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

3   M.L. Villamizar[1], C.D. Brown

4   Environment Department, The University of York, Heslington, York, YO10 5NG, UK

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^2 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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[1] Corresponding author: Environment Department, University of York, Wentworth Way, Heslington, York, YO10 5NG, UK. Email address: martha.villamizarvelez@york.ac.uk; marthaluvv@gmail.com (M.L. Villamizar).

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

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

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

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

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

2   Methods
2.1   Site description and data acquisition

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

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

95 correspond to an average K_{oc} value of 292 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

4

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 m^3) and pesticide leaching mass that reaches the groundwater

146 ($m_{i,t}$ in mg), predicted by MACRO at a daily time-step ($t \geq 1\ day$). 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 m^3, mg and

149 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 m^3, mg and 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 $Tank\ (T) \begin{cases} V_{T,t};\quad m_{T,t} = m_{i,t};\ C_{T,t} = m_{T,t}/V_{T,t}, & if\ t = 1 \\ V_{T,t} = V_{T,t-1} - V_{o,t-1} + V_{i,t};\ m_{T,t} = m_{T,t-1} - m_{o,t-1} + m_{i,t};\ C_{T,t} = m_{T,t}/V_{T,t}, & if\ t > 1 \end{cases}$ (1)

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

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 θ, and mm h^{-1} for all
195 other terms) at an hourly time step t is calculated from Equation 2:

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

197 where θ 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^{-1} for all other terms) at an hourly time step t for each layer is given by Equation 3.

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

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^3. 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).

2.4 Model evaluation

244
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 1st to
249 August 31st) using Equation 4.

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

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 -∞ 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

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

263 where *PestL* is the daily pesticide load in kg, Q is the daily water flow in m^3 and *PestC* is the
264 measured daily pesticide concentration in µg l^{-1} multiplied by a conversion factor of 10^{-6}. 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^{-1} 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^{-1}, 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^{-1}, 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^{-1} 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

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

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

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

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

10

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

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

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

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

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

3.3 Uncertainty analysis for SPIDER and MACRO simulations

3.3.1 Uncertainty in the rainfall data

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

3.3.2 Uncertainty in the application date

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

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

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3.3.3 Uncertainty in pesticide sorption and degradation

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

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

4 Discussion
4.1 Simulation of water flow

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

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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

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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 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 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

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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

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.

624 **6 References**

625 Allen, R.G. (1998) Crop evapotranspiration: guidelines for computing crop water requirements.

626 FAO, Rome.

627 Arias-Estevez, M., Lopez-Periago, E., Martinez-Carballo, E., Simal-Gandara, J., Mejuto, J.C.,

628 Garcia-Rio, L. (2008) The mobility and degradation of pesticides in soils and the pollution of

629 groundwater resources. Agriculture Ecosystems & Environment 123, 247-260.

630 Bardossy, A., Das, T. (2008) Influence of rainfall observation network on model calibration and

631 application. Hydrology and Earth System Sciences 12, 77-89.

632 Besien, T.J., Jarvis, N.J., Williams, R.J. (1997) Simulation of water movement and isoproturon

633 behaviour in a heavy clay soil using the MACRO model. Hydrology and Earth System Sciences 1,

634 835-844.

635 Beulke, S., Renaud, F., Brown, C.D., (2002) Development of guidance on parameter estimation for

636 the preferential flow model MACRO 4.2. Report to the Department for Environment, Food & Rural

637 Affairs. DEFRA project L0538. Cranfield Centre for EcoChemistry Contract No. JA3749E, 68pp.

638 Boithias, L., Sauvage, S., Srinivasan, R., Leccia, O., Sanchez-Perez, J.M. (2014) Application date as

639 a controlling factor of pesticide transfers to surface water during runoff events. Catena 119, 97-103.

640   Brock, T.C.M., Alix, A., Brown, C.D., Capri, E., Gottesbüren, B.F.F., Heimbach, F., Lythgo, C.M.,

641   Schulz, R., Streloke, E. (2010) Linking aquatic exposure and effects: Risk assessment of pesticides.

642   SETAC Press & CRC Press, Taylor & Francis, London.

643   Brown, C.D., Bellamy, P.H., Dubus, I.G. (2002) Prediction of pesticide concentrations found in

644   rivers in the UK. Pest Manag Sci 58, 363-373.

645   Brown, C.D., Rose, D.A., Syers, J.K., Hodgkinson, R.A. (1995) Effects of Preferential Flow Upon

646   the Movement of Pesticides and a Conservative Tracer from a Heavy Clay Soil. Pesticide Movement

647   to Water, 93-98.

648   Carsel, R.F., Mulkey, L.A., Lorber, M.N., Baskin, L.B. (1985) The Pesticide Root Zone Model

649   (PRZM) - a Procedure for Evaluating Pesticide Leaching Threats to Groundwater. Ecological

650   Modelling 30, 49-69.

651   Carter, A. (2000) How pesticides get into water - and proposed reduction measures. Pesticide

652   Outlook 11, 149-156.

653   Ciach, G.J. (2003) Local random errors in tipping-bucket rain gauge measurements. Journal of

654   Atmospheric and Oceanic Technology 20, 752-759.

655   CSF, (2012) Pesticides in Catchment Sensitive Farming catchments 2006-2012. Catchment Sensitive

656   Farming. Evidence Directorate. Environment Agency, UK.

657   Dubus, I.G., Brown, C.D. (2002) Sensitivity and first-step uncertainty analyses for the preferential

658   flow model MACRO. Journal of Environmental Quality 31, 227-240.

659   Dubus, I.G., Brown, C.D., Beulke, S. (2003) Sources of uncertainty in pesticide fate modelling.

660   Science of the Total Environment 317, 53-72.

661   Evans, S.P., Mayr, T.R., Hollis, J.M., Brown, C.D. (1999) SWBCM: a soil water balance capacity

662   model for environmental applications in the UK. Ecological Modelling 121, 17-49.

663   FOCUS, (2000) "FOCUS groundwater scenarios in the EU review of active substances" Report of

664   the FOCUS Groundwater Scenarios Workgroup, EC Document Reference SANCO/321/2000 rev.2,

665   202pp.

666   Gardner, R., (2014) The problem of leaching. Accessed on 30 July 2014. Availabe at:

667   http://pesticidestewardship.org/water/Pages/Leaching.aspx. Cornell University - Cooperative

668   extension, The Pesticide Environmental Stewardship (PES) Website.

669 Garthwaite, D.G., Barker, I., Parrish, G., Smith, L., Chippindale, C., (2010) Pesticide usage survey
670 report 232: Grassland and fodder crops in Great Britain 2005 (including aerial applications 2009).
671 Defra, London.

672 Garthwaite, D.G., Barker, I., Parrish, G., Smith, L., Chippindale, C., Pietravalle, S., (2011) Pesticide
673 usage survey report 235: Arable crops in Great Britain 2010 (including aerial applications 2010).
674 Defra, London.

675 Garthwaite, D.G., Hudson, S., Barker, I., Parrish, G., Smith, L., Pietravalle, S., (2013) Pesticide
676 usage survey report 250: arable crops in the United Kingdom 2012 (including aerial applications
677 2012). Defra, London.

678 Garthwaite, D.G., Hudson, S., Barker, I., Parrish, G., Smith, L., Pietravalle, S., (2014) Pesticide
679 usage survey report 255: Grassland and fodder crops in the United Kingdom 2013. Defra, London.

680 Garthwaite, D.G., Thomas, M.R., Anderson, M., Battersby, A., (2006) Pesticide usage survey report
681 210: Grassland and fodder crops in Great Britain 2005 (including aerial applications 2003-2005).
682 CSL, London.

683 Garthwaite, D.G., Thomas, M.R., Heywood, E., Battersby, A., (2007) Pesticide usage survey report
684 213: Arable crops in Great Britain 2006 (including aerial applications 2003-2006). Defra, London.

685 Garthwaite, D.G., Thomas, M.R., Parrish, G., Smith, L., Barker, I., (2009) Pesticide usage survey
686 report 224: Arable crops in Great Britain 2008 (including aerial applications 2007-2008). Defra,
687 London.

688 Gericke, D., Nekovar, J., Horold, C. (2010) Estimation of plant protection product application dates
689 for environmental fate modeling based on phenological stages of crops. Journal of Environmental
690 Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes 45, 639-647.

691 Hallett, S.H., Thanigasalam, P., Hollis, J.M. (1995) Seismic - a Desk-Top Information-System for
692 Assessing the Fate and Behavior of Pesticides in the Environment. Computers and Electronics in
693 Agriculture 13, 227-242.

694 Harris, G.L., Catt, J.A. (1999) Overview of the studies on the cracking clay soil at Brimstone Farm,
695 UK. Soil Use and Management 15, 233-239.

696 Hodge, C.A.H., Burton, R.G.O., Corbett, W.M., Evans, R., Seale, R.S. (1984) Soils and their use in
697 Eastern England. Soil Survey of England and Wales.

698   Holvoet, K., van Griensven, A., Seuntjens, P., Vanrolleghem, P.A. (2005) Sensitivity analysis for
699   hydrology and pesticide supply towards the river in SWAT. Physics and Chemistry of the Earth 30,
700   518-526.

701   Holvoet, K.M.A., Seuntjens, P., Vanrolleghem, P.A. (2007) Monitoring and modeling pesticide fate
702   in surface waters at the catchment scale. Ecological Modelling 209, 53-64.

703   Jarvis, N.J., Hollis, J.M., Nicholls, P.H., Mayr, T., Evans, S.P. (1997) MACRO-DB: a decision-
704   support tool for assessing pesticide fate and mobility in soils. Environmental Modelling & Software
705   12, 251-265.

706   Jarvis, N.J., Jansson, P.E., Dik, P.E., Messing, I. (1991) Modeling Water and Solute Transport in
707   Macroporous Soil .1. Model Description and Sensitivity Analysis. Journal of Soil Science 42, 59-70.

708   Johnson, A.C., Haria, A.H., Bhardwaj, C.L., Williams, R.J., Walker, A. (1996) Preferential flow
709   pathways and their capacity to transport isoproturon in a structured clay soil. Pesticide Science 48,
710   225-237.

711   Laliberte, G., Brooks, R., Corey, A. (1968) Permeability calculated from desaturation data. Irrig
712   Drain Div ASCE 94, 57-69.

713   Lewis, K.A., Green, A., Tzilivakis, J., Warner, D., (2015) The Pesticide Properties DataBase (PPDB)
714   developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire,
715   2006-2015.

716   Lindahl, A.M.L., Kreuger, J., Stenstrom, J., Gardenas, A.I., Alavi, G., Roulier, S., Jarvis, N.J. (2005)
717   Stochastic modeling of diffuse pesticide losses from a small agricultural catchment. Journal of
718   Environmental Quality 34, 1174-1185.

719   Ma, Q., Wauchope, R.D., Rojas, K.W., Ahuja, L.R., Ma, L., Malone, R.W. (2004) The pesticide
720   module of the Root Zone Water Quality Model (RZWQM): testing and sensitivity analysis of
721   selected algorithms for pesticide, fate and surface runoff. Pest Management Science 60, 240-252.

722   Monteith, J.L. (1965) Evaporation and environment. Symp Soc Exp Biol 19, 205-234.

723   Moulin, L., Gaume, E., Obled, C. (2009) Uncertainties on mean areal precipitation: assessment and
724   impact on streamflow simulations. Hydrology and Earth System Sciences 13, 99-114.

725   Nash, J.E., Sutcliffe, J.V. (1970) River flow forecasting through conceptual models. Part I - A
726   discussion of principles. Journal of Hydrology 10, 282-290.

727 Netherton, M., Brown, C.D., (2010) Review of current knowledge on pesticides with potential for
728 non-compliance under the Water Framework Directive. Defra Project PS2242, University of York,
729 Environment Department, Heslington, York.

730 Obled, C., Wendling, J., Beven, K. (1994) The Sensitivity of Hydrological Models to Spatial Rainfall
731 Patterns - an Evaluation Using Observed Data. Journal of Hydrology 159, 305-333.

732 Pedersen, H.J., Kudsk, P., Helweg, A. (1995) Adsorption and Ed(50) Values of 5 Soil-Applied
733 Herbicides. Pesticide Science 44, 131-136.

734 Pistocchi, A. (2013) Some considerations on the use of simple box models of contaminant fate in
735 soils. Environ Monit Assess 185, 2855-2867.

736 Renaud, F.G., Bellamy, P.H., Brown, C.D. (2008) Simulating pesticides in ditches to assess
737 ecological risk (SPIDER): I. Model description. Science of the Total Environment 394, 112-123.

738 Renaud, F.G., Brown, C.D. (2008) Simulating pesticides in ditches to assess ecological risk
739 (SPIDER): II. Benchmarking for the drainage model. Science of the Total Environment 394, 124-
740 133.

741 Rushton, K.R., Youngs, E.G. (2010) Drainage of recharge to symmetrically located downstream
742 boundaries with special reference to seepage faces. Journal of Hydrology 380, 94-103.

743 Sear, D.A., Newson, M., Old, J.C., Hill, C., (2006) Geomorphological appraisal of the River
744 Wensum Special Area of Conservation, English Nature Research Reports, 685.

745 Sloan, P.G., Moore, I.D. (1984) Modeling Subsurface Stormflow on Steeply Sloping Forested
746 Watersheds. Water Resources Research 20, 1815-1822.

747 Sohrabi, T.M., Shirmohammadi, A., Montas, H. (2002) Uncertainty in nonpoint source pollution
748 models and associated risks. Environmental Forensics 3, 179-189.

749 Tediosi, A., Whelan, M.J., Rushton, K.R., Gandolfi, C. (2013) Predicting rapid herbicide leaching to
750 surface waters from an artificially drained headwater catchment using a one dimensional two-domain
751 model coupled with a simple groundwater model. Journal of Contaminant Hydrology 145, 67-81.

752 UK Meteorological Office, (2010) National Meteorological Library and Archive. Fact sheet 17.
753 Weather observations over land. UK Meteorological Office, Devon, UK.

754 Villamizar, M., (2014) Modelling non-point source pollution of rivers in the UK and Colombia,
755 Environment department. The University of York, York.

756 Wang, J.X., Fisher, B.L., Wolff, D.B. (2008) Estimating rain rates from tipping-bucket rain gauge
757 measurements. Journal of Atmospheric and Oceanic Technology 25, 43-56.

758 Wood, E.F., Sivapalan, M., Beven, K., Band, L. (1988) Effects of Spatial Variability and Scale with
759 Implications to Hydrologic Modeling. Journal of Hydrology 102, 29-47.

760 Zhang, H., Haan, C.T., Nofziger, D.L. (1993) An Approach to Estimating Uncertainties in Modeling
761 Transport of Solutes through Soils. Journal of Contaminant Hydrology 12, 35-50.

762 Zhu, Y., Shi, L.S., Yang, J.Z., Wu, J.W., Mao, D.Q. (2013) Coupling methodology and application
763 of a fully integrated model for contaminant transport in the subsurface system. Journal of Hydrology
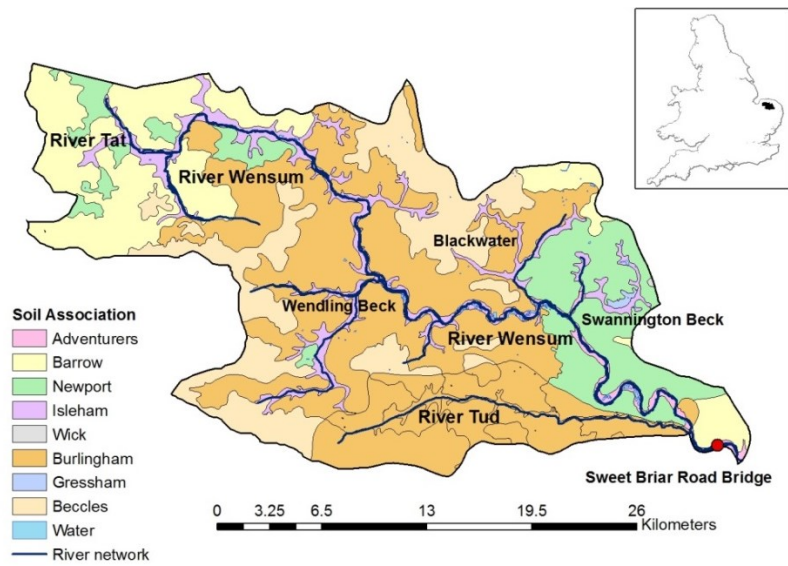764 501, 56-72.

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

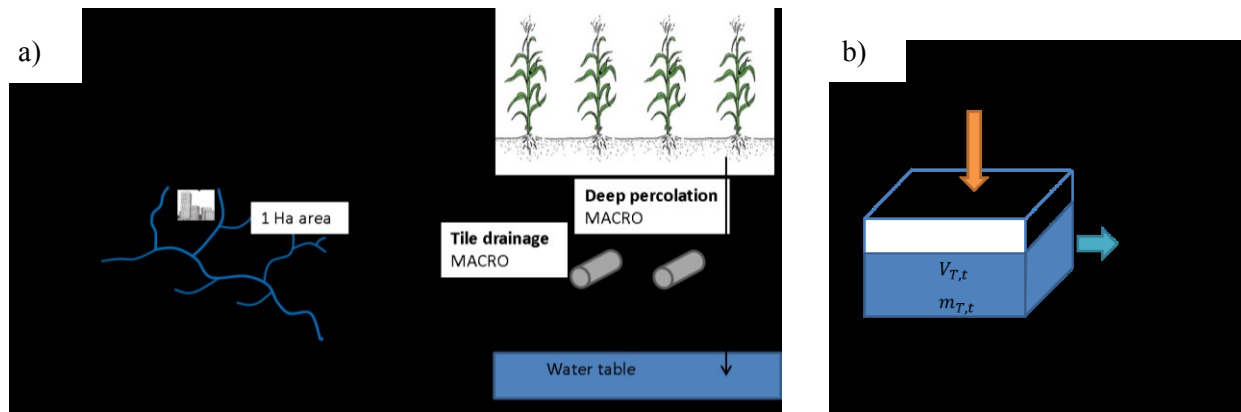768 Inset: location of the Wensum catchment within England and Wales.

769

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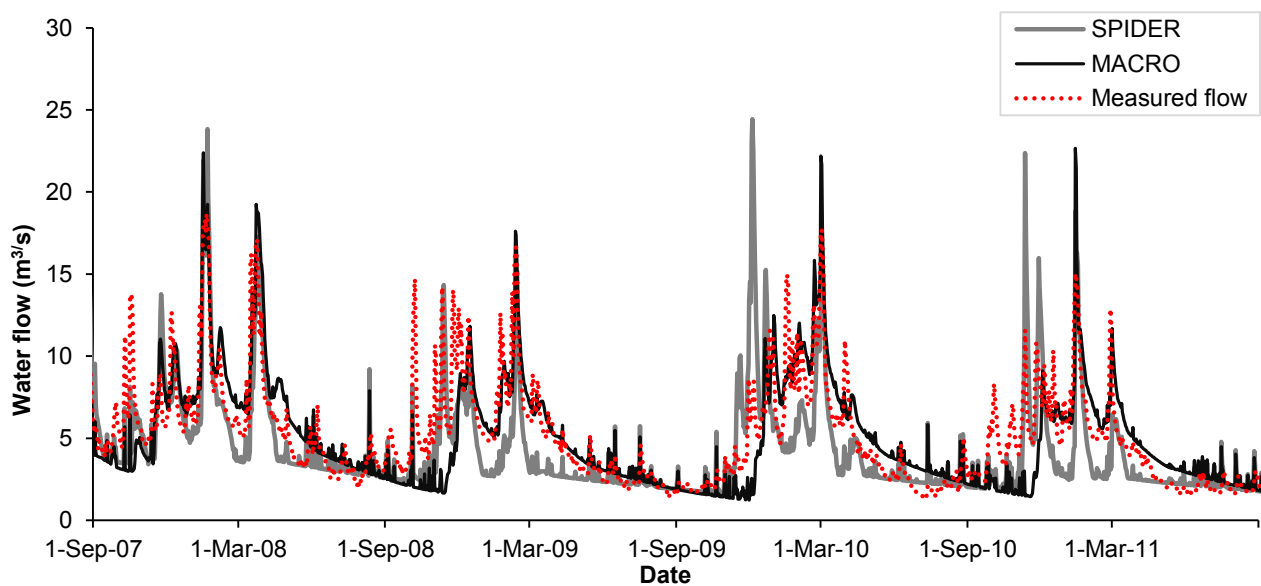

771
772 **Figure 3** Comparison of the measured and simulated water flow (calibrated simulations) by MACRO and
773 SPIDER. Measured flow supplied by the Environment Agency.
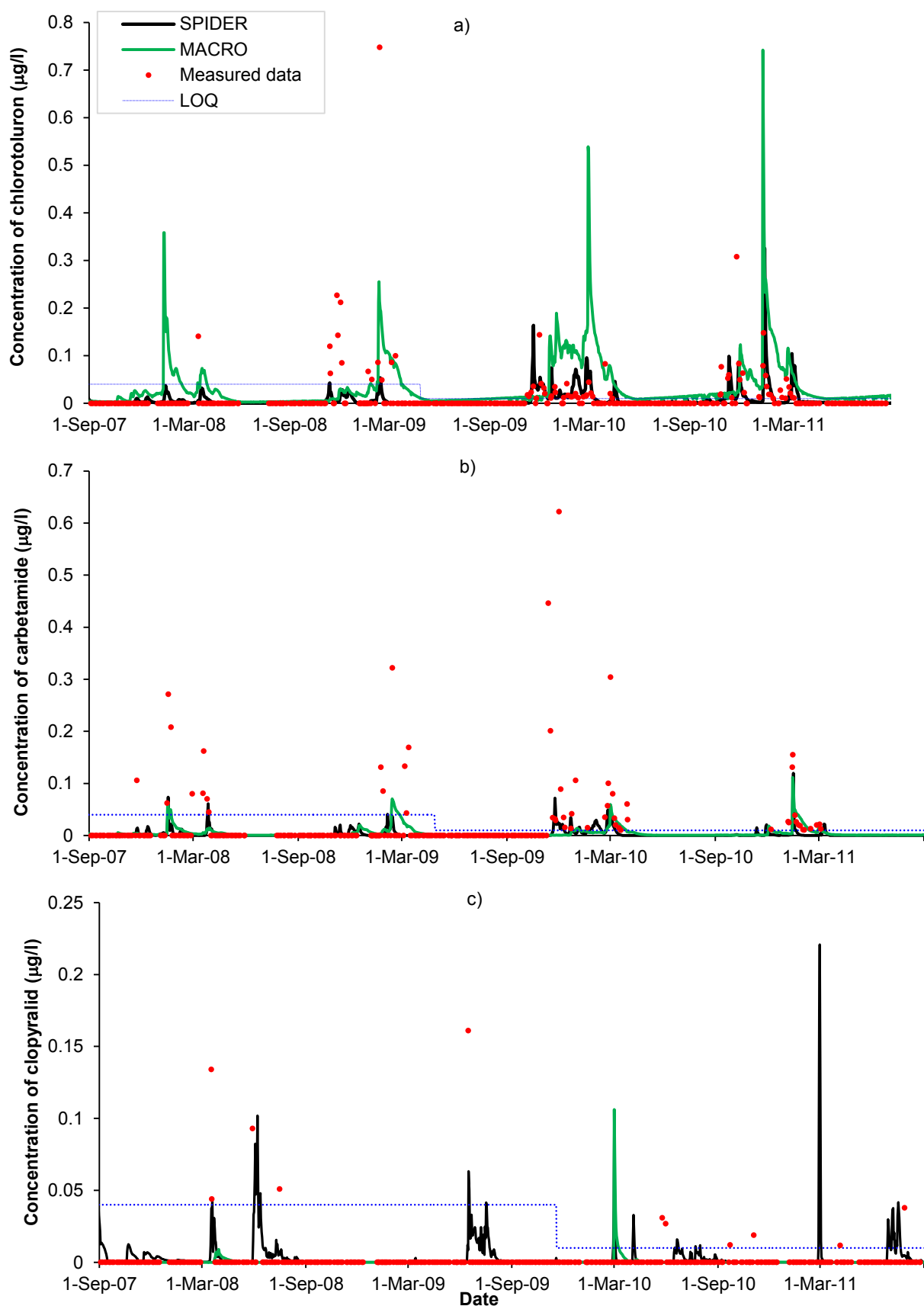
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777 **Figure 4** Comparison of measured pesticide concentrations with those simulated by SPIDER and MACRO for

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
	Loads (kg/4 years)							
SPIDER	6.05	9.99	14.1	19.3	17.3	21.7	22.7	23.3
MACRO	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
	Loads (kg/4 years)					
SPIDER	6.05	11.3	0.14	43.1	0.48	23.3
MACRO	11.5	28.6	1.56	74.1	1.83	

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^{-1})[a]	DT$_{50}$ soil[a] (days)	Koc range[a] (mL g^{-1})	DT$_{50}$ soil range[a] (days)	TREF (°C)	TRESP (K^{-1})	EXPB	Freundlich coefficient[b]
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[d]	3.43 - 7.34	2 – 24[d]	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[c]	47	-	-	20	0.08	0.7	0.90[c]

794 TREF: Reference temperature. TRESP: Exponent in the temperature response function. EXPB: Exponent in
795 the degradation water response function. [a]Lewis et al. (2015), [b]Netherton and Brown (2010), [c]Pedersen et al.
796 (1995). [d]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[a]	2008[b]	2010[c]	2012[d]
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[e]	2009[f]	2013[g]	
Grassland	29,137	36,103	37,065	

799 OSR: Oilseed rape. * Including set-aside
800 [a]Garthwaite et al. (2007); [b]Garthwaite et al. (2009); [c]Garthwaite et al. (2011); [d]Garthwaite et al. (2013);
801 [e]Garthwaite et al. (2006); [f]Garthwaite et al. (2010); [g]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)
Chlorotoluron **Cereals**			**Carbetamide** **OSR**		
2006[a]	19,548	32,607	2006[a]	12,121	25,086
2008[b]	44,697	96,841	2008[b]	30,383	61,725
2010[c]	101,014	178,711	2010[c]	26,066	49,453
2012[d]	58,293	84,938	2012[d]	27,229	45,596
Clopyralid **Cereals**			**Clopyralid** **Beet**		
2006[a]	811	151	2006[a]	65,273	4,810

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

[a]Garthwaite et al. (2007); [b]Garthwaite et al. (2009); [c]Garthwaite et al. (2011); [d]Garthwaite et al. (2013); [e]Garthwaite et al. (2006); [f]Garthwaite et al. (2010)

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

| Pesticide	LOQ (μg/l) September 2006 to April 2009/*April 2010	LOQ (μg/l) 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

Table A–5 Pesticide degradation values in water and sediment obtained from laboratory studies and Freundlich coefficients used in SPIDER

Pesticide	DT_{50} water (days)[a]	DT_{50} sediment (days)[a]	Freundlich coefficient[a]
Carbetamide	9.1	55.5	0.93
Chlorotoluron	42	352	0.90
Clopyralid	148	1000[b]	0.85*
MCPA	13.5	17	0.85*
Mecoprop	37	50	0.90
Propyzamide	21	94	0.90

[a]Lewis et al. (2015), [b]Netherton and Brown (2010). *Values adjusted to avoid sorption conflicts in the model because the reported values were to small (0.76 and 0.68 for clopyralid and MCPA, respectively).

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815 **Figure A–1** Location of meteorological stations.
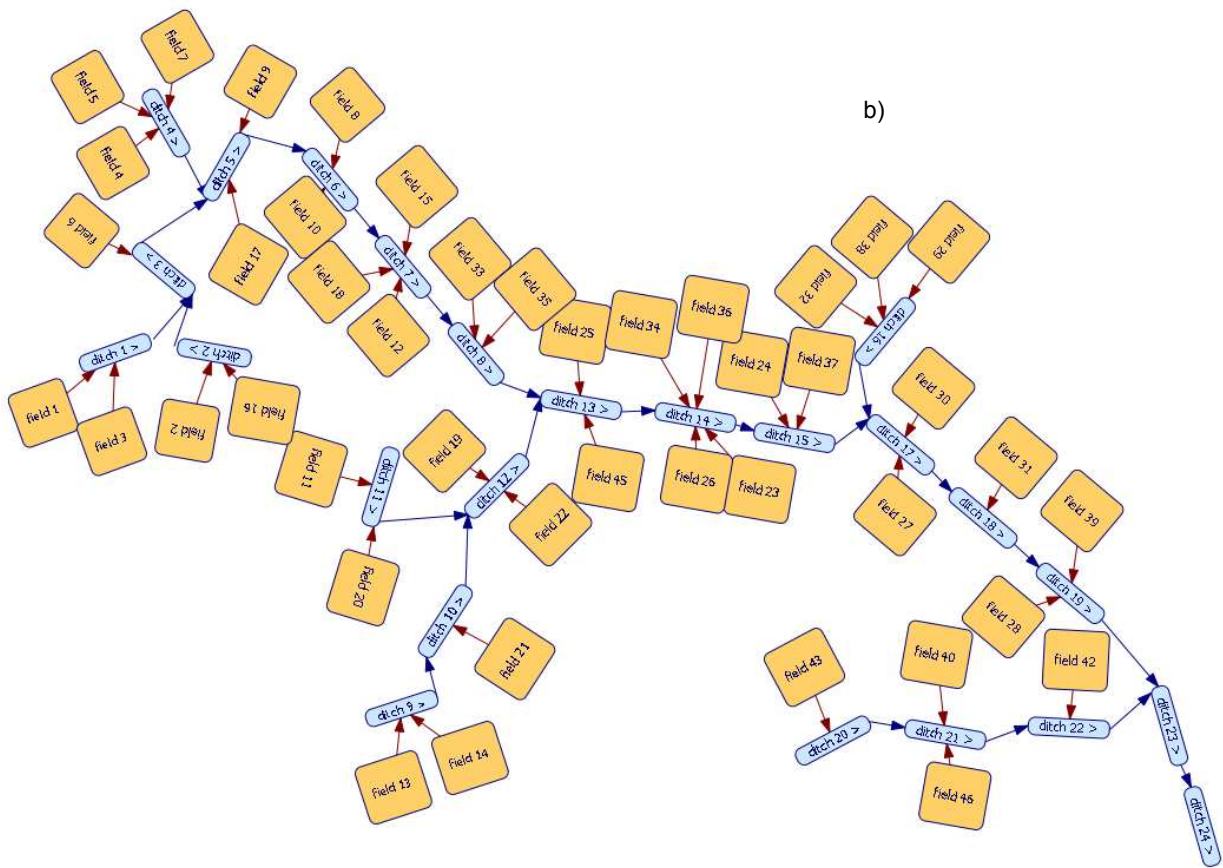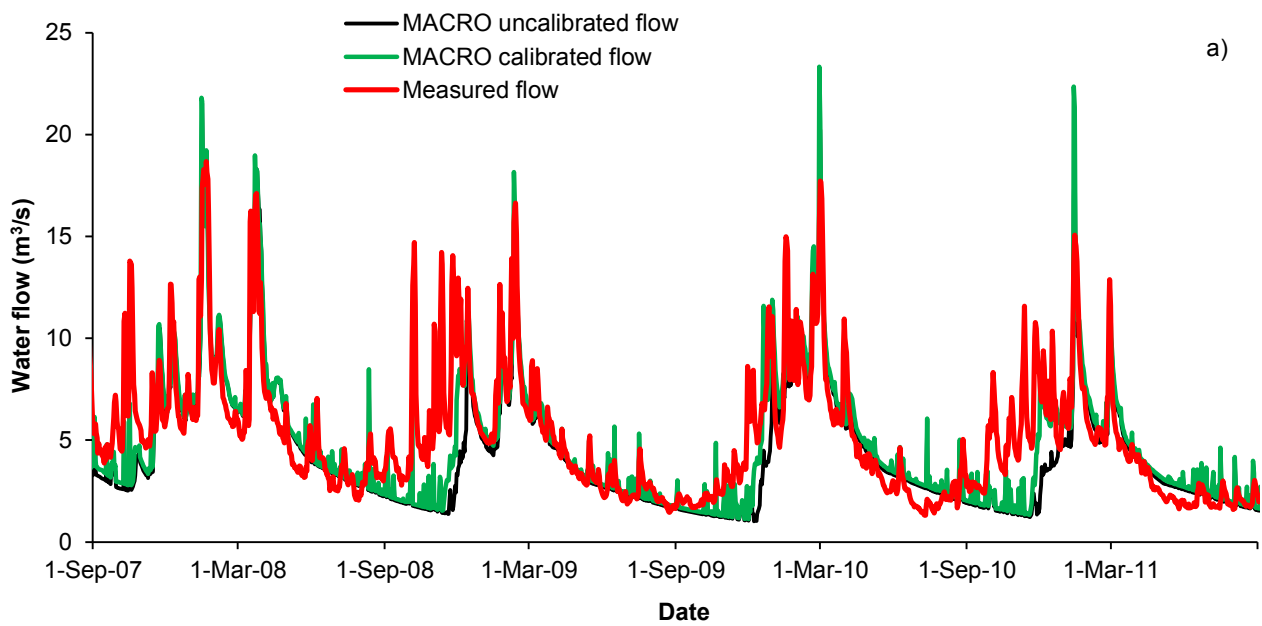816
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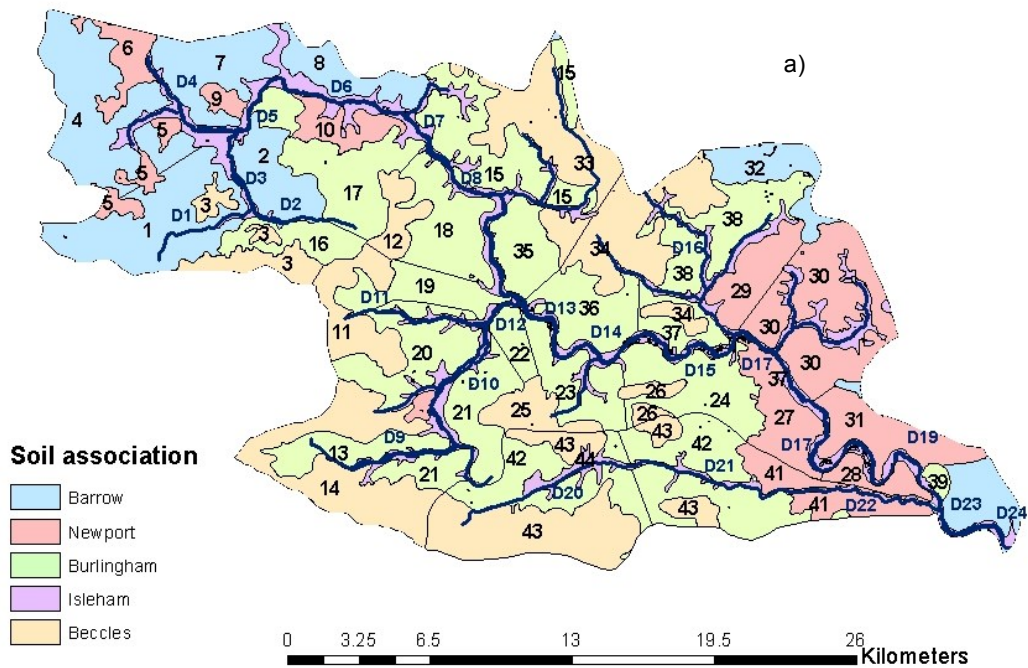
820 **Figure A–2** a) Division of the Wensum catchment into 44 land blocks and 24 streams reaches. b) Conceptual

821 scheme using SPIDER for the Wensum catchment.
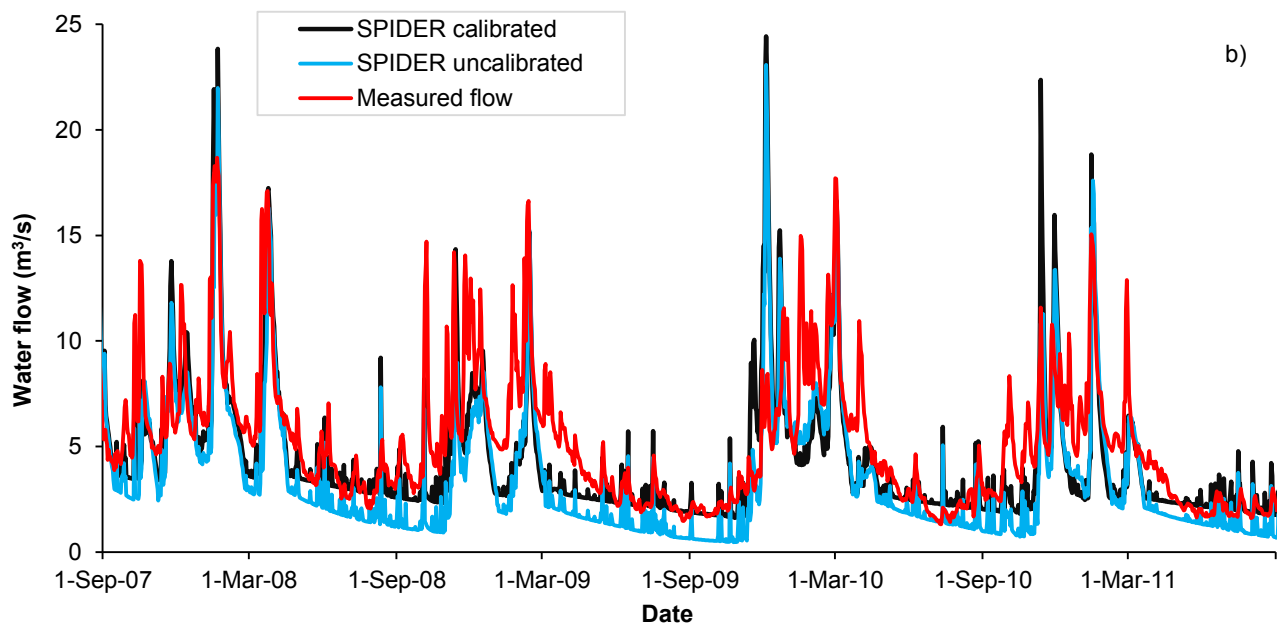
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825

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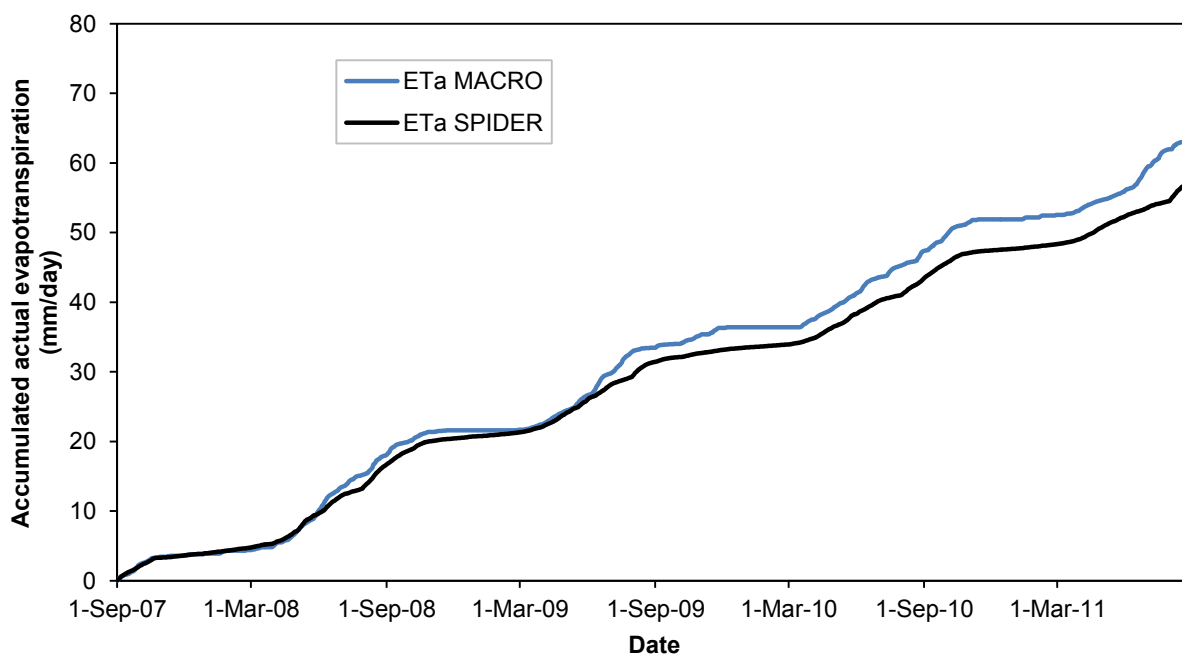827   b) SPIDER with the measured flow in the Wensum catchment. Measured flow supplied by the Environment
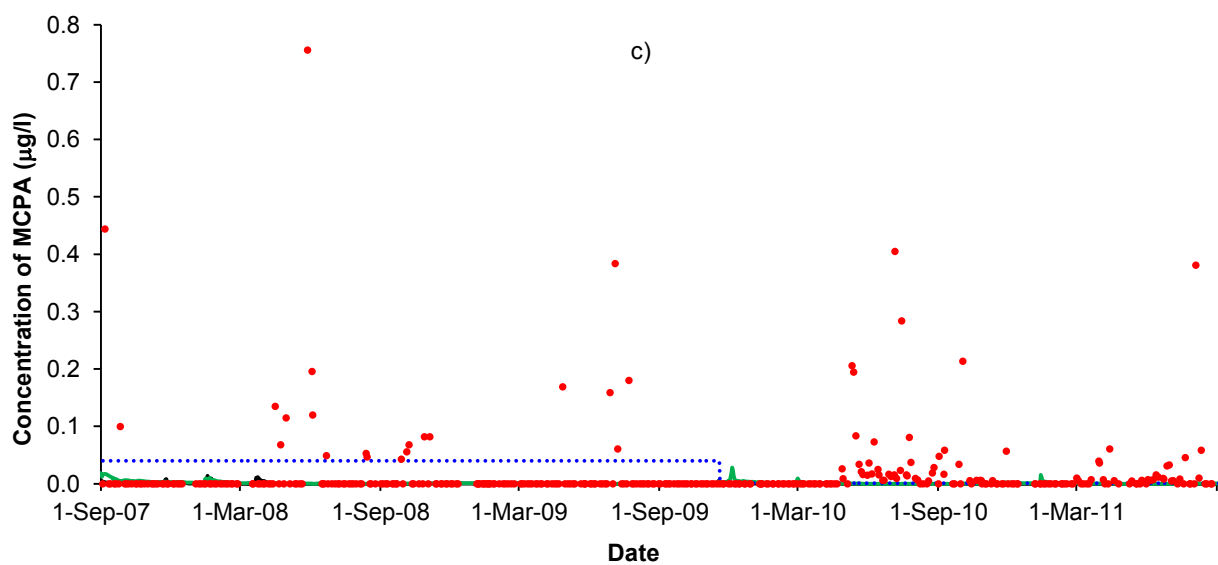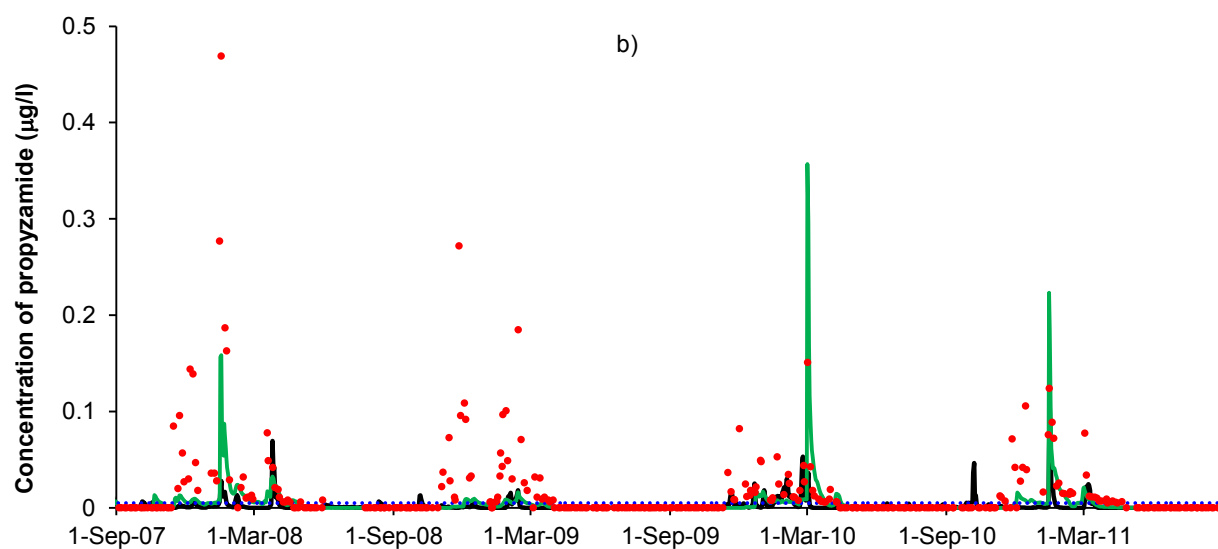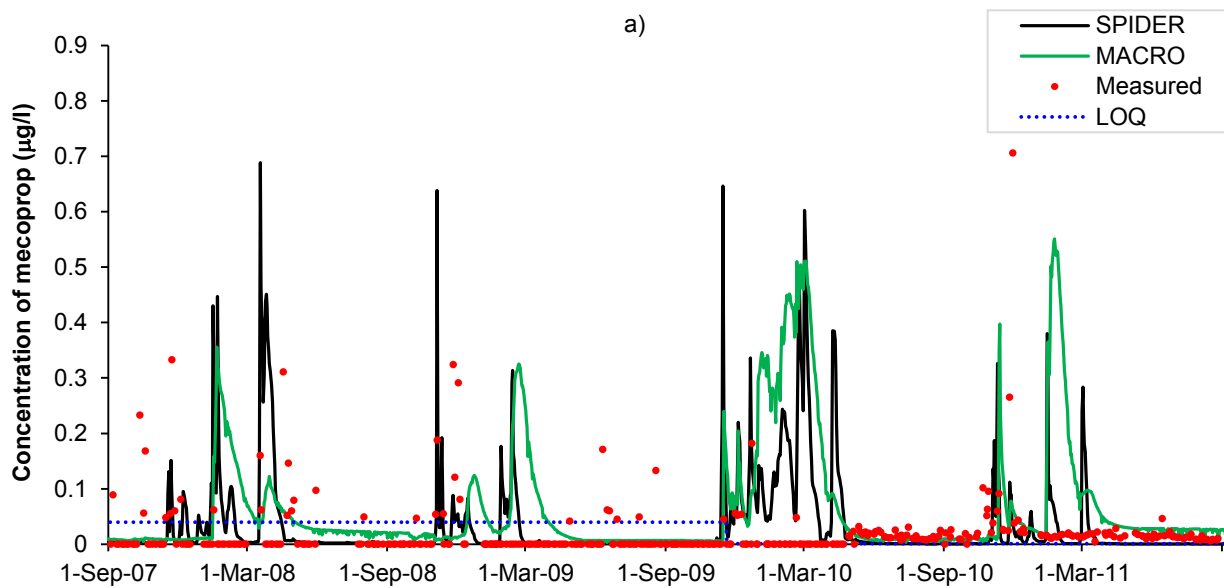828   Agency.

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

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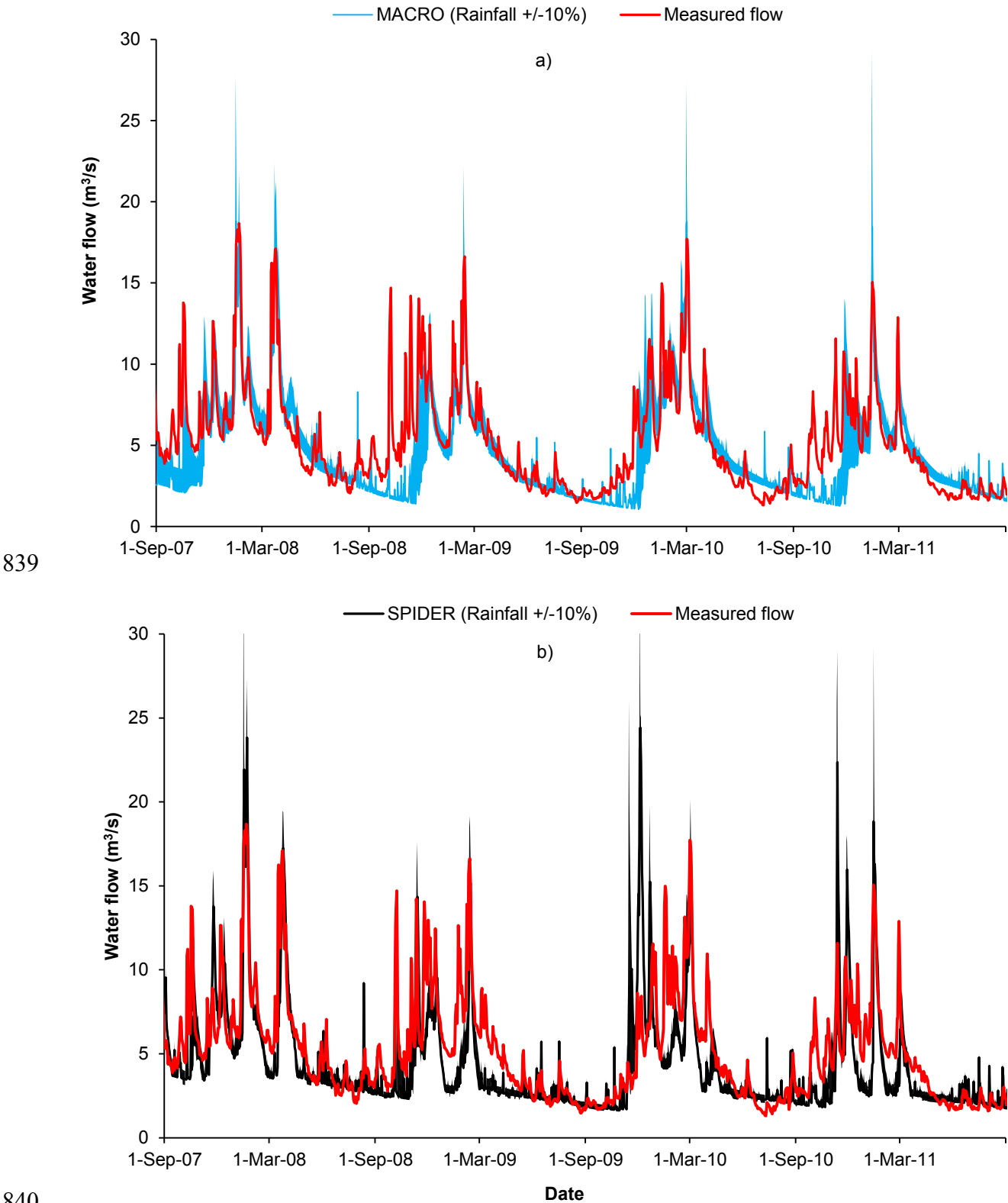
Figure A–6 Effect on the simulated water flow when decreasing and increasing the rainfall data by 10% using a) MACRO and b) SPIDER compared to the measured flow. Measured flow supplied by the Environment Agency.
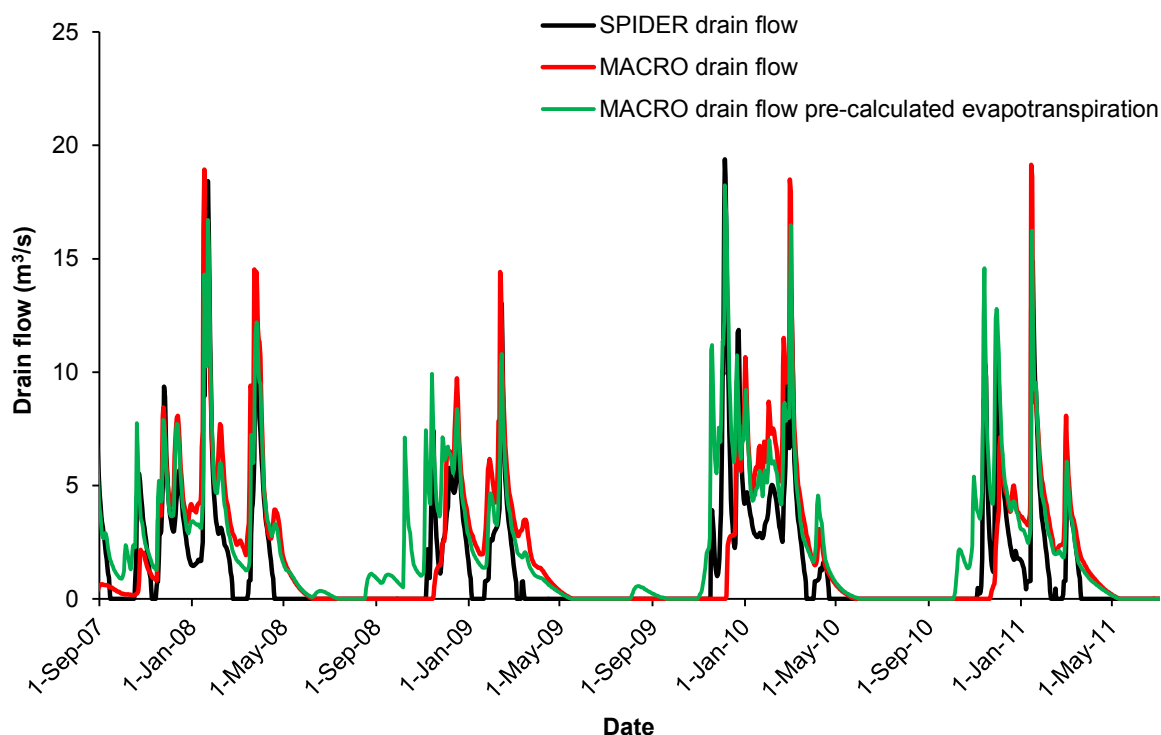
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845 **Figure A–7** Effect on the simulation of drain flow in MACRO from using the pre-calculated

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. (μg/l)		
Chlorotoluron						
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	**16.3**	**8.68**	**37.1**			
Mecoprop						
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	**30.7**	**38.6**	**68.6**			
Carbetamide						
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

36

Total 4 years	**19.0**	**3.12**	**5.77**			
Propyzamide						
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	**21.4**	**2.57**	**7.63**			
Clopyralid						
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	**19.0**	**12.3**	**1.76**			
MCPA						
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	**28.3**	**0.346**	**0.983**			

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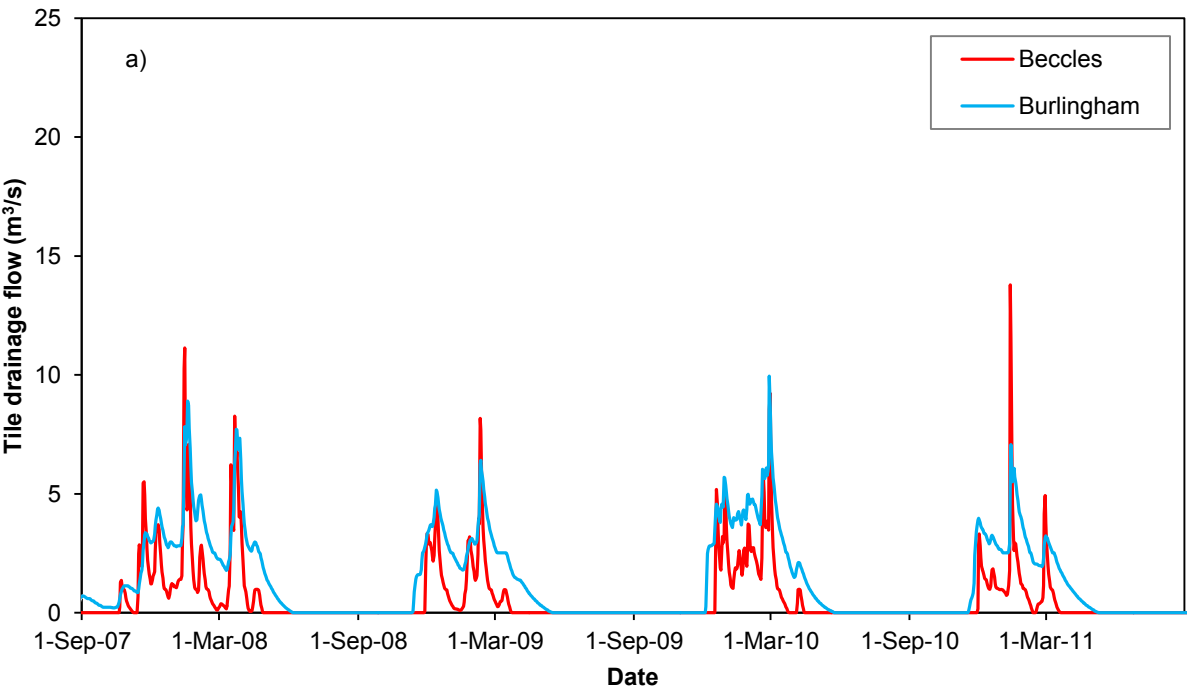853 with the observed value.

Pesticide/ Model	Loads (kg/4 years)							
	20 Oct	**25 Oct***	**30 Oct**	**4 Nov**	**9 Nov**	**14 Nov**	**19 Nov**	Observed data
Chlorotoluron								
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
Mecoprop								
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
Propyzamide								
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	

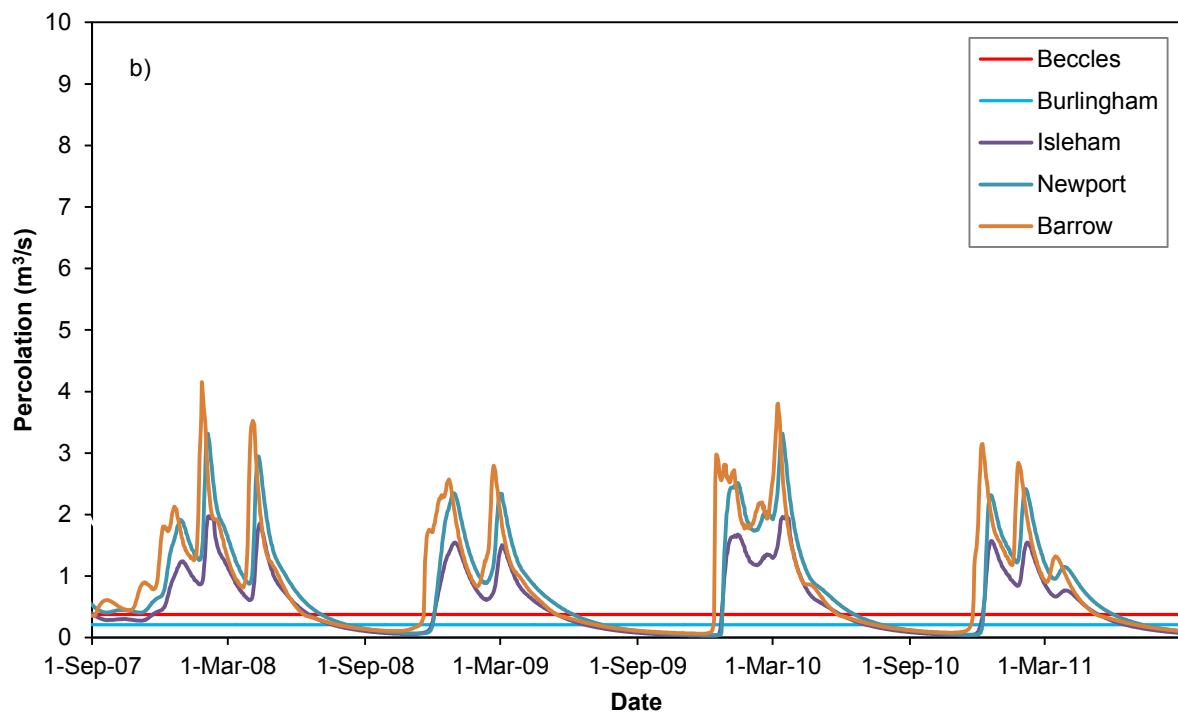|	**17 Mar** **5 May**	**17 Mar** **15 May**	**7 Mar** **15 May**	**17 Mar** **25 May**	**7 Mar** **5 May**	**25 Feb** **15 May**	**7 Mar** **25 May**	**25 Feb*** **25 May**	**25 Feb** **5 May**	**Observed data**
Clopyralid										
SPIDER	0.855	1.17	1.24	1.96	11.8	12.3	12.9	13.0	22.8	19.0
MACRO	0.186	0.186	0.230	0.186	0.230	0.670	0.230	0.669	0.669	

854 * Typical application date

855

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
Loads (kg/4 years)						
Chlorotoluron						
SPIDER	8.68	2.33	1.91	30.0	22.5	16.3
MACRO	37.1	14.5	14.1	137	88.5	
MCPA						
SPIDER	0.346	0.230	0.000	9.53	0.036	28.2
MACRO	0.983	1.14	0.002	6.52	0.007	
Clopyralid						
SPIDER	13.0	18.0	9.07	22.8	9.32	19.0
MACRO	0.669	0.878	0.176	1.76	0.183	

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861   **Figure A–8** Hydrographs simulated by MACRO for different soil types for a) drain flow and b) percolation.
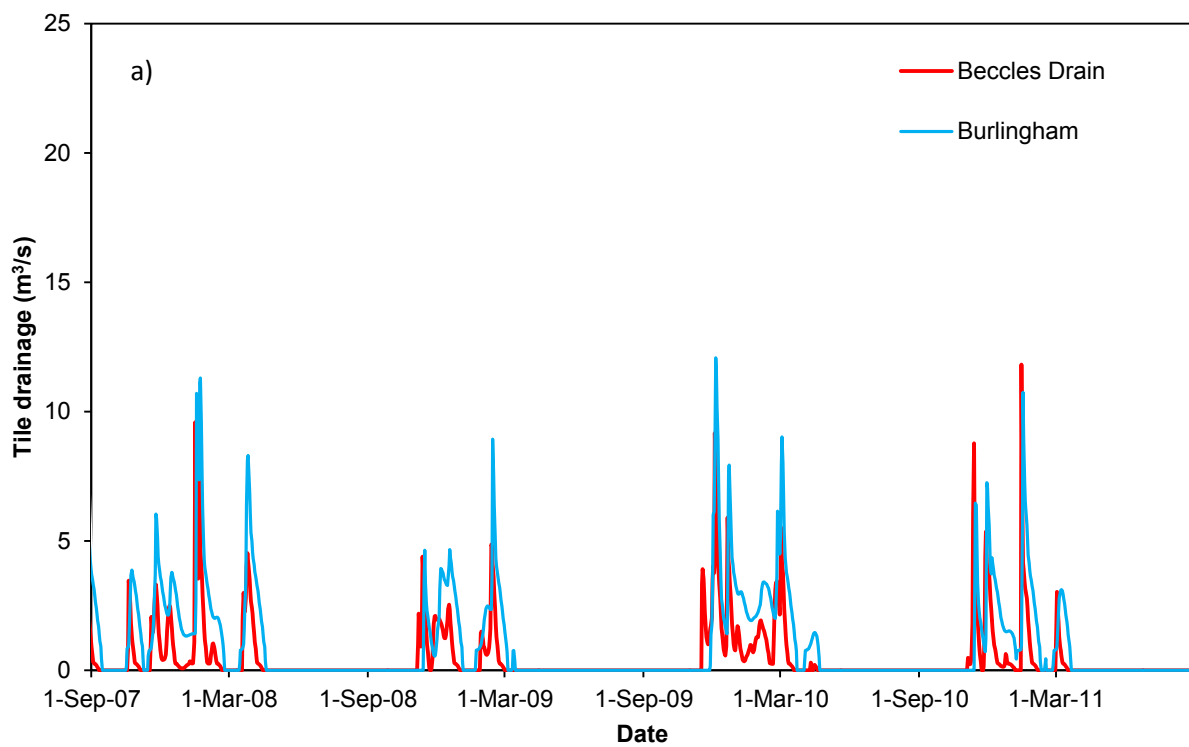
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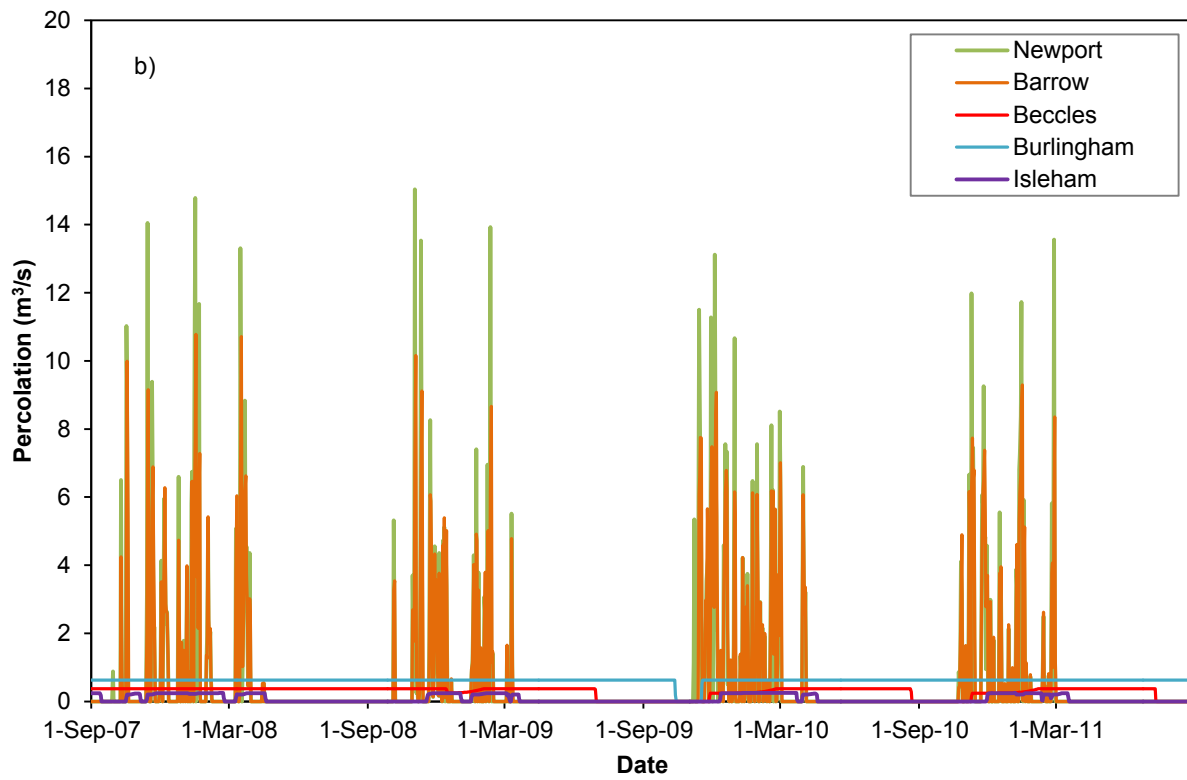
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864   **Figure A–9** Hydrographs simulated by SPIDER for different soil types for a) drain flow and b) percolation.