations.  
503 Apart from the peaks that MACRO missed in early autumn due to under-estimation in the flow, most  
504 of the simulations showed reasonable agreement with measured behaviour; however, some  
505 disagreements were observed in the timing and magnitude of peaks. The exception was for  
506 clopyralid and MCPA where significant differences in the simulations were observed both relative to  
507 measured data and between models.

508 Holvoet et al. (2007) considered that in-stream processes and state variables (e.g. microbial activity,  
509 dissolved oxygen concentration, pH, sedimentation, re-suspension) have a significant impact on

510 modelling pesticides at the catchment-scale. However, in the present study, the modelling framework  
511 was able to satisfactorily simulate water flow from a relatively large catchment like the Wensum and  
512 predict reasonably well the pattern of pesticide concentrations even though the framework ignored  
513 in-stream processes suggesting that the river system had a relatively minor influence on patterns of  
514 pesticide concentrations at the catchment outlet. Modelling results suggested that pesticide  
515 concentrations in water were driven primarily by field-scale processes. There was no major  
516 difference between simulations from a modelling framework composed of field-scale models and  
517 from a catchment-scale model when applied to a medium-sized catchment in Eastern England. An  
518 implication is that provided field-scale processes are well captured by a model, then it should be  
519 possible to approximate pesticide export at the catchment scale. This is in agreement with other  
520 studies that have suggested the possibility to predict the order of magnitude of pesticide losses from  
521 catchments based on information on pesticide and soil properties plus pesticide usage (Pistocchi,  
522 2013).

523 The best simulations were observed for pesticides that are normally applied in late autumn such as  
524 chlorotoluron, mecoprop, carbetamide and propyzamide. These pesticides are mainly applied to a  
525 single crop type, so uncertainty in their usage patterns (i.e. application date and amount) is relatively  
526 small. For instance, chlorotoluron is exclusively applied as a pre- or early post-emergence herbicide  
527 to winter cereals to control annual grasses and broad leaved weeds. In addition, the relatively large  
528 degradation half-life (59 days) means that differences in the application date will have relatively little  
529 impact on the timing and magnitude of pesticide peaks simulated by the models.

530 Propyzamide and carbetamide showed a good agreement between the pattern of the simulated  
531 concentrations and the measured data but with some disagreements in the magnitude of the peaks.  
532 These pesticides are mainly used to control broadleaved weeds and blackgrass that is resistant to  
533 other herbicides. Pesticide application takes place between October and the end of February  
534 depending on soil moisture and temperature. The relatively wide window of time for application and  
535 the specific environmental conditions required mean that the use of a uniform and fixed application  
536 date would generate uncertainty that will mainly affect the magnitude of the peaks. This uncertainty  
537 in the application date had a greater impact on the simulation of carbetamide than propyzamide  
538 losses. The moderately large  $K_{oc}$  ( $292 \text{ ml g}^{-1}$ ) and half-life (47 days) selected to simulate  
539 propyzamide mean that the pesticide binds strongly to soils and persists for a long time. In contrast,  
540 carbetamide has both weaker soil sorption ( $K_{oc} = 89 \text{ ml g}^{-1}$ ) and shorter half-life (10.9 days) so if  
541 there is a delay between application date and a storm event, pesticide transfers to tile drains would be  
542 reduced due to pesticide degradation.

543 Clopyralid and MCPA concentrations proved difficult to simulate due to the complex and uncertain  
544 usage pattern of these pesticides. Clopyralid is applied to a wide range of crops including cereals,  
545 grassland, amenity grass/lawns, OSR, brassicas and maize and MCPA is used on cereals, grassland  
546 and amenity grass/lawns. These post-emergence herbicides are mainly applied during spring and  
547 throughout the summer when weeds are actively growing. Since these herbicides can be applied  
548 during a very wide window of time, the uncertainty generated by the use of fixed application dates  
549 can greatly affect the simulation. Different authors have suggested supplying application date as a  
550 probability distribution in fate models (Holvoet et al., 2005; Lindahl et al., 2005). However, this  
551 approach also requires knowledge of the distribution of application dates throughout the catchment.  
552 Gericke et al. (2010) used phenological data for different crops along with climate data to estimate  
553 application dates in Germany and the Czech Republic; satisfactory results were obtained when  
554 comparing estimated to actual application dates. This approach can provide a broader amount of  
555 information to estimate application dates but the methodology requires further development and  
556 validation under different environmental conditions.

557 For clopyralid, MACRO only predicted three small peaks that were due to pesticide drainflow, whilst  
558 the model missed other events that SPIDER simulated. It was observed that important losses of  
559 clopyralid could be due to sub-lateral flow (through-flow); SPIDER simulates this whereas MACRO  
560 does not account for pesticide loss by this route. Clopyralid was different from other compounds  
561 where drainflow dominated because losses occurred in late spring when drains may not be flowing  
562 and sub-lateral flow may be a relatively important contributor to catchment hydrology.

563 The uncertainty analyses for the simulation pesticide losses in the present study showed that  
564 uncertainty from individual input parameters could explain some of the observed disagreements in  
565 the simulation from the two models. Simulated loads from both uncertainty analyses (application  
566 date and sorption and degradation data) using both models generally covered the observed load for  
567 the simulation period. However, a combination of different sources of uncertainties might be the best  
568 explanation of discrepancies in simulated concentrations. The exception was for MCPA due to the  
569 lack of simulated drainflow on days when emissions were observed and for clopyralid using  
570 MACRO for the reasons explained above.

571 The impact on the simulated loads of uncertainty in both application timing and pesticide properties  
572 was model- and compound-specific. Boithias et al. (2014) carried out a sensitivity study using  
573 plausible ranges of application dates for two contrasting pre-emergence herbicides in SWAT. The  
574 authors also found that the effect of the application date was a pesticide-specific factor influenced by  
575 their bioavailability and hence by sorption and degradation. For runoff models like SWAT pesticide

576 sorption was shown to be more important than degradation in determining the availability of  
577 pesticides in the runoff interaction zone. For preferential flow models, the availability for pesticide  
578 loss would depend on the leaching potential of pesticides to reach tile drains where both parameters  
579 (degradation and sorption) are known to be important (Arias-Estevez et al., 2008; Carter, 2000).  
580 Pesticides with high leaching potential likely to reach tile drains via preferential flow are  
581 characterised by having slower degradation rates and weaker soil sorption (Gardner, 2014).

582 Model evaluation was in some cases affected by the resolution of the measured pesticide  
583 concentrations. Some important emissions predicted by the models could not be evaluated due to the  
584 absence of monitoring data for those days. Monitoring frequency varies within crop years and a large  
585 proportion of none detections was observed for most herbicides. For instance, only 73 of the 395  
586 samples taken between September 2007 and November 2011 for the analysis of chlorotoluron  
587 contained residues above the LoQ; however, during this period SPIDER predicted 139 days with  
588 emissions on days when samples were not taken. The CSF monitoring programme has a moderate  
589 sampling frequency (an average of one sample every four days) and this resolution is useful to  
590 analyse pesticide trends and to undertake model evaluation; however, modelling results show that the  
591 monitoring programme could be made more efficient by applying a more variable sampling  
592 frequency during the year. A report from the CSF (2012) explains that the monitoring design was  
593 based on the major crop types present in the catchment and highlights that a large proportion of the  
594 pesticides analysed are not detected in the samples. This report notes that predicting the likelihood of  
595 occurrence of a pesticide is a complex task that is influenced by many factors such as pesticide  
596 properties, soil types, and pesticide usage and drainage systems (CSF, 2012). Pesticide fate  
597 modelling takes into account all these factors and helps avoid bias and speculative methodologies.  
598 Fate models have been shown to be a useful tool to improve the design of monitoring programmes  
599 (e.g. by focusing sampling collection on days when pesticides are most likely to be present) and can  
600 be easily incorporated into programmes without a big financial investment.

601

## 602 **5 Conclusions**

603 The modelling framework simulated fairly well the main sources of water flow contributing to the  
604 river network in the Wensum catchment and their associated pesticide losses though there was  
605 variable performance between individual pesticides. As the framework excluded the simulation of in-  
606 stream processes, results suggest that field-scale processes may be important in determining patterns  
607 of pesticide contamination at the catchment outlet. The models showed a better performance for  
608 pesticide losses coming from pre- or early post-emergence herbicides normally applied during

609 autumn probably because of their less complex usage patterns; an alternative explanation is that  
610 important hydrological pathways resulting in pesticide losses during spring and summer periods were  
611 poorly simulation by the models. Uncertainty analyses of sensitive input parameters showed that the  
612 impact of parameter variation on pesticide simulations was compound-specific. The simulation of  
613 low-flow periods was greatly affected by uncertainty from rain gauge measurements and the  
614 simulation of evapotranspiration. More studies into the combined effect of uncertainties in fate  
615 modelling as well as in pesticide-specific uncertainty would strengthen the understanding of their  
616 impact on simulations.

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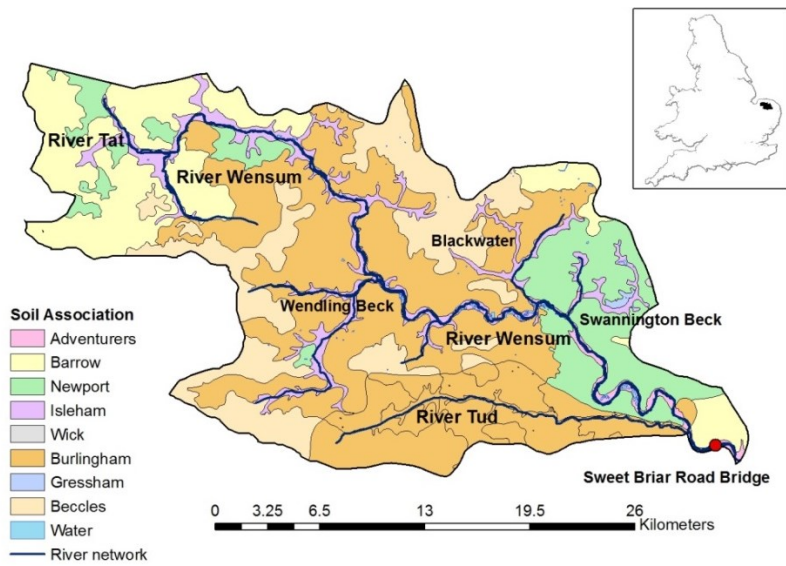
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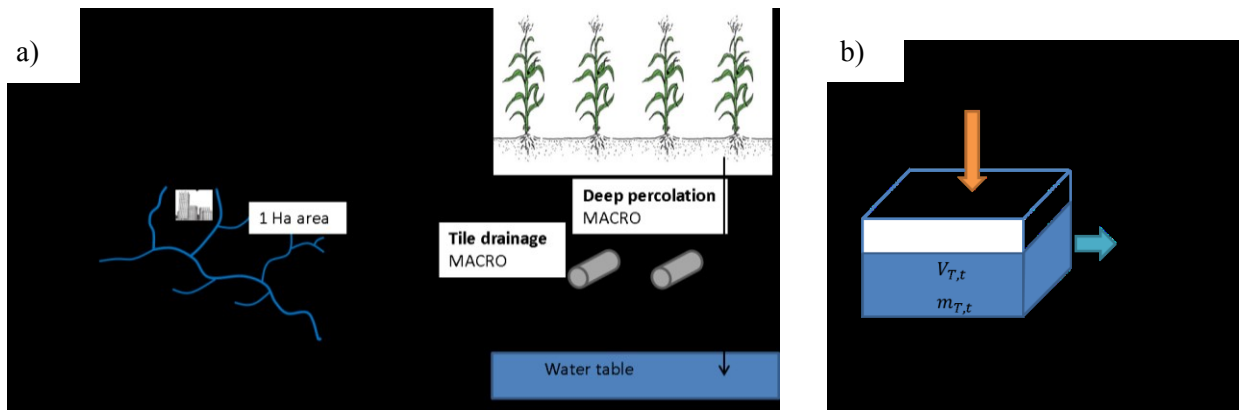
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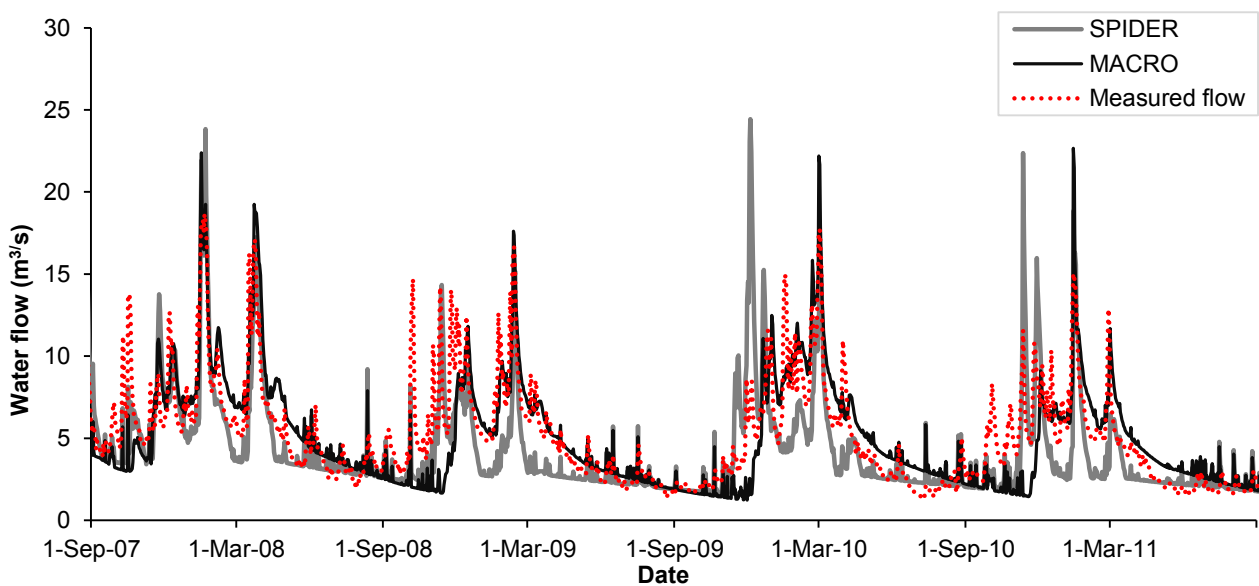
767 **Figure 1** Wensum catchment showing the river network and the catchment outlet at Sweet Briar Road Bridge.

768 Inset: location of the Wensum catchment within England and Wales.



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770 **Figure 2** Conceptual model of a) the framework using MACRO and b) the groundwater mixing model.

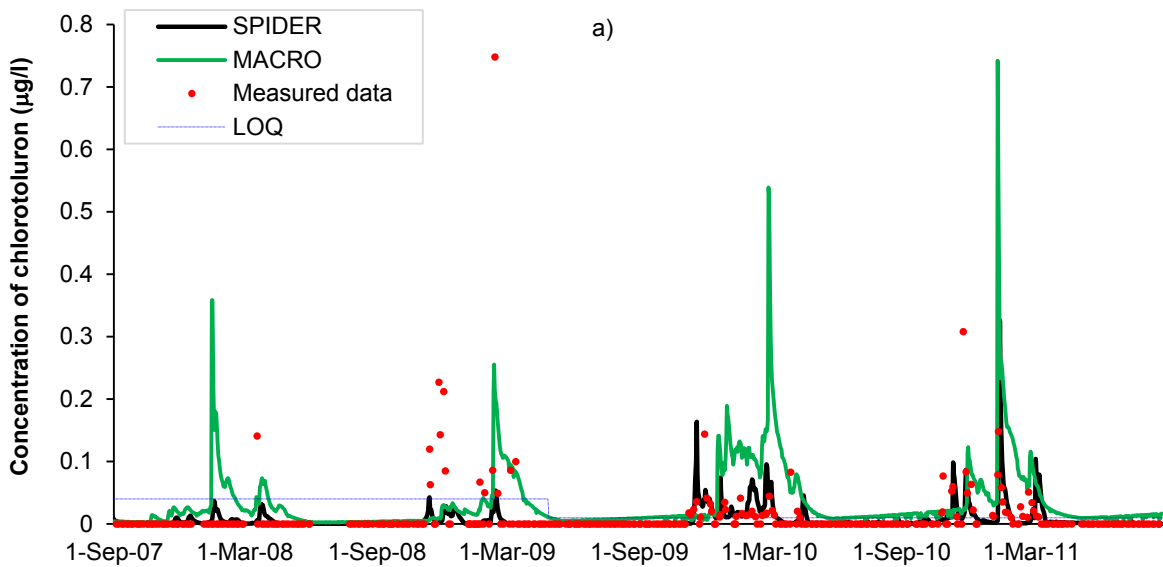


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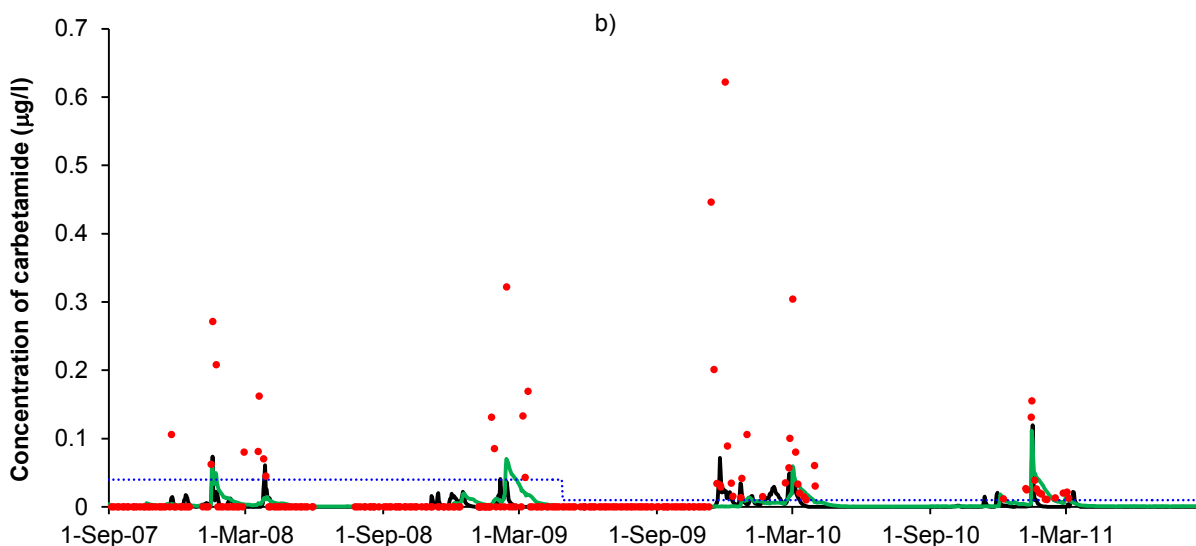
772 **Figure 3** Comparison of the measured and simulated water flow (calibrated simulations) by MACRO and

773 SPIDER. Measured flow supplied by the Environment Agency.

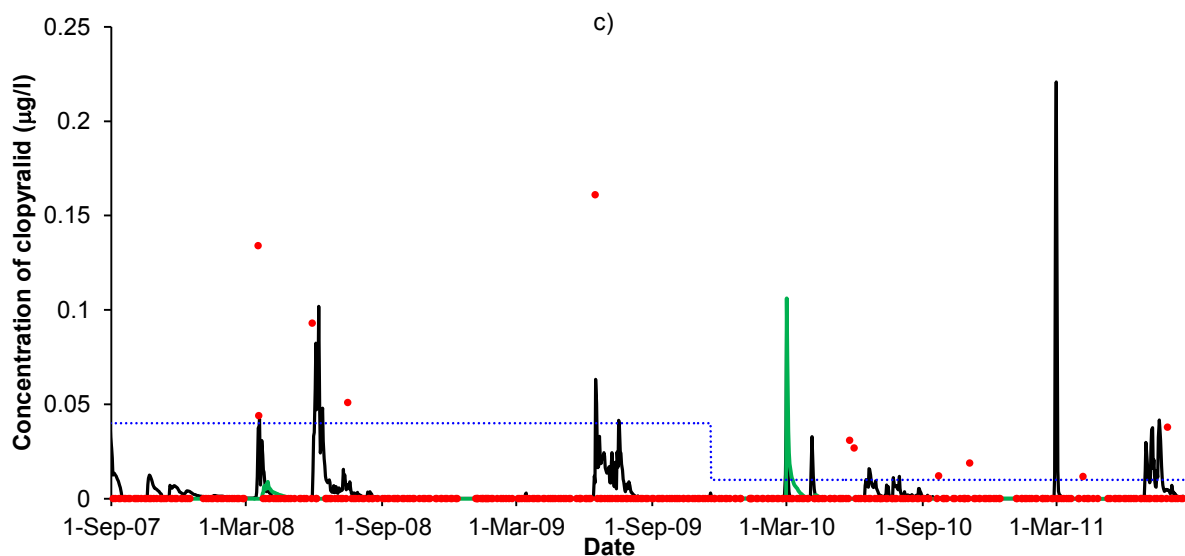
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777 **Figure 4** Comparison of measured pesticide concentrations with those simulated by SPIDER and MACRO for  
 778 a) chlorotoluron, b) carbetamide and c) clopyralid. The dotted line indicates the LoQ. Pesticide concentrations  
 779 <LOQ represented with a value of zero. Measured pesticide data supplied by the Environment Agency.

780 **Table 1** Comparison between observed and simulated flow for each hydrological year from the model  
 781 framework using MACRO and SPIDER before and after calibration including their NSE values and the  
 782 measured rainfall.

Hydrological year	Rainfall (mm)	Uncalibrated				Calibrated			
		Simulated flow (% of the observed flow)		NS		Simulated flow (% of the observed flow)		NS	
		MACRO	SPIDER	MACRO	SPIDER	MACRO	SPIDER	MACRO	SPIDER
2007/08	671.2	96.3	74.8	0.61	0.35	98.6	89.6	0.63	0.59
2008/09	543.3	73.5	50.2	0.10	-0.22	81.0	69.0	0.33	0.22
2009/10	593.0	91.2	77.3	0.64	0.33	100.7	91.9	0.72	0.15
2010/11	586.3	80.5	65.7	0.19	0.15	91.1	80.8	0.39	0.22
Total 4 years	2,393.8	85.9	67.2	0.45	0.23	93.0	83.0	0.56	0.34

783

784 **Table 2** Loads of carbetamide simulated by SPIDER and MACRO for different application dates in  
 785 November and comparison with the observed value.

	1 Nov	5 Nov	10 Nov	15 Nov	20 Nov	25 Nov	30 Nov	Observed data
<b>Loads (kg/4 years)</b>								
<b>SPIDER</b>	6.05	9.99	14.1	19.3	17.3	21.7	22.7	23.3
<b>MACRO</b>	11.5	14.5	21.5	22.5	15.3	14.2	20.1	

786

787 **Table 3** Loads of carbetamide simulated by SPIDER and MACRO using combinations of maximum and  
 788 minimum sorption and degradation values, together with the simulated load using average inputs and the  
 789 observed value.

	Avg. $K_{oc}$ Avg. $DT_{50}$	Max. $K_{oc}$ Max $DT_{50}$	Max. $K_{oc}$ Min. $DT_{50}$	Min. $K_{oc}$ Max $DT_{50}$	Min. $K_{oc}$ Min. $DT_{50}$	Measured data
<b>Loads (kg/4 years)</b>						
<b>SPIDER</b>	6.05	11.3	0.14	43.1	0.48	23.3
<b>MACRO</b>	11.5	28.6	1.56	74.1	1.83	

790 **Supplementary information**

791 Methodology

792 **Table A–1** Pesticide properties used in the models and sorption and degradation ranges used for the  
793 uncertainty analysis.

Pesticide	Koc (mL g <sup>-1</sup> ) <sup>a</sup>	DT <sub>50</sub> soil <sup>a</sup> (days)	Koc range <sup>a</sup> (mL g <sup>-1</sup> )	DT <sub>50</sub> soil range <sup>a</sup> (days)	TREF (°C)	TRESP (K <sup>-1</sup> )	EXPB	Freundlich coefficient <sup>b</sup>
Carbetamide	89	10.9	59 - 118	4 - 29	20	0.08	0.7	0.93
Chlorotoluron	184	59	108 - 384	52 - 66	20	0.08	0.7	0.90
Clopyralid	4.9	11 <sup>d</sup>	3.43 - 7.34	2 - 24 <sup>d</sup>	10	0.001	0.01	0.76
MCPA	74	24	38 - 157	7 - 41	20	0.08	0.7	0.68
Mecoprop	20	8.2	-	-	20	0.08	0.7	0.90
Propyzamide	292 <sup>c</sup>	47	-	-	20	0.08	0.7	0.90 <sup>c</sup>

794 TREF: Reference temperature. TRESP: Exponent in the temperature response function. EXPB: Exponent in  
795 the degradation water response function. <sup>a</sup>Lewis et al. (2015), <sup>b</sup>Netherton and Brown (2010), <sup>c</sup>Pedersen et al.  
796 (1995). <sup>d</sup>Field-based degradation rate.

797

798 **Table A–2** Crop areas in the Eastern region for target crops and arable land between 2005 and 2013.

	Crop area (ha)			
	2006 <sup>a</sup>	2008 <sup>b</sup>	2010 <sup>c</sup>	2012 <sup>d</sup>
Cereals	471,706	534,735	502,081	513,356
OSR	103,488	130,181	140,960	168,241
Beet	72,656	80,732	75,918	82,346
Total arable land	1,017,084*	987,447	967,621	990,137
	2005 <sup>e</sup>	2009 <sup>f</sup>	2013 <sup>g</sup>	
Grassland	29,137	36,103	37,065	

799 OSR: Oilseed rape. \* Including set-aside

800 <sup>a</sup>Garthwaite et al. (2007); <sup>b</sup>Garthwaite et al. (2009); <sup>c</sup>Garthwaite et al. (2011); <sup>d</sup>Garthwaite et al. (2013);

801 <sup>e</sup>Garthwaite et al. (2006); <sup>f</sup>Garthwaite et al. (2010); <sup>g</sup>Garthwaite et al. (2014)

802

803

**Table A–3** Pesticide usage information for the Eastern region of the UK.

Pesticide / Crop / Year	Total area treated with pesticide (ha)	Total pesticide weight applied (kg)	Pesticide / Crop / Year	Total area treated with pesticide (ha)	Total pesticide weight applied (kg)
<b>Chlorotoluron</b>	<b>Cereals</b>		<b>Carbetamide</b>	<b>OSR</b>	
2006 <sup>a</sup>	19,548	32,607	2006 <sup>a</sup>	12,121	25,086
2008 <sup>b</sup>	44,697	96,841	2008 <sup>b</sup>	30,383	61,725
2010 <sup>c</sup>	101,014	178,711	2010 <sup>c</sup>	26,066	49,453
2012 <sup>d</sup>	58,293	84,938	2012 <sup>d</sup>	27,229	45,596
<b>Clopyralid</b>	<b>Cereals</b>		<b>Clopyralid</b>	<b>Beet</b>	
2006 <sup>a</sup>	811	151	2006 <sup>a</sup>	65,273	4,810

2008 <sup>b</sup>	1,964	175	2008 <sup>b</sup>	64,532	4,856
2010 <sup>c</sup>	7,797	255	2010 <sup>c</sup>	107,283	7,835
2012 <sup>d</sup>	12,152	830	2012 <sup>d</sup>	58,830	4,673
<b>Clopyralid</b>	<b>Grassland</b>		<b>MCPA</b>	<b>Grassland</b>	
2005 <sup>e</sup>	9,233	1,311	2005 <sup>e</sup>	103,504	131,101
2009 <sup>f</sup>	23,988	4,597	2009 <sup>f</sup>	20,997	20,469
<b>Clopyralid</b>	<b>ORS</b>		<b>MCPA</b>	<b>Cereals</b>	
2006 <sup>a</sup>	34,848	2,767	2006 <sup>a</sup>	19,977	14,910
2008 <sup>b</sup>	94,076	7,729	2008 <sup>b</sup>	9,826	5,867
2010 <sup>c</sup>	98,711	7,794	2010 <sup>c</sup>	21,980	13,016
2012 <sup>d</sup>	137,486	11,781	2012 <sup>d</sup>	17,575	16,128
<b>Mecoprop</b>	<b>Cereals</b>		<b>Propyzamide</b>	<b>OSR</b>	
2006 <sup>a</sup>	167,289	98,793	2006 <sup>a</sup>	81,144	60,493
2008 <sup>b</sup>	187,286	102,590	2008 <sup>b</sup>	110,357	83,970
2010 <sup>c</sup>	180,532	95,611	2010 <sup>c</sup>	161,367	125,987
2012 <sup>d</sup>	135,446	77,745	2012 <sup>d</sup>	215,375	171,889

804 <sup>a</sup>Garthwaite et al. (2007); <sup>b</sup>Garthwaite et al. (2009); <sup>c</sup>Garthwaite et al. (2011); <sup>d</sup>Garthwaite et al. (2013);  
805 <sup>e</sup>Garthwaite et al. (2006); <sup>f</sup>Garthwaite et al. (2010)

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807

**Table A-4** Limits of quantification for the pesticides data supplied by the Environment Agency

<b>Pesticide</b>	LOQ (µg/l)	
	September 2006 to April 2009/*April 2010	May 2009/*May2010 to December 2011
Carbetamide	0.04	0.01
Chlorotoluron	0.04	0.01
Clopyralid	0.04*	0.01*
MCPA	0.04*	0.005*
Mecoprop	0.04*	0.005*
Propyzamide	0.005	0.005

808

809 **Table A-5** Pesticide degradation values in water and sediment obtained from laboratory studies and  
810 Freundlich coefficients used in SPIDER

<b>Pesticide</b>	<b>DT<sub>50</sub> water (days)<sup>a</sup></b>	<b>DT<sub>50</sub> sediment (days)<sup>a</sup></b>	<b>Freundlich coefficient<sup>a</sup></b>
Carbetamide	9.1	55.5	0.93
Chlorotoluron	42	352	0.90
Clopyralid	148	1000 <sup>b</sup>	0.85*
MCPA	13.5	17	0.85*
Mecoprop	37	50	0.90
Propyzamide	21	94	0.90

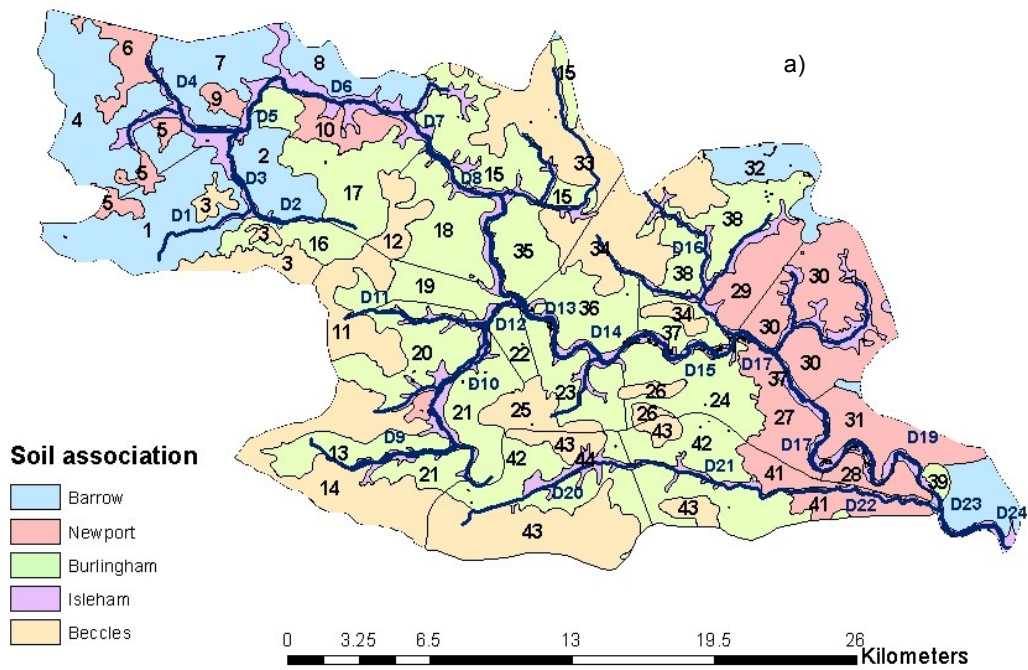
811 <sup>a</sup>Lewis et al. (2015), <sup>b</sup>Netherton and Brown (2010). \*Values adjusted to avoid sorption conflicts in the model  
812 because the reported values were too small (0.76 and 0.68 for clopyralid and MCPA, respectively).

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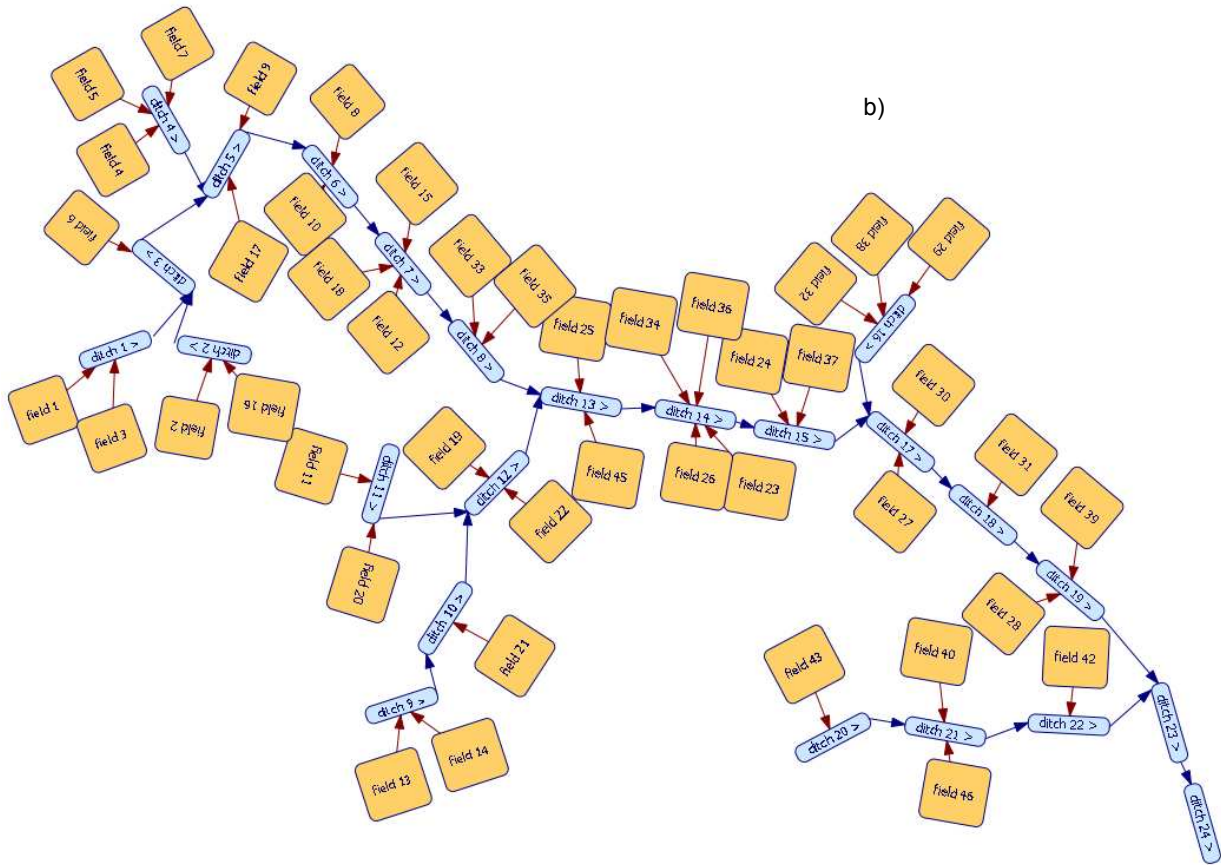
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Figure A-1 Location of meteorological stations.



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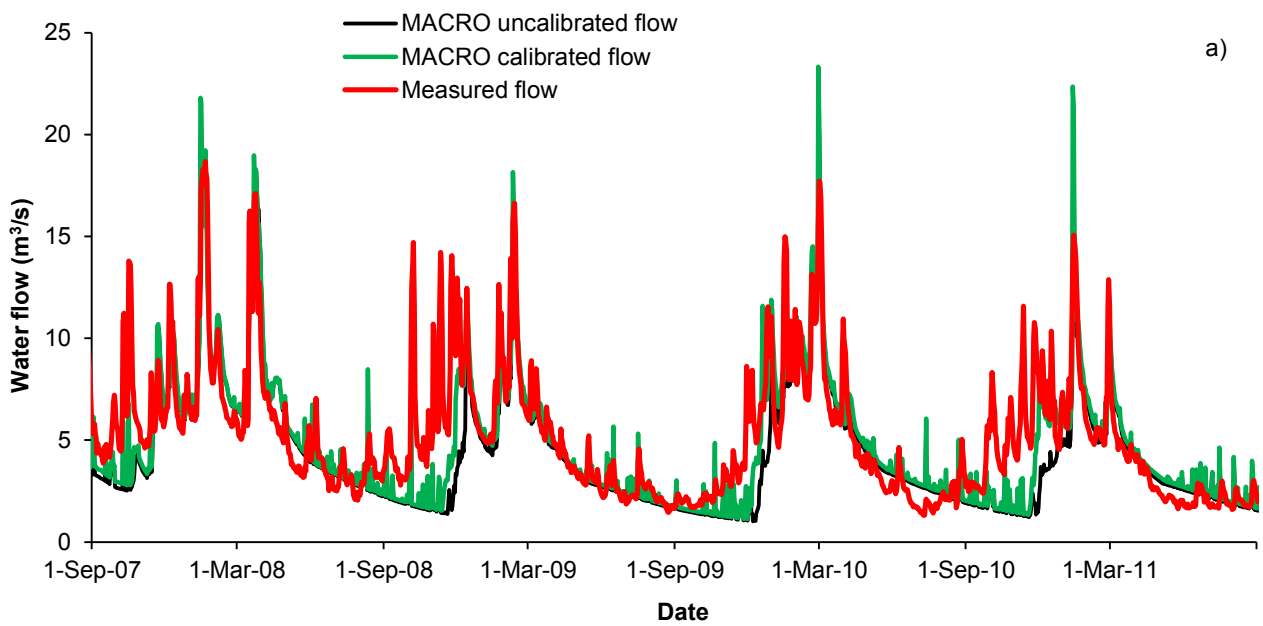


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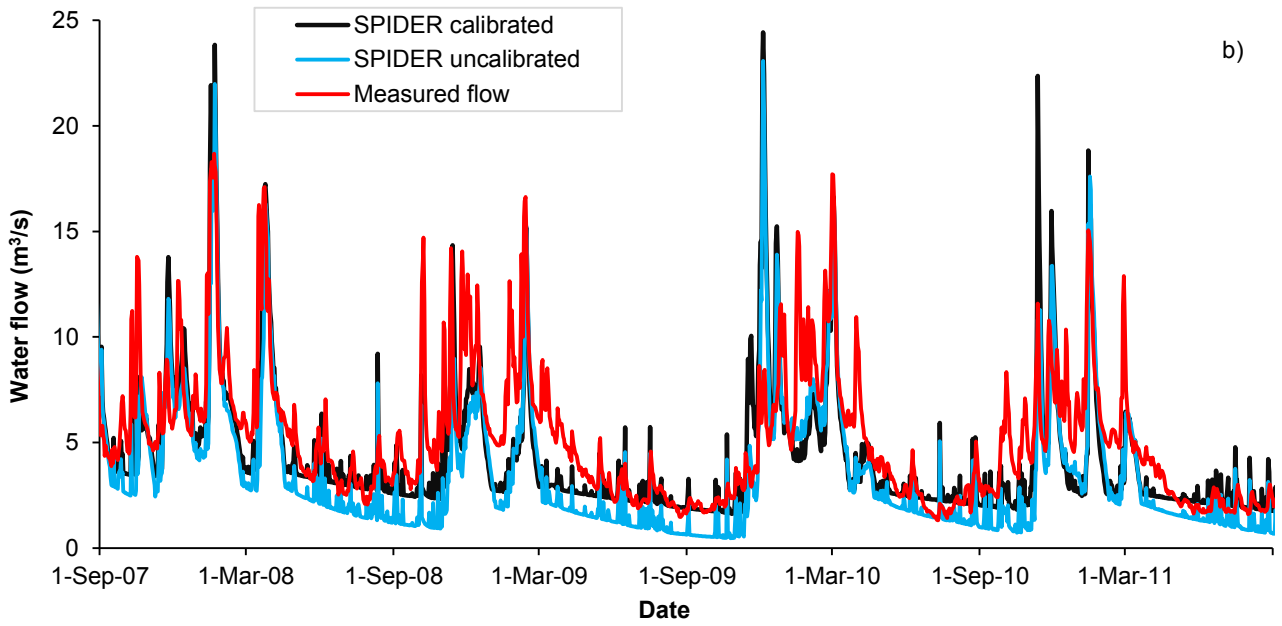
820 **Figure A-2** a) Division of the Wensum catchment into 44 land blocks and 24 streams reaches. b) Conceptual  
 821 scheme using SPIDER for the Wensum catchment.

822

823 **Results**



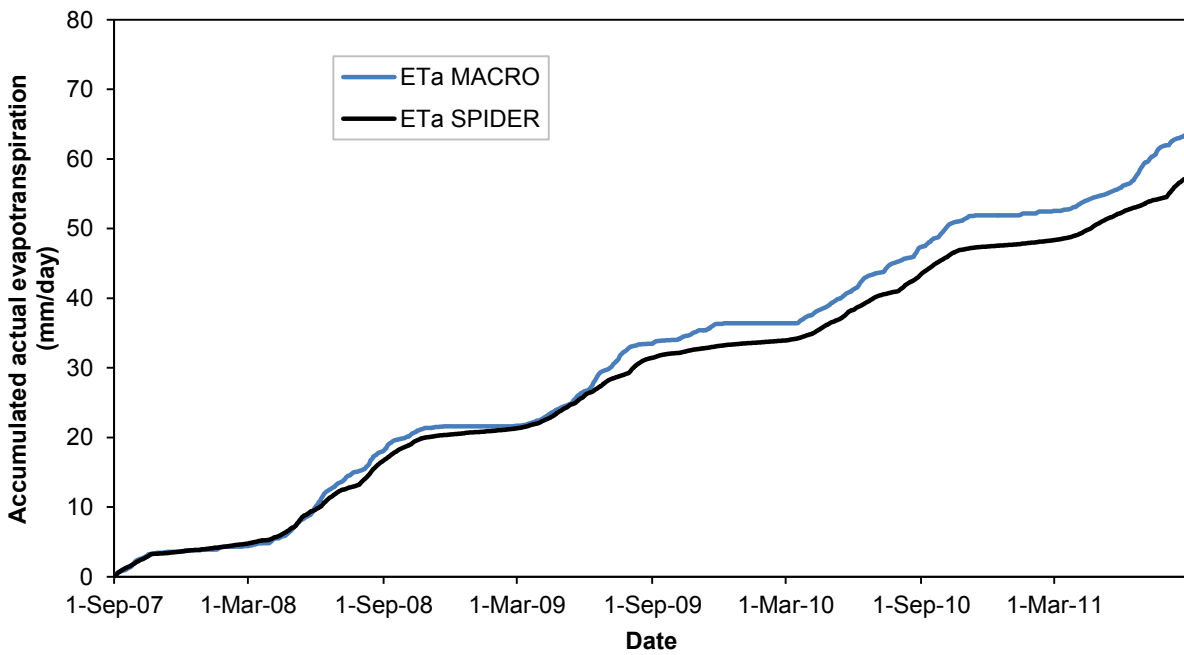
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825

826 **Figure A-3** Comparison of the uncalibrated and calibrated simulation of the water flow using a) MACRO and  
 827 b) SPIDER with the measured flow in the Wensum catchment. Measured flow supplied by the Environment  
 828 Agency.

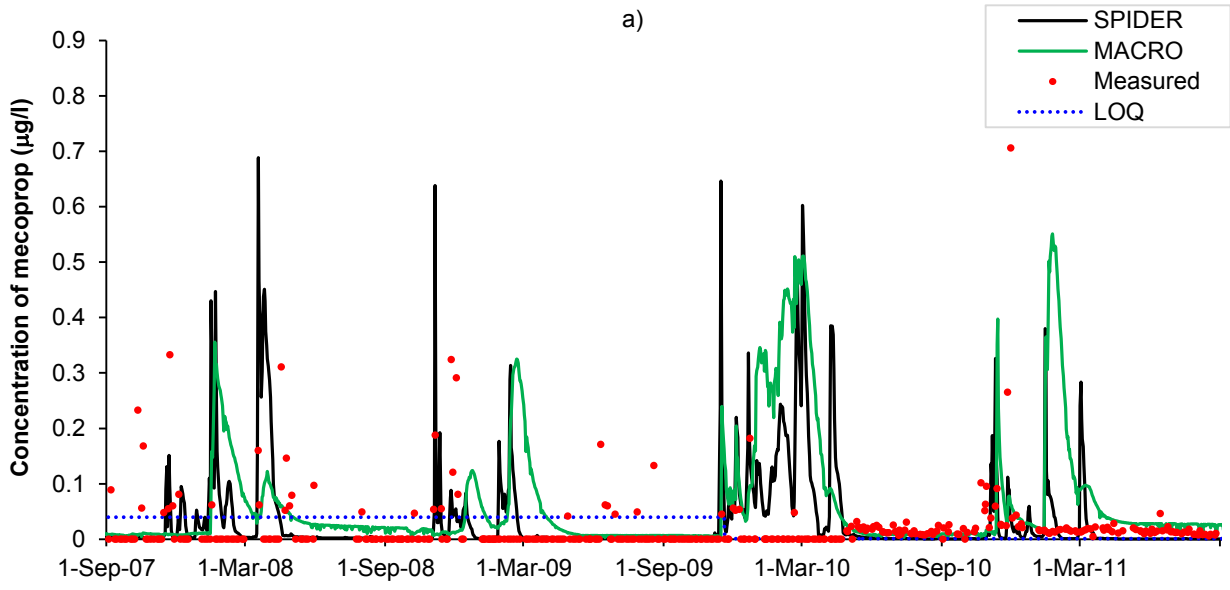
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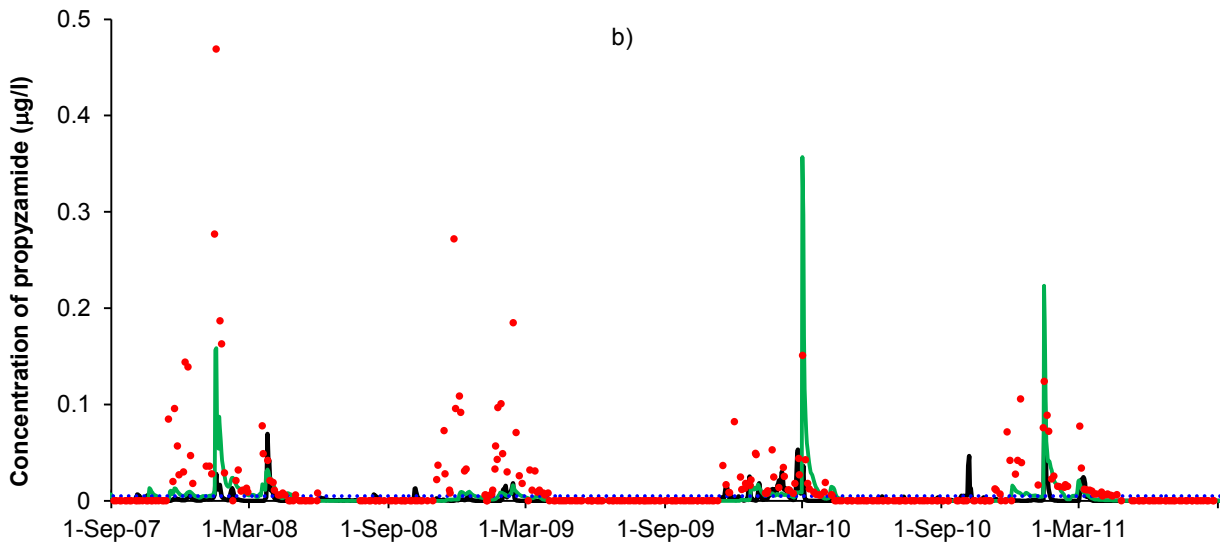
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831 **Figure A-4** Comparison of the accumulated actual evapotranspiration simulated by MACRO and SPIDER.

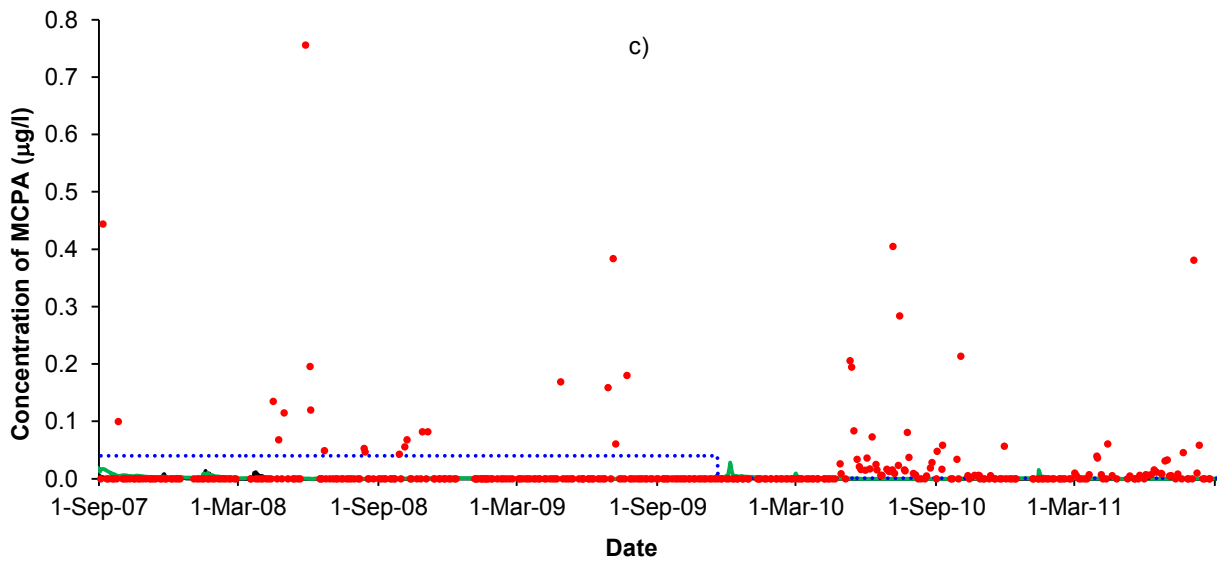
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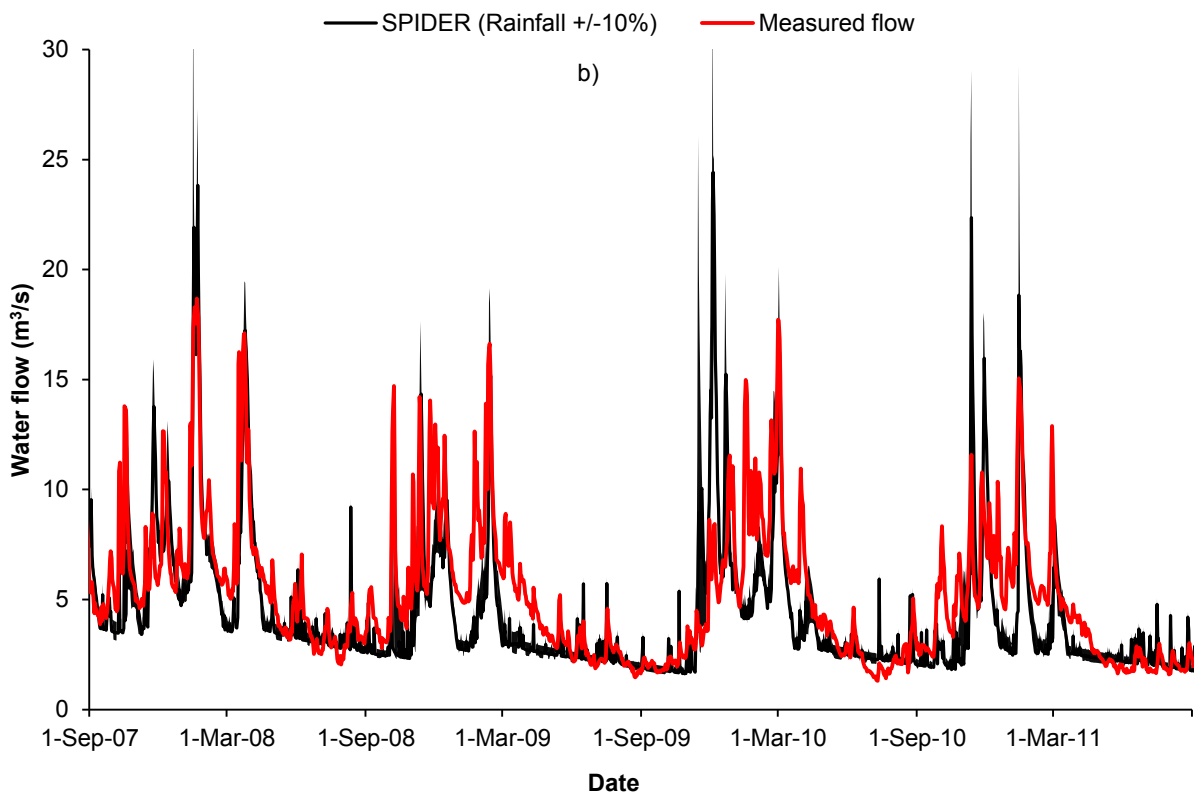
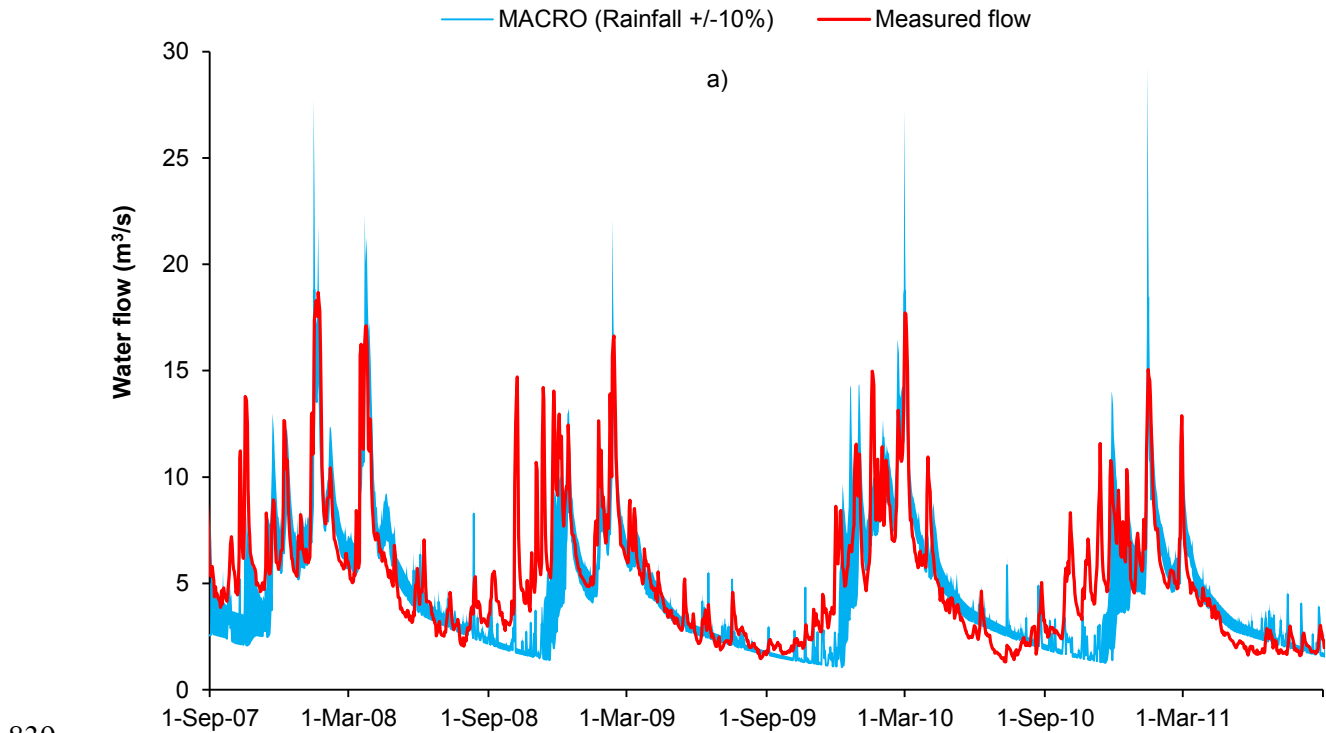


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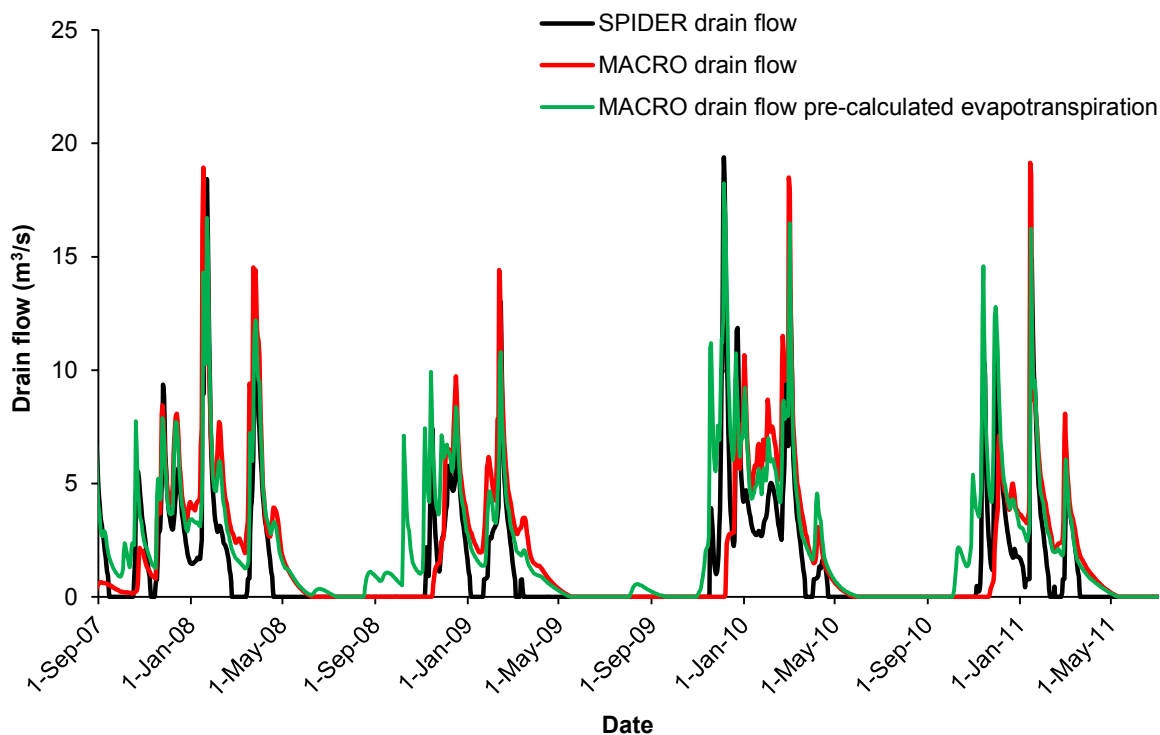
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836 **Figure A-5** Comparison of measured pesticide concentrations with those simulated by SPIDER and MACRO  
 837 for a) mecoprop, b) propyzamide and c) MCPA. Measured pesticide concentration supplied by the  
 838 Environment Agency.



840

841 **Figure A-6** Effect on the simulated water flow when decreasing and increasing the rainfall data by 10% using  
 842 a) MACRO and b) SPIDER compared to the measured flow. Measured flow supplied by the Environment  
 843 Agency.



844

845 **Figure A-7** Effect on the simulation of drain flow in MACRO from using the pre-calculated  
 846 evapotranspiration from SPIDER and comparison with SPIDER and MACRO original simulation.

847

848 **Table A-6** Loads and maximum concentrations of pesticides simulated by MACRO and SPIDER for different  
 849 hydrological years and comparison with observed values.

	Observed	SPIDER	MACRO	Observed	SPIDER	MACRO
	Load (kg/year)			Max. Conc. ( $\mu$ g/l)		
<b>Chlorotoluron</b>						
2007/08	3.12	1.09	7.61	0.141	0.037	0.359
2008/09	8.83	0.933	5.48	0.227	0.053	0.256
2009/10	1.33	3.34	14.0	0.144	0.163	0.539
2010/11	3.06	3.32	10.1	0.308	0.326	0.742
Total 4 years	<b>16.3</b>	<b>8.68</b>	<b>37.1</b>			
<b>Mecoprop</b>						
2007/08	12.5	14.1	13.1	0.311	0.688	0.355
2008/09	9.70	3.86	8.94	0.324	0.638	0.325
2009/10	3.12	16.4	31.3	0.182	0.646	0.511
2010/11	5.37	4.26	15.2	0.706	0.380	0.551
Total 4 years	<b>30.7</b>	<b>38.6</b>	<b>68.6</b>			
<b>Carbetamide</b>						
2007/08	6.71	0.804	1.42	0.271	0.074	0.064
2008/09	3.95	0.488	1.56	0.322	0.041	0.071
2009/10	6.44	1.27	1.34	0.622	0.072	0.060
2010/11	1.85	0.557	1.45	0.155	0.120	0.112

Total 4 years	<b>19.0</b>	<b>3.12</b>	<b>5.77</b>			
<b>Propyzamide</b>						
2007/08	9.12	0.841	2.74	0.469	0.069	0.158
2008/09	5.88	0.272	0.463	0.272	0.018	0.016
2009/10	3.24	0.724	2.67	0.151	0.053	0.357
2010/11	3.21	0.737	1.758	0.124	0.108	0.223
Total 4 years	<b>21.4</b>	<b>2.57</b>	<b>7.63</b>			
<b>Clopyralid</b>						
2007/08	8.74	3.35	0.945	0.134	0.242	0.009
2008/09	6.81	2.57	0.011	0.161	0.325	0.000
2009/10	2.00	3.26	0.722	0.031	0.239	0.106
2010/11	1.42	3.17	0.086	0.038	0.456	0.000
Total 4 years	<b>19.0</b>	<b>12.3</b>	<b>1.76</b>			
<b>MCPA</b>						
2007/08	14.7	0.314	0.517	3.76	0.014	0.018
2008/09	7.48	0.007	0.038	0.384	0.001	0.002
2009/10	3.96	0.020	0.320	1.76	0.005	0.028
2010/11	2.11	0.005	0.108	3.76	5.32	0.015
Total 4 years	<b>28.3</b>	<b>0.346</b>	<b>0.983</b>			

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852 **Table A–7** Pesticide loads simulated by MACRO and SPIDER for different application dates and comparison  
 853 with the observed value.

Pesticide/ Model	Loads (kg/4 years)								Observed data	
	20 Oct	25 Oct*	30 Oct	4 Nov	9 Nov	14 Nov	19 Nov	Observed data		
<b>Chlorotoluron</b>										
SPIDER	6.88	8.68	7.12	7.18	7.08	6.74	6.34		16.3	
MACRO	31.5	37.1	45.5	45.8	52.9	43.7	39.5			
	25 Oct*	30 Oct	4 Nov	9 Nov	14 Nov	19 Nov	24 Nov	Observed data		
<b>Mecoprop</b>										
SPIDER	38.6	60.2	90.3	139	186	198	188		30.7	
MACRO	68.6	83.7	96.1	125	172	96.9	102			
	1 Nov	5 Nov	10 Nov	15 Nov	20 Nov	25 Nov	30 Nov*	Observed data		
<b>Propyzamide</b>										
SPIDER	2.60	2.67	2.69	2.57	2.61	2.43	2.57		21.4	
MACRO	12.2	12.5	14.4	10.8	10.5	8.91	7.63			
	17 Mar	17 Mar	7 Mar	17 Mar	7 Mar	25 Feb	7 Mar	25 Feb*	25 Feb	Observed data
	5 May	15 May	15 May	25 May	5 May	15 May	25 May	25 May	5 May	
<b>Clopyralid</b>										
SPIDER	0.855	1.17	1.24	1.96	11.8	12.3	12.9	13.0	22.8	19.0
MACRO	0.186	0.186	0.230	0.186	0.230	0.670	0.230	0.669	0.669	

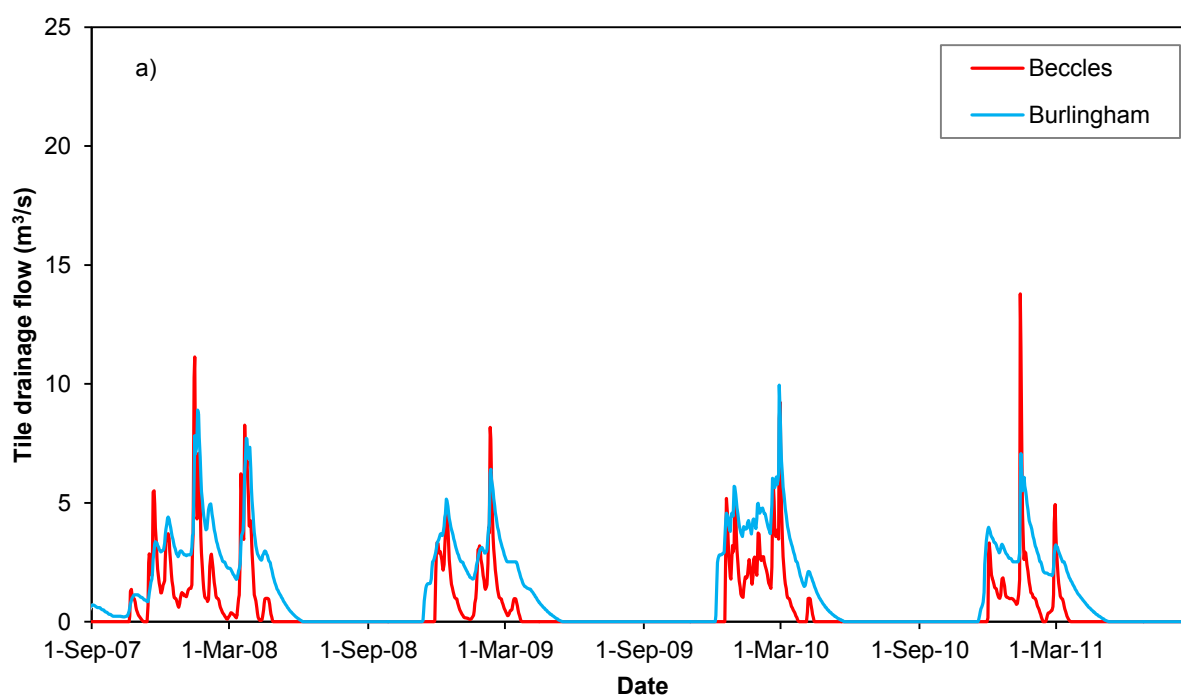
854 \* Typical application date

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856 **Table A-8** Simulated pesticide loads for combinations of maximum and minimum sorption and degradation  
 857 values, together with the simulated load using average inputs and the observed value.

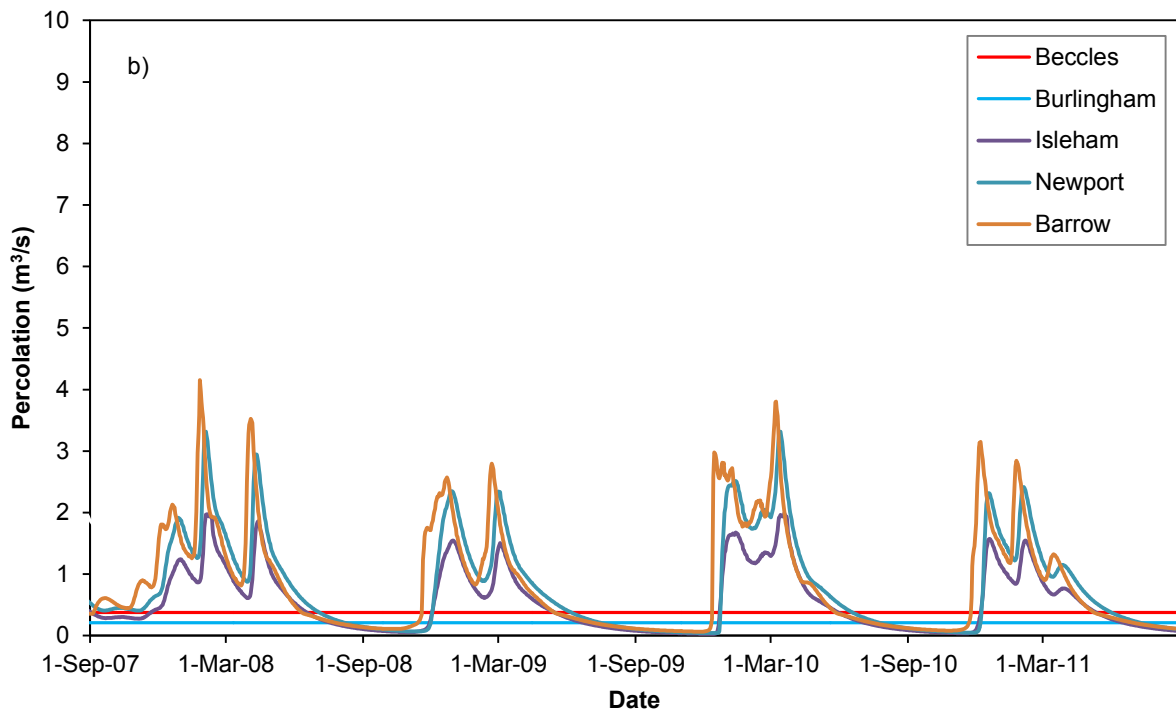
	Avg. $K_{oc}$ Avg. $DT_{50}$	Max. $K_{oc}$ Max $DT_{50}$	Max. $K_{oc}$ Min. $DT_{50}$	Min. $K_{oc}$ Max $DT_{50}$	Min. $K_{oc}$ Min. $DT_{50}$	Observed load
<b>Loads (kg/4 years)</b>						
<b>Chlorotoluron</b>						
<b>SPIDER</b>	8.68	2.33	1.91	30.0	22.5	16.3
<b>MACRO</b>	37.1	14.5	14.1	137	88.5	
<b>MCPA</b>						
<b>SPIDER</b>	0.346	0.230	0.000	9.53	0.036	28.2
<b>MACRO</b>	0.983	1.14	0.002	6.52	0.007	
<b>Clopyralid</b>						
<b>SPIDER</b>	13.0	18.0	9.07	22.8	9.32	19.0
<b>MACRO</b>	0.669	0.878	0.176	1.76	0.183	

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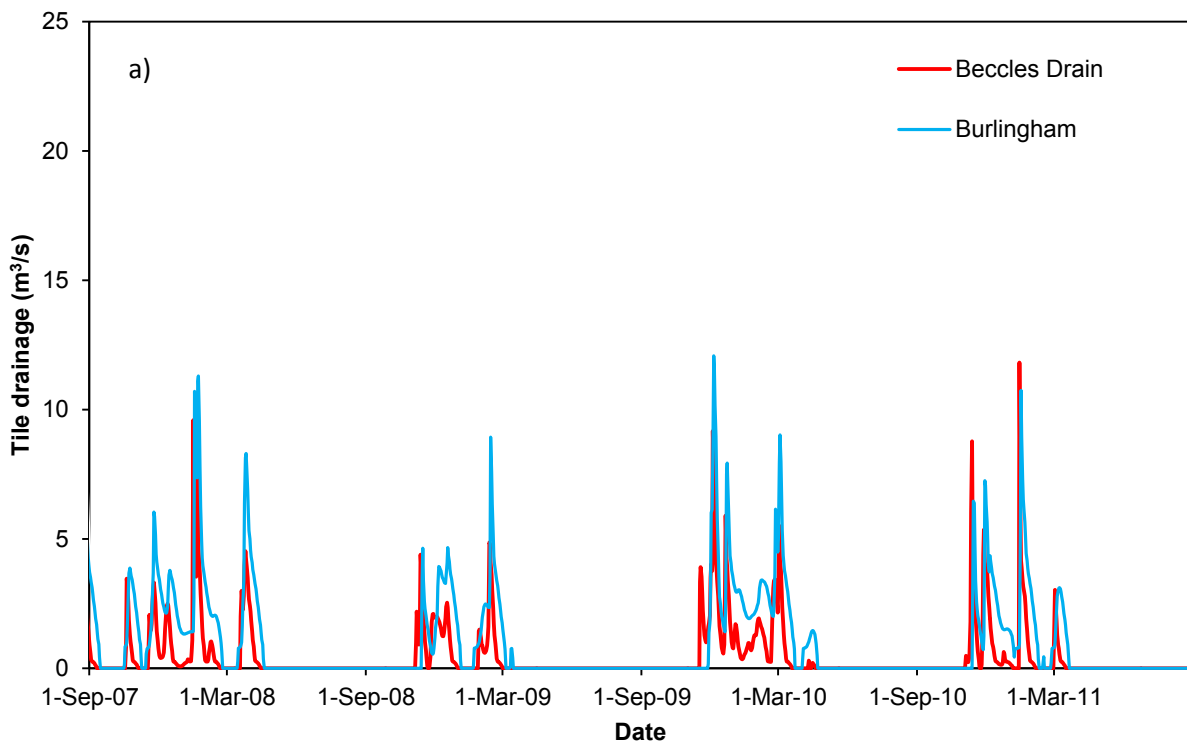
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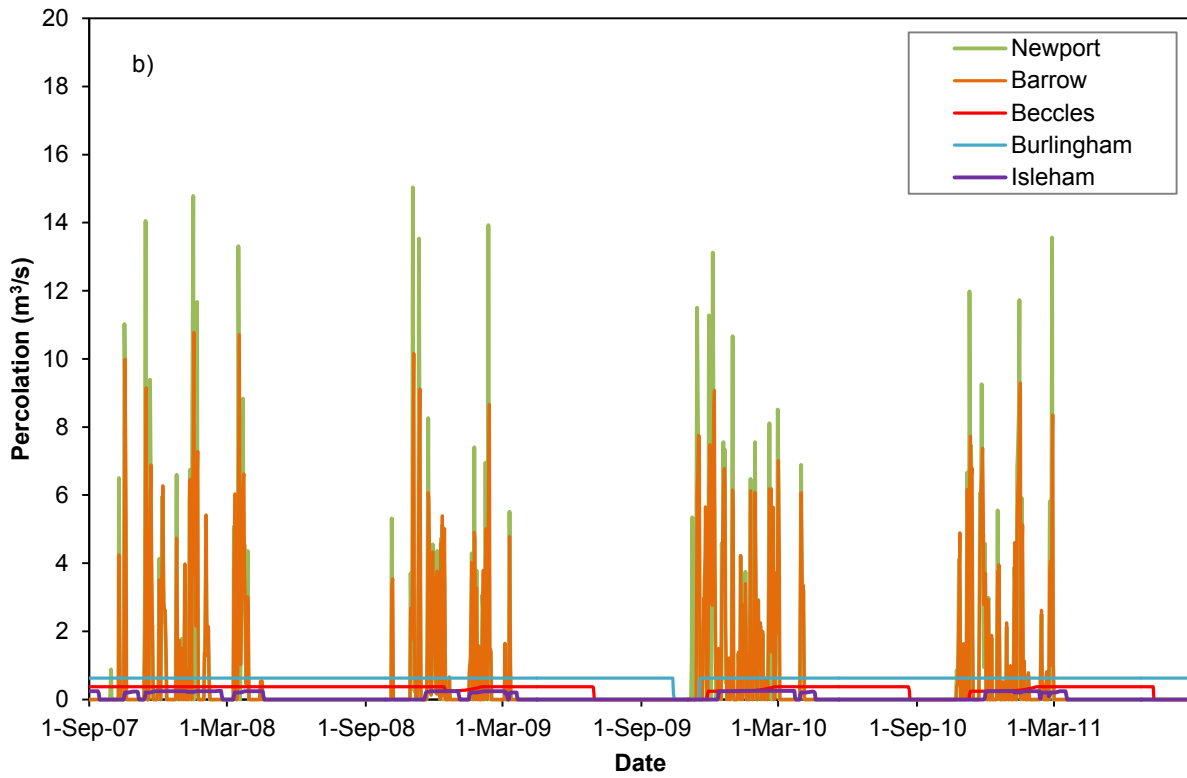


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861 **Figure A-8** Hydrographs simulated by MACRO for different soil types for a) drain flow and b) percolation.



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864 **Figure A-9** Hydrographs simulated by SPIDER for different soil types for a) drain flow and b) percolation.