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# Development and application of a catchment scale pesticide fate and transport model for use in drinking water risk assessment

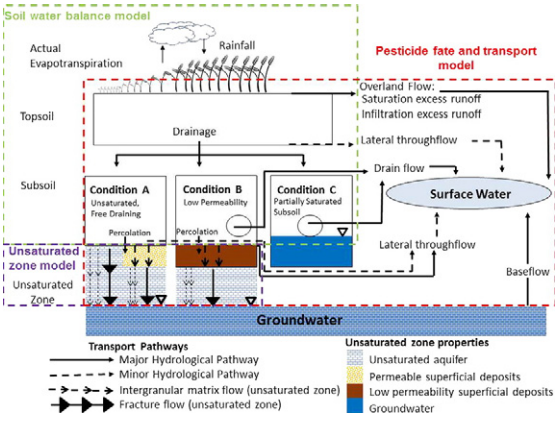
S.P. Pullan [a,b], M.J. Whelan [c,*], J. Rettino [d], K. Filby [d], S. Eyre [e], I.P. Holman [a]

[a] Cranfield University, Cranfield, Bedfordshire, UK
[b] TSGE Consulting, UK
[c] Department of Geography, University of Leicester, Leicester, UK
[d] Severn Trent Water, Coventry, UK
[e] Anglian Water, Cambridge, UK

## HIGHLIGHTS

- A new parameter-efficient catchment-scale pesticide exposure model is presented.
- Soil-type-specific boundary conditions determine active hydrological pathways.
- Applied and evaluated at the small sub-catchment and large catchment scales.
- Predicted exposure can inform water company risk assessments.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This paper describes the development and application of IMPT (Integrated Model for Pesticide Transport), a parameter-efficient tool for predicting diffuse-source pesticide concentrations in surface waters used for drinking water supply. The model was applied to a small UK headwater catchment with high frequency (8 h) pesticide monitoring data and to five larger catchments (479–1653 km$^2$) with sampling approximately every 14 days. Model performance was good for predictions of both flow (Nash Sutcliffe Efficiency generally >0.59 and PBIAS <10%) and pesticide concentrations, although low sampling frequency in the larger catchments is likely to mask the true episodic nature of exposure. The computational efficiency of the model, along with the fact that most of its parameters can be derived from existing national soil property data mean that it can be used to rapidly predict pesticide exposure in multiple surface water resources to support operational and strategic risk assessments.



* Corresponding author.
*E-mail address:* mjw72@le.ac.uk (M.J. Whelan).

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## 1. Introduction

Pesticides are widely used in modern conventional agriculture and contribute to increased yield and quality. However, a small fraction of some active ingredients can be transported, via a range of different pathways, to ground and surface waters. If the receiving water body is used for drinking water supply, then these substances may periodically present compliance risks for water companies if the treatment technologies in place are unable to reduce concentrations to the limits required by the prevailing legislation. In the European Union (EU), individual pesticides must not have concentrations >0.1 μg $L^{-1}$ in drinking water supplies (post treatment) and the total concentration of all pesticides must be <0.5 μg $L^{-1}$ (Drinking Water Directive - DWD; EC, 1998). In order to anticipate the levels of exposure which will be experienced at different drinking water abstraction points under current or future land use and meteorological scenarios, water companies are increasingly employing numerical models (Bloodworth et al., 2015). These models can help to assess DWD compliance risks and guide timing of sampling and the choice of analytical methods used on samples collected at water intakes. They can also be used to explore the potential of different catchment management interventions for mitigating pesticide exposure (e.g. changing crop rotations, switching active ingredients, using different dose rates), as required by Article 7 of the Water Framework Directive (WFD; EC, 2000).

There are a number of pesticide fate models that describe pesticide transfers from soil to surface and ground waters that could be used at the catchment scale (understood in this context to be over 100 ha or 1 $km^2$; Köhne et al., 2009). These range from simple screening models such as the Groundwater Ubiquity Score (GUS) developed by Gustafson (1985), the soil fugacity model (SoilFug) of Di Guardo et al. (1994) and the Pesticide Risk Management Profiling Tool (PRoMPT: Whelan et al., 2007), all based largely on pesticide properties, through to detailed field-scale one dimensional models, such as MACRO (a model of water flow and solute transport in macroporous soil: Larsbo and Jarvis, 2003; Larsbo et al., 2005), Pesticide Emission Assessment at Regional and Local scales (PEARL: Tiktak et al., 2000), PEsticide Leaching Model (PELMO: Klein, 1991) and the Pesticide Root Zone Model (PRZM: Mullins et al., 1993). Many simpler models (e.g. GUS) are not dynamic (i.e. they are not able to make predictions in time) and often lack good description of spatial variations in leaching due to varying soil characteristics, weather, topography and land use. The latter one-dimensional models are all employed as risk screening tools using standardised scenarios in the pesticide registration process in the EU (e.g. FOCUS, 2000, 2001) but can also be up-scaled to catchment and regional scales (e.g. GeoPEARL: Tiktak et al., 2003 and MACRO-SE: Steffens et al., 2015). Although such up-scaling can be successful, detailed models typically have high data requirements and incur long run times to solve the partial differential equations describing one-dimensional transport of water and solutes by numerical methods. This is exacerbated when applied to large heterogeneous catchments which require simulations to be performed for various (independent or connected) units representing different soil type and land use combinations and topographic locations. They are, therefore, often unsuitable for catchment-scale applications where evaluations may be required for many different pesticides (possibly all feasible combinations of active ingredients currently on the market) and for many different combinations of weather, soil types and land uses.

The aim of the model described here is to predict pesticide transport from agricultural land to surface waters in order to inform and support water company risk assessments in multiple catchments over a range of scales. This application requires a model that contains a sufficient description of process complexity to yield realistic concentrations in a wide range of catchment types (i.e. it should be process-based rather than empirically-based) using readily available input data (e.g. on soil properties and meteorological data). However, it also needs to be computationally efficient so that it can be run for a wide range of pesticides, crops, soils and weather combinations over large heterogeneous areas. This problem of finding an optimal combination between fidelity to real process operation and simplicity (to reduce run times) is a perennial problem in environmental modelling and has recently been attempted for pesticides by, inter alia, Gassmann et al. (2013) and Steffens et al. (2015). In the case of ZIN-AgriTra, the model described by Gassmann et al. (2013), a fully distributed approach was taken with soil water and pesticide dynamics represented at 10 min time steps in 10 m grid cells across a 1.95 $km^2$ catchment in Switzerland. The explicit representation of material transfers within and between many grid cells in this catchment resulted in long run times which would be problematical for exposure assessments for several pesticides in larger catchments. In contrast, the one dimensional MACRO model is used in MACRO-SE model (Steffens et al., 2015) to calculate leaching to 2 m depth for a set of independent soil and crop combinations, which are then integrated at the catchment scale via weighted averaging. This approach is more efficient than running computations for all grid cells in a catchment (although it lacks the ability to account for landscape connectivity) but still requires a number of computationally intensive one-dimensional runs to be performed. Furthermore, whilst MACRO is based on a realistic and mechanistic representation of water and material transfers in one dimension, accurate catchment scale up of such models is not always straightforward and may require additional calibration (e.g. Beven, 1989).

This paper presents the development of IMPT (Integrated Model for Pesticide Transport), a conceptual, parameter efficient model for predicting pesticide fate and transport at the catchment outlet. It is intended to fill the gap between one dimensional aspatial leaching models such as the ones used in FOCUS and fully distributed catchment scale models which have yet to be employed widely for operational environmental management. The model was initially applied to a small (0.15 $km^2$) sub-catchment for which detailed data on flows and pesticide concentrations were available in order to demonstrate its ability to predict concentrations at the 'edge of field' scale and to underpin confidence in process representation. The model was then applied to five larger catchments (479–1653 $km^2$) to assess its performance under a range of different soil, land use, pesticide use and climatic conditions.

## 2. Model description

The underlying philosophy of the model is to represent soil-to-water transport in a simple, but physically realistic, way. This necessitates the implementation of a good hydrological model as catchment hydrological response plays a critical role in determining how solutes, including agriculturally-applied pesticides, are transported from land to water (Holvoet et al., 2005).

### 2.1. Soil water balance

The model is "semi-distributed" and performs calculations for homogenous soil type and land use combinations (sometimes referred to as Hydrological Response Units). A soil water balance model is used to predict the hydrological (and pesticide) transport pathways. For each soil type, the soil is divided into two discrete stores: the top soil and the subsoil. A separate moisture balance (e.g. Ward and Robinson, 1999) is calculated for each store i.e.

$$\frac{dS_{TOP}}{dt} = P - f_{TOP}.ET_a - q_{OLF} - q_{DRAIN} - q_{LAT\_top} \quad (1)$$

$$\frac{dS_{SUB}}{dt} = q_{DRAIN} - f_{SUB}.ET_a - q_{GW} - q_{LAT\_sub} \quad (2)$$

where $_{TOP}$ and $_{SUB}$ refer to the topsoil and subsoil stores, respectively, $S$ is the storage in each layer (mm), $t$ is time (days), $P$ is the precipitation, $ET_a$ is the actual evapotranspiration, $f_{TOP}$ and $f_{SUB}$ are the fractions of

total root mass in the topsoil and subsoil layers, respectively, $q_{OLF}$ is the overland flow rate, $q_{LAT\_top}$ is the rate of lateral water transfer through the topsoil, $q_{DRAIN}$ is the rate of vertical water transfer from the top soil layer to the subsoil later, $q_{GW}$ is percolation to groundwater and $q_{LAT\_sub}$ is the rate of lateral water transfer through the subsoil, either as throughflow or as artificial drainage. All flux terms have units of mm $d^{-1}$. Both equations are solved via Euler's method of integration with a small time step (e.g. 1 h).

A gravity flow approximation to soil water flow (Whelan and Gandolfi, 2002; Whelan et al., 2002; Jury and Horton, 2004) is used to represent drainage, in which a unit hydraulic gradient is assumed and where the unsaturated hydraulic conductivity is predicted using the Mualem-van Genuchten model (van Genuchten, 1980) from $(S - S_r) / (S_{MAX} - S_r)$ where $S_r$ (mm) is the residual moisture storage (assumed here to be the storage at the permanent wilting point - i.e. the water content at −1500 kPa tension) and $S_{MAX}$ (mm) is the storage at saturation over the depth of the soil store under consideration. Note that the residual moisture content employed in the application of the Mualem-van Genuchten model in soil physics is often lower than the wilting point but here the equations are used in a different way and with different physical significance for the parameters, which represent effective area responses rather than describing hydraulic properties at the Darcy scale.

#### 2.1.1. Evapotranspiration

For many catchments, the full set of meteorological variables required for the Penman-Monteith equation is not available. Reference evapotranspiration is, therefore, calculated from air temperature data using the Hargreaves equation (Hargreaves and Samani, 1985):

$$ET_O = 0.135 \cdot K_T \cdot (T + 17.8) \cdot (T_{max} - T_{min})^{0.5} \cdot R_a \quad (3)$$

where $ET_O$ is reference evapotranspiration (mm $d^{-1}$), $K_T$ is an empirical coefficient (−) assumed to be fixed at 0.17 (Hargreaves and Allen, 2003; Weiß and Menzel, 2008), $T_{max}$ is the maximum monthly temperature (°C), $T$ is daily average temperature (°C), $T_{min}$ is the minimum monthly temperature (°C) and $R_a$ is extra-terrestrial radiation flux density in units of equivalent water evaporation (i.e. the flux density divided by the latent heat of evaporation: mm $d^{-1}$).

Potential crop evapotranspiration is calculated as:

$$ET_C = ET_O \cdot K_C \quad (4)$$

where $ET_C$ is the potential evapotranspiration (mm $d^{-1}$) and $K_C$ is a crop coefficient (−) intended to adjust $ET_O$ to account for crop characteristics at particular growth stages. $K_C$ values are taken from Holman et al. (2005) for key stages in the plant growth cycle. Linear interpolation is used to provide daily estimates of $K_C$ between stages.

Actual evapotranspiration ($ET_a$) is calculated from Allen et al. (1998) as:

$$ET_a = ET_C \cdot K_S \quad (5)$$

where $ET_a$ is the actual evapotranspiration (mm $d^{-1}$) and $K_s$ is the water stress coefficient (−) i.e. the $ET_a$:$ET_C$ ratio is assumed to decrease below unity at a fixed threshold soil moisture content and reach zero at the permanent wilting point.

The contribution of the topsoil and subsoil stores to total daily evapotranspiration depends on the fraction of the total root length assumed in each store (Finch, 1998). Assuming water uptake is proportional to the root density (Huang and Fry, 2000) and root zone density decreases with depth, Hansen et al. (1979) proposed a triangular function to describe root water extraction with depth, with the greatest water-uptake taking place near the surface (Finch, 1998; Ragab et al., 1997). This approach has been adopted here.

In autumn and winter, bare soil is common in arable environments in the UK. The potential evaporation from bare soil is calculated as:

$$E_S = ET_O \cdot K_e \quad (6)$$

where $E_S$ is evaporation from bare soil (mm $d^{-1}$) and $K_e$ is a bare soil evaporation coefficient (−), set at 1.10 (Rushton, 2003). In Eq. (1), $ET_a$ is replaced by $E_S$ and $f_{TOP}$ is set to 1. In the subsoil, loss of water via evaporation from bare soil is considered to be negligible (i.e. $f_{SUB} = 0$). Actual evaporation from bare soil is adjusted for water availability in the topsoil via $K_S$ (see Eq. (5)).

### 2.2. Modelling hydrological pathways from the soil to surface water

The hydrological pathways (overland flow, lateral throughflow, drainflow and/or percolation to groundwater) from soil to surface waters are assumed to drive pesticide transport. Each soil type is assigned to one of three broad (but physically realistic) classes representing contrasting boundary conditions at the base of the subsoil (A: unsaturated and free draining; B: low permeability with and without drains; and C: partially saturated subsoil; Fig. 1). The boundary condition assigned is based on a soil's Hydrology of Soil Type (HOST) class (Boorman et al., 1995), a widely-accepted classification of hydrological settings of soil in the UK, which has also been applied across Europe (Schneider et al., 2007). A similar approach was taken by Steffens et al. (2015) in MACRO-SE where soil types are assigned to four classes (rather than three).

In the unsaturated, free-draining bottom boundary condition (A) there are no restrictions to vertical percolation into the unsaturated zone, which represents the major drainage pathway out of the soil. Percolation is calculated assuming a gravity flow approximation to soil water flow in which a unit hydraulic gradient is assumed. The saturated hydraulic conductivity and parameters describing the shape of the water retention curve (van Genuchten, 1980) were derived from soil type-specific data in the National Soil Map database.

In the low permeability bottom boundary condition (B), the principal pathway for water movement is lateral (Fig. 1). In the UK, approximately 66% of arable land is drained (De la Cueva, 2006). Where artificial field drains are assumed to be in place, this is the principal transport pathway to surface water. In such situations drainflow from the subsoil store is calculated using an exponential equation similar to that employed in TOPMODEL (Beven et al., 1984; Beven and Kirkby, 1979):

$$q_{AD} = C_d \cdot exp^{(-D_{sub}/C_m)} \quad (7)$$

where $q_{AD}$ is the flow generated from artificial drainage (mm $d^{-1}$), $D_{sub}$ is a deficit from saturation (mm) calculated from the water balance in the subsoil ($D_{sub} = 0$ when the subsoil is saturated), $C_d$ is the maximum drainflow rate (mm $d^{-1}$) and $C_m$ is a drainflow parameter that controls the shape of the recession curve (mm).

When drains are not present, lateral throughflow is considered to be the dominant pathway from the subsoil (Carter, 2000). The generation of lateral throughflow in the topsoil store of IMPT is predicted to occur only when the subsoil is temporarily saturated, thereby restricting drainage from the topsoil store, or when predicted drainage from the topsoil store exceeds the saturated hydraulic conductivity of the subsoil store. An exponential storage model is also used to describe lateral throughflow in the subsoil:

$$q_{LT} = K_{lat} \cdot exp^{(-D_{sub}/C_{lat})} \quad (8)$$

where $q_{LT}$ is the lateral flow generated in the subsoil (mm $d^{-1}$), $K_{lat}$ is the saturated lateral hydraulic conductivity (mm $d^{-1}$) and $C_{lat}$ is a parameter that controls the shape of the curve (mm).

Percolation into the unsaturated zone in the presence of low permeability material is possible (Jackson and Rushton, 1987; Klinck et al.,

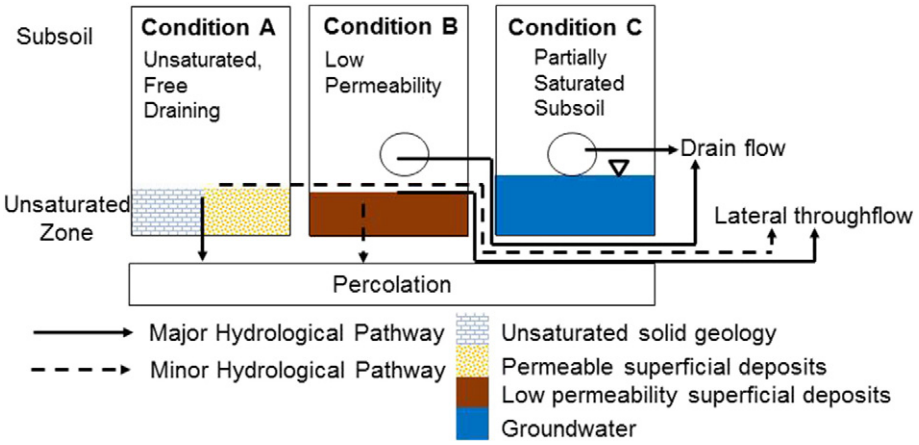


**Fig. 1.** Schematic diagram of the three boundary conditions considered in IMPT at the base of the subsoil store.

1996) and is conceptualised in IMPT as described for condition A but with a low value for the saturated hydraulic conductivity which reduces its importance as a hydrological pathway.

The partially-saturated bottom boundary condition C is assumed to occur in soils that have a permanent groundwater table within 2 m of the soil surface, typical of alluvial soils. No percolation is assumed under this boundary condition and the pathway for water is assumed to be entirely via field drains (Fig. 1).

Overland flow (saturation excess and infiltration excess) can occur in the topsoil under all three boundary conditions. Overland flow, as saturation excess, is generated in IMPT when the available storage in the topsoil reaches zero. Infiltration excess overland flow occurs when rainfall intensity is greater than the soil infiltration rate. This is difficult to estimate using daily data because high intensity rainfall events tend to occur for short durations which can only be predicted using hourly or sub-hourly data. Such data are often not available in many catchments. In their absence, infiltration excess overland flow is approximated by assuming that a fraction of rainfall above a certain threshold cannot infiltrate sufficiently quickly. This threshold is set as a proportion ($p_2$; −) of the Minimum Standard Rainfall Volume (*MSRV*; mm) – a parameter associated with the HOST class (Brown and Hollis, 1996). Thus, for an event of magnitude $R$ which is greater than $MSRV.p_2$, infiltration excess overland flow ($q_{OF}$) is:

$$q_{IEOF} = (R - MSRV \cdot p_2) \cdot f_R \quad (9)$$

where $q_{IEOF}$ is the infiltration excess overland flow generated (mm $d^{-1}$) and $f_R$ is the fraction of the "excess" rainfall that flows over the surface (−). This is similar to the storage threshold approach used by Kirkby et al. (2008). A low *MSRV* is associated with soils which are expected to require only a small volume of rainfall to induce a stream response.

### 2.3. Modelling solute transport

The pesticide mass balance in the soil takes the form:

$$\frac{dM_{SOIL}}{dt} = E - k.M_{SOIL} - J \quad (10)$$

where $M_{SOIL}$ is the mass of pesticide in a soil layer (μg $m^{-2}$) at any particular time $t$ (d), $E$ is the application rate (μg $m^{-2}$ $d^{-1}$), $k$ is first-order dissipation rate constant ($d^{-1}$) and $J$ is the mass flux of pesticides out of the soil in mobile soil water (μg $m^{-2}$ $d^{-1}$). Again, this is solved numerically via Euler's method with a sufficiently small time step to avoid significant integration errors.

The fate of pesticides in the soil after application is accounted for in two stages: (1) pesticide fate and transport between "significant" rainfall events and (2) pesticide displacement during such events. Significant rainfall events are considered to be those capable of transferring a fraction of the soil pore water and associated pesticide to an adjacent surface water body. Following a significant rainfall event any remaining pesticide is assumed to continue undergoing internal redistribution.

#### 2.3.1. Pesticide fate in the soil

On application, pesticide is assumed to immediately penetrate the soil uniformly to a given depth – nominally 2 mm (Brown and Hollis, 1996). There is no consideration of crop interception. The pesticide is assumed to diffuse through the 'non-excluded' water filled pore space (Brown and Hollis, 1996) and to equilibrate between water and the soil solid phase (assuming hydrophobic interactions dominate resulting in a linear sorption isotherm). Pesticide partitioning between the gas phase and other phases is not considered so the model is only applicable to non-volatile compounds (although most modern pesticides are not volatile to any extent which would affect significantly their concentrations in water). The non-excluded water filled pore volume is defined as the difference between the current volumetric water content of the soil and 50% of the volumetric water content at permanent wilting point. Pesticides are assumed to be excluded from the most strongly held water due to slow diffusion and size exclusion phenomena (Brown and Hollis, 1996).

In the soil water phase a pesticide is assumed to be subject to vertical advective transport due to gravity as long as the soil is wet enough (Kördel et al., 2008). This is assumed to be proportional to the unsaturated hydraulic conductivity, calculated using the Mualem-van Genuchten (1980) equation, subject to retardation due to sorption to the surrounding soil matrix. The concentration of pesticide in the non-excluded pore water ($C_{NE}$, μg $L^{-1}$) is calculated as the ratio of the mass of pesticide in the dissolved phase and the non-excluded water volume, i.e.:

$$C_{NE} = \frac{M_{soilwater}}{(\theta_{NE} \cdot Z)} = \frac{M_{soil}}{Z \cdot (\theta_{NE} + K_d \cdot \rho_B)} \quad (11)$$

where $M_{soilwater}$ is the mass of pesticide in the dissolved phase (μg $m^{-2}$), $\theta_{NE}$ is the volumetric non-excluded fraction (assumed to be uniform throughout the topsoil store; $m^3$ $m^{-3}$), $Z$ is the soil depth (mm) to which pesticide has penetrated, $Kd$ is the linear sorption coefficient (L $kg^{-1}$) and $\rho_B$ is the soil bulk density (kg $L^{-1}$).

At the time of a rainfall event, a fraction ($f_d$) of the so-called 'mobile' water-filled pore volume ($\theta_{mob}$) is assumed to be displaced by rainfall. This mobile water refers to the largest water filled pores and is defined as the difference between the current volumetric water content and a mobile threshold (i.e. the volumetric water content at 200 kPa tension: again, after Brown and Hollis, 1996). If the volumetric water content is

less than $\theta_{200}$ (i.e. the volumetric water content at 200 kPa) then the volume of mobile water is zero. This mobility threshold has also been used by Addiscott et al. (1986).

The fraction of the mobile water displaced, $f_d$, is assumed to be a function of the ratio of the unsaturated hydraulic conductivity $K(\theta)$ and the saturated hydraulic conductivity ($K_{sat}$), such that a larger volume of water will be displaced the closer the soil is to saturation:

$$f_d = \left(\frac{V_d}{\theta_{mob}.Z}\right) = \frac{K(\theta)}{K_{sat}} \tag{12}$$

where $V_d$ is the volume of displaced water from the most mobile pores (L $m^{-2}$) i.e.:

The pesticide mass, $J$ (μg $m^{-2}$), generated by the displacement of $V_d$ is calculated as:

$$J = C_{NE} \cdot V_d. \tag{13}$$

This mass is assumed to be transported to surface water and/or to the water table based on the relative importance of different hydrological pathways.

Between subsequent rainfall events the remaining mass of pesticide is assumed to undergo further equilibrium partitioning, first order degradation and vertical advective transport.

*2.3.2. Pesticide transport from the soil*

Pesticide transport from soil is intrinsically linked to hydrological response. The pathways of pesticide transport through the soil during a rainfall event (i.e. via macropores or through the bulk matrix) are not explicitly represented due to their complexity and associated uncertainties, which bedevil description using only a few readily-available parameters. Instead, we make an implicit assumption that the displaced pesticide mass bypasses the soil matrix during an event and is transported directly to surface water (e.g. by overland flow, drainflow or lateral throughflow and/or to the top of the unsaturated zone). We recognise that this is probably not realistic for all soil types and may lead to an overestimation of pesticide transport for sandy soils where bypass flow tends to be less important. However, it is also important to recognise that $V_d$ will depend on $\theta_{mob}$ and the ratio $K(\theta)$: $K_{SAT}$ (Eq. (12)) and will be lower for coarse textured soils which tend to be drier in spring and summer.

Pesticide at the top of the unsaturated zone is available for further transfer to the water table but this is not covered further here (see Pullan, 2014 for more information). The pesticide flux to surface water ($J_{sw,\,i,\,j}$; μg $m^{-2}d^{-1}$) is calculated as:

$$J_{sw,i,j} = J_{i,j}.\left(\frac{q_{OLFi,j} + q_{LATi,j}}{q_{OLFi,j} + q_{LATi,j} + q_{GWi,j}}\right) \tag{14}$$

where $i$ and $j$ are indices for soil type and crop type, respectively, $q_{OLF}$ is overland flow, $q_{LAT}$ is the water flux generated from drainflow and lateral throughflow (from both the topsoil and subsoil) and $q_{GW}$ is the water percolating through the base of the subsoil in boundary conditions A and B which is not assumed to reach the receiving water body (all in mm $d^{-1}$).

Total flow in the river ($Q_{CATCH}$, mm $d^{-1}$) is calculated as the sum of baseflow from a groundwater store ($Q_{BASE}$, mm $d^{-1}$) and a weighted contribution of runoff from different soil type and crop combinations within the catchment.

$$Q_{CATCH} = Q_{BASE} + \left(\sum_{i=1}^{Nsoil}\sum_{j=1}^{Ncrop}\left(q_{OLFi,j} + q_{LATi,j}\right).w_{i,j}\right) \tag{15}$$

where *Nsoil* and *Ncrop* are the numbers of soil types and crop types in the catchment and $w_{i,j}$ is the relative area of soil type $i$ covered by crop type $j$. It is assumed that

$$Q_{BASE} = C_g.\exp^{(-GW_t/BF)} \tag{16}$$

where $C_g$ is the groundwater flow constant (mm $d^{-1}$), $GW_t$ is a groundwater storage deficit (mm) which is depleted by percolation from the soil and augmented by baseflow to the river, and $BF$ is a baseflow constant that controls the shape of the recession (mm). The groundwater store is assumed to have the same catchment boundary as the surface water catchment.

The pesticide mass at the catchment outlet ($J_{CATCH}$, μg $m^{-2}$ $d^{-1}$) is calculated as a weighted average flux from different soil type and land use combinations.

$$J_{CATCH} = \sum_{i=1}^{Nsoil}\sum_{j=1}^{Ncrop}\left(J_{SWi,j}.w_{i,j}.f_{TREAT,i}\right) \tag{17}$$

where $f_{TREAT,\,i}$ is the fraction of crop type $i$ which is treated with the pesticide in question.

The pesticide concentration at the catchment outlet ($C_{CATCH}$; μg $L^{-1}$) will be subject to dilution from water originating from soil type and land use combinations where pesticides have not been applied, as well as dilution from baseflow:

$$C_{CATCH} = \frac{J_{CATCH}}{Q_{CATCH}}. \tag{18}$$

## 3. Model set-up, calibration and validation

The model was applied to a small head-water sub-catchment and in five larger catchments representing a range of sizes, land use distributions and physical characteristics.

### 3.1. Study catchments and monitoring data

*3.1.1. Headwater sub-catchment*

A 15.5 ha sub-catchment in the upper reaches of the river Cherwell in central England was described in detail by Tediosi et al. (2012, 2013). Briefly, it is comprised of two fields: a drained arable field (8.6 ha) and, upslope, an undrained interfluve area (6.9 ha). The arable field is primarily underlain by heavy clay soil of the Denchworth series. On the interfluve, the soils are lighter and made up of soils of the Banbury Association which overlie the Northampton Sand. The flows at the drain outlet also include a baseflow component from the Northampton Sand, which is assumed to be recharged solely in the interfluve area (Tediosi et al., 2013). The arable field was cropped with oilseed rape in 2009/10 and two pesticides were applied: propyzamide on the 7th of November 2009 at a rate of 800 g $ha^{-1}$ and carbetamide on the 15th of February 2010 at a rate of 2100 g $ha^{-1}$ (Tediosi et al., 2012). This is not normal agricultural practice, as the carbetamide was applied for experimental reasons only.

Hourly rainfall and temperature data were collected, together with 5 min flow data from a Venturi flume connected to the main drain via a stainless steel collecting tank. Samples were collected every 8 h for pesticide analysis. $DT_{50}$ values of 56 days and 8 days and $K_{OC}$ values of 840 L $kg^{-1}$ and 89 L $kg^{-1}$ were assumed for propyzamide and carbetamide, respectively (Tediosi et al., 2012, 2013). IMPT was run at an hourly time-step for this system.

*3.1.2. Larger catchments*

The model was also applied to five larger surface water catchments in England and Wales covering a range of size, climate, runoff, land use, soil types and geology: the Lugg, Teme, Waveney, Wensum and

**Table 1**
Characteristics of the five catchments (Lugg, Teme, Waveney, Wensum and Yare).

| | Lugg | | Teme | | Waveney | | Wensum | | Yare | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Flow monitoring point[a] | Pesticide monitoring point[f] | Flow monitoring point[b] | Pesticide monitoring point[f] | Flow monitoring point[c] | Pesticide monitoring point[f] | Flow monitoring point[d] | Pesticide monitoring point[f] | Flow monitoring point[e] | Pesticide monitoring point[f] |
| Size ($km^2$) | 885 | 1077 | 1484 | 1653 | 376 | 670 | 560 | 699 | 229 | 479 |
| Monitoring location | Lugwardine | Mordiford Bridge | Knightsford Bridge | Powick | Needham Mill | Ellingham Mill | Costessey Mill | Sweet Briar road Bridge | Colney | Trowse Mill |
| Mean annual rainfall ($mm\ y^{-1}$) | 812 (1961–1990) | n/a | 818 (1961–1990) | n/a | 594 (1961–1990) | n/a | 672 (1960–1990) | n/a | 635 (1960–1990) | n/a |
| Rainfall station | Lyonshall | | Pennerly | | Uplands Farm | | North Creake | | Browick Hall | |
| Temperature weather station | Lyonshall | | Pennerly | | Charsfield | | Santon Downham | | Santon Downham | |
| Mean annual flow ($mm\ y^{-1}$) | 383 (1939–2013) | n/a | 381 (1970–2013) | n/a | 152 (1963–2014) | n/a | 226 (1960–2014) | n/a | 200 (1959–2014) | n/a |
| Dominant geology | Low permeability bedrock (mudstone, siltstone and sandstone) | | Low permeability bedrock (mudstone, siltstone and sandstone) | | High permeability bedrock (chalk) covered by mixed permeability drift | | High permeability bedrock (chalk) covered by mixed permeability drift | | High permeability bedrock (chalk) covered by mixed permeability drift | |
| Dominant soil association | Escrick | | Bromyard | | Beccles | | Burlingham | | Burlingham | |
| Dominant land use[g] | Grassland (47%) | Arable (50%) | Grassland (47%) | Arable (46%) | Arable (93%) | Arable (91%) | Arable (88%) | Arable (83%) | Arable (94%) | Arable (91%) |

[a] http://www.ceh.ac.uk/data/nrfa/data/station.html?55003.
[b] http://www.ceh.ac.uk/data/nrfa/data/station.html?54029.
[c] http://www.ceh.ac.uk/data/nrfa/data/station.html?34006.
[d] http://www.ceh.ac.uk/data/nrfa/data/station.html?34004.
[e] http://www.ceh.ac.uk/data/nrfa/data/station.html?34001.
[f] CSF Pesticides Report (2012) (http://www.wensumalliance.org.uk/publications/CSFpesticidesreport_2006_2012_061112.pdf).
[g] CORINE Land Cover 2000.

Yare for eight pesticides: 2,4-D, carbetamide, clopyralid, chlorotoluron, isoproturon, MCPA, mecoprop and propyzamide.

Regular pesticide monitoring has been conducted in these catchments as part of Catchment Sensitive Farming (CSF Evidence Team, 2011). Daily flow data were available for all five catchments. However, in all cases, the flow monitoring point is located a short distance upstream of the pesticide monitoring point resulting in different catchment sizes (see Table 1). Dominant geology and soil associations in each catchment are shown in Table 1 although it should be stressed that each catchment contains a complex mosaic of soils and parent materials which are not always reflected by the dominant class.

All flows are calculated on an area-normalised basis (i.e. in $mm\ d^{-1}$) and the land use and soil type distributions in both the gauged and sampled catchments were assumed to be the same. Similarly, the groundwater store is assumed to have the same catchment boundary as the surface water catchment. IMPT was run at a daily time-step for these catchments.

### 3.2. Input data at the catchment scale

In order to be applicable to a wide range of catchment types in the UK, IMPT has been designed to run with readily available data: the database of the National Soil Map (available from http://www.landis.org.uk/data/natmap.cfm) and CORINE land cover data (CLC, 2000). Rainfall and temperature data were taken from the British Atmospheric Data Centre (BADC), with a single weather station chosen to represent each catchment (Table 1).

The distribution of soil types in each catchment was determined from the 1:250,000 scale National Soil Map for England and Wales, with the soil properties (Table 2) of the dominant soil type used to represent all soils in each mapping unit. Soil properties are available for four broad land uses: arable, long-term 'permanent' grassland, short-term rotational 'ley' grassland, and 'other' (i.e. land that is semi-natural). Soil properties for arable land were used unless arable land is not found on that soil type in the catchment. In this instance, the most suitable land use group is used instead. Each soil type was assigned a priori into one of the three contrasting boundary condition classes (A, B or C) by expert judgement on the basis of their HOST class. This allocation can be found in the Supplementary Material File (Table SM3).

The land cover in each catchment was determined using CORINE Land Cover 2000 which was grouped into four broad categories: arable, grassland, urban and other (e.g. forests, moorland and estuaries). The arable land cover category in each catchment was further divided into the two most common arable crop types in England: winter wheat and winter oilseed rape, based on the DEFRA June Survey statistics (DEFRA, 2010). Grass is used to represent all grass-based land uses as well as the urban and other land use categories. Although in urban areas, vegetated surfaces, such as gardens and parks, can cover significant areas (Grimmond and Oke, 1999) and affect hydrological response (e.g. Huang et al., 2008), their extent in the predominantly rural study catchments was small. Pesticides are only assumed to be applied in the "grassland" and "arable" land use categories and not in the urban and other land use categories.

The following vegetation-specific parameters are required to calculate actual evapotranspiration: rooting depth at emergence, maximum rooting depth, *Kc* (initial, mid growth and end), the depletion factor ($p$) and growth stage dates (planting, emergence, 10% cover, 100% cover, senescence and harvest). Crop development parameters and evapotranspiration parameters (e.g. *Kc* for various stages) were taken from Holman et al. (2005). The parameters for grass are assumed to be constant all year round, i.e. a constant root depth and $K_C$ are assumed.

Pesticide properties ($K_{OC}$ and $DT_{50}$) were taken from the Pesticide Properties Database (University of Hertfordshire, 2013), manufacturers' safety data sheets and EFSA conclusions (European Food Safety Authority, 2010). $K_{OC}$ and $DT_{50}$ exhibit a large degree of variability (Table 3) which can lead to issues of subjectivity about which values to choose

**Table 2**
Soil properties required in IMPT.

| Soil property | Symbol |
|---|---|
| Water content at saturation (0 kPa; $cm^3\ cm^{-3}$) | $\theta_{sat}$ |
| −5 kPa, −10 kPa, −200 kPa and −1500 kPa tension; $cm^3\ cm^{-3}$) | $\theta_5, \theta_{10}, \theta_{200}, \theta_{1500}$, |
| Bulk density ($g\ cm^{-3}$) | *pb* |
| Sub-vertical saturated hydraulic conductivity ($mm\ d^{-1}$) | $K_{sat}$ |
| Lateral saturated hydraulic conductivity ($mm\ d^{-1}$) | $K_{lat}$ |
| van Genuchten *n* parameter (−) | *n* |
| Organic carbon content (%) | *OC* |
| Depth of topsoil and subsoil layer (mm) | $Z_{top}, Z_{sub}$ |
| Drain installation depth (mm) | $Z_{drain}$ |
| Maximum hydraulic conductivity of the last soil horizon ($mm\ d^{-1}$) | $K_{BC}$ |
| *For each soil type* | |
| Hydrology of soil type classification (−) | HOST |
| Minimum standard rainfall volume (mm) | MSRV |
| Baseflow index (−) | BFI |

(Boesten and Gottesbüren, 2000; Dubus et al., 2003). Therefore, IMPT was run using a best case combination (a high $K_{OC}$ and a low $DT_{50}$) and a worst case combination (a low $K_{OC}$ and a high $DT_{50}$) to capture the edges of the pesticide property envelope (see Table 3).

The treated area of winter wheat and winter oilseed rape was estimated from the national average usage using data from 2008 (Garthwaite et al., 2010) and crop statistics (DEFRA, 2009). The grass treated area was estimated from 2005 data (Garthwaite et al., 2006) and the crop statistics from DEFRA (2006). The application window for each pesticide was estimated using product labels and Whitehead (2006). In each catchment, the percentage of the catchment treated with a pesticide is split equally over the application window. For example, propyzamide has a 17 week application window. If 34% of the oilseed rape in each catchment is assumed to receive propyzamide, this equates to 2.0% applied each week across the catchment. In the model the application day is assumed to be a Monday, unless rainfall is $>2\ mm\ d^{-1}$, in which case the application day moves forward to the next day, assuming that most farmers will not spray during rainfall events. The application rate is assumed to be the maximum label rate for a single application (Table 3).

### 3.3. Model calibration and validation

In the upper Cherwell sub-catchment the model run was split into a calibration period (October 2009–December 2009) and a validation period (February 2010–March 2010). A "warm-up" period was also used, which employed a copy of the rainfall and temperature data from the calibration period.

In the other catchments, model runs were split into a two year warm-up period (1989–1991 in the Lugg, Teme, Wensum and Yare and 1991–1993 in the Waveney), a calibration period (1992–2011 in the Lugg, Teme, Wensum and Yare and 1994–2002 in the Waveney) and a validation period (2002–2010 in the Lugg, Teme, Wensum and Yare and 2003–2010 in the Waveney). Seven catchment-specific parameters were adjusted in calibration: drainflow parameters (*Cm* and *Cd*), baseflow parameters (*Cg* and *BF*), infiltration excess overland flow parameters (*p2* and *fractR*) and a subsoil lateral throughflow parameter (*Clat*). Calibration was performed via a manual trial and error procedure with parameter values adjusted one at a time. Although this involves a certain degree of subjectivity and may result in identifying local rather than global optima, the physical significance of parameters is often eroded by any optimisation routine – even automated ones (Beven, 1989). Furthermore, there may be several combinations of parameter values which result in similar goodness of fit (equifinality: Beven, 2006).

Two model performance statistics: Nash Sutcliffe Efficiency (NSE; Nash and Sutcliffe, 1970) and Percent Bias (PBIAS) were used to assess goodness-of-fit. In the calibration period the parameter set was chosen so as to maximise the NSE, whilst minimising the PBIAS (see Tables SM1 and SM2 in the supplementary material). No calibration of pesticide-specific parameters or the parameters pertaining to the moisture retention curve (e.g. $\theta_{mob}$) was performed at either scale.

Validation of model performance for predicting pesticide concentrations was relatively straightforward at the headwater scale due to the high frequency of sampling. However, in the larger catchments, measured data were only available at approximately fortnightly intervals and sometimes longer. This presents challenges for evaluating IMPT predictions which are made on a daily time step. Results were evaluated against the measured data via a combination of visual comparisons and comparing cumulative frequency distributions.

## 4. Results and discussion

### 4.1. Upper Cherwell

Observed and predicted drainflow and pesticide concentrations in the Cherwell sub-catchment are shown in Fig. 2, split between the calibration (Fig. 2a) and validation periods (Fig. 2b). The overall performance of IMPT for predicting drainflow was good: NSE values were 0.66 and 0.56 for the calibration and validation periods, respectively, and BIAS values were 12.6% and −20.5%, respectively. These metrics compare favourably with the performance of MACRO (Larsbo and Jarvis, 2003; Larsbo et al., 2005), a one-dimensional dual permeability solute transport model combined with baseflow contributions from the Northampton Sand in the same catchment (Tediosi et al., 2012, 2013). The timing and magnitude of peak drainflow prediction during the calibration period was particularly good with only a slight overprediction of the first two events (Fig. 2a). In the validation period, there was a general underestimation in drainflow by IMPT. This could

**Table 3**
Pesticide properties ($K_{OC}$ and $DT_{50}$), main uses in the UK, typical application rate and typical application window. OSR = Oil Seed rape. Ranges given for $K_{OC}$ and Soil $DT_{50}$ denote the lowest and highest values reported for each compound (University of Hertfordshire, 2013).

| Pesticide active ingredient | Organic carbon to water partition coefficient $K_{OC}$ ($L\ kg^{-1}$) | Soil $DT_{50}$ (days) | Main uses in the UK | Application rate | Application windows | Treated area (%)[a] |
|---|---|---|---|---|---|---|
| 2,4-D | 5–212 | 2–59 | Grass | 1.65 kg/ha | 15 Mar–15 Apr | 0.5% |
| | | | Cereal | 1.25 kg/ha | 31 Mar–5 Apr | 0.3% |
| Carbetamide | 45–180 | 15–60 | OSR | 3.5 kg/ha | 15 Oct–28 Feb | 10% |
| Chlorotoluron | 108–384 | 26–40 | Cereals | 3.5 kg/ha | 1 Oct–25 Mar | 5% |
| Clopyralid | 2–30 | 14–56 | OSR | 0.2 kg/ha | 20 Feb–29 Apr | 6% |
| Isoproturon | 67–235 | 13–40 | Cereals | 1.5 kg/ha | 1 Oct–20 Apr | 41% |
| Mecoprop | 10–40 | 7–21 | Grass | 1.3 kg/ha | 1 Mar–31 Jul | 0.6% |
| | | | Cereal | 1.3 kg/ha | 25 Mar–30 Apr | 21% |
| MCPA | 10–57 | 6–43 | Grass | 1.6 kg/ha | 1 Mar–31 May | 1.7% |
| | | | Cereal | 1.6 kg/ha | 15 Oct–15 Apr | 1.5% |
| Propyzamide | 128–990 | 16–54 | OSR | 0.8 kg/ha | 1 Oct–31 Jan | 34% |

[a] Treated area for grass estimated with pesticide usage statistics from 2005 (Garthwaite et al., 2006) and crop statistics from DEFRA (2006). Treated area for winter wheat and winter oilseed rape estimated from pesticide use statistics from 2008 (Garthwaite et al., 2010) and crop statistics from DEFRA (2009).

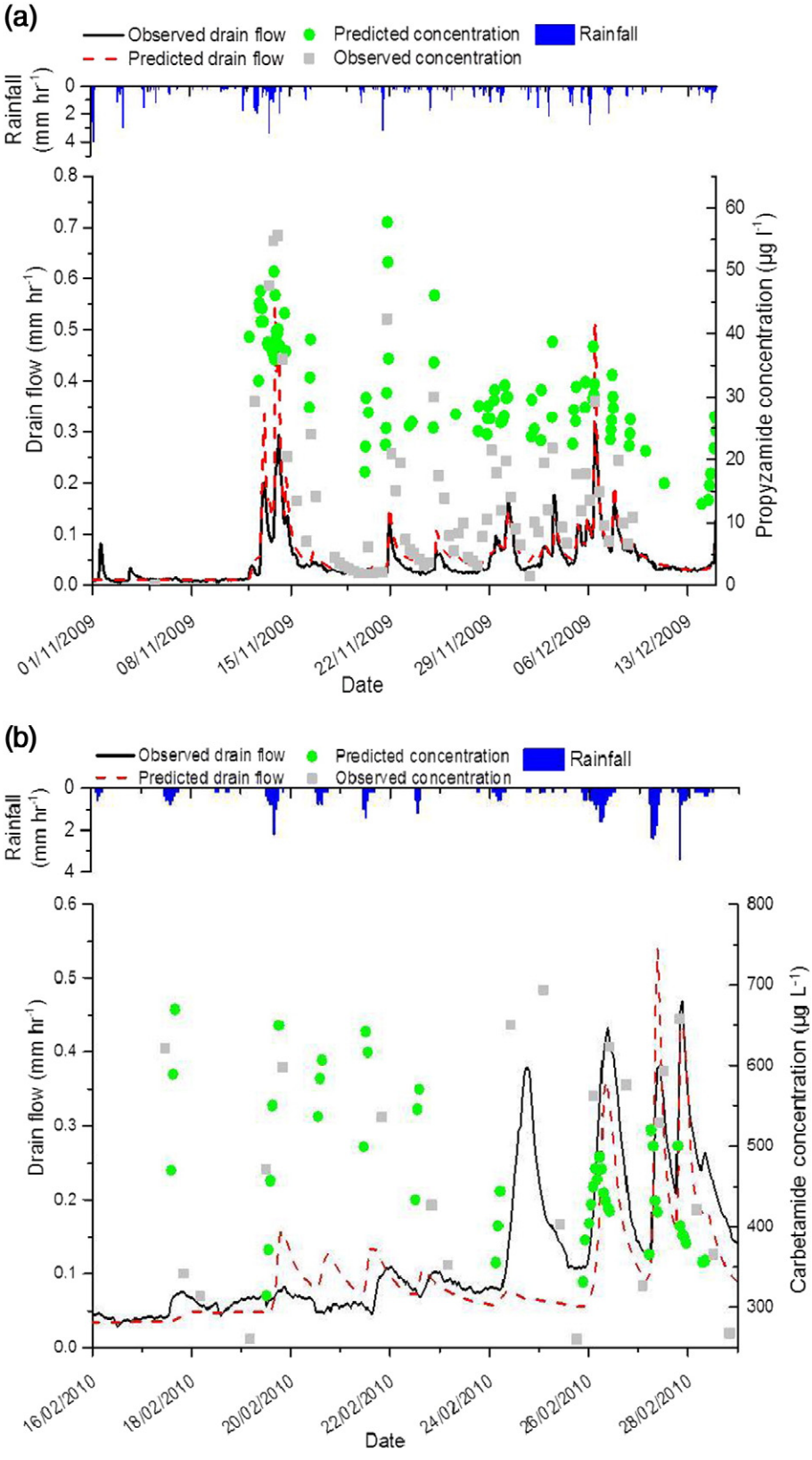


**Fig. 2.** Rainfall, observed (solid line) and predicted (dashed line) drainflow in the Cherwell sub-catchment during (a) the calibration period and (b) the validation period. Observed and predicted concentrations of (a) propyzamide and (b) carbetamide are also shown.

be attributed to high snow fall in this period resulting in both snowmelt contributing to observed drainflow and a probable under-estimation of precipitation by the rain gauge (Tediosi et al., 2013).

The prediction of timing and magnitude of peak propyzamide concentrations (Fig. 2a) and peak carbetamide concentrations (Fig. 2b) in comparison with the measured data are also reasonable suggesting

that the IMPT model structure is able to predict the chemograph peaks accurately. However, the clear quasi-exponential post-storm recessions in concentrations for both pesticides do not appear to be well captured by IMPT. This is because pesticide displacement out of the soil profile is not predicted at times when there is no rainfall (although internal redistribution via vertical advective transport is predicted to occur: Section 2.3.1).

### 4.2. Hydrograph simulations in the larger catchments

The model's ability to reproduce the hydrograph in both the calibration and validation periods was good in four out of five cases in the

**Table 4**
Model performance statistics and overall model performance of IMPT for the prediction of flow at the catchment outlet in the five larger catchments.

| Catchment | Calibration | | | Validation | | |
|---|---|---|---|---|---|---|
| | NSE | *PBIAS* | Overall model performance[a] | NSE | *PBIAS* | Overall model performance[a] |
| Lugg | 0.71 | 3.6 | Very good | 0.72 | 9.3 | Very good |
| Teme | 0.71 | 19.6 | Good | 0.72 | 9.1 | Very good |
| Waveney | 0.54 | −14.8 | Good | 0.59 | −11.3 | Good |
| Wensum | 0.25 | 29.6 | Poor | 0.19 | 1.7 | Poor |
| Yare | 0.53 | 12.8 | Good | 0.45 | 2.1 | Poor |

[a] Adapted from Henriksen et al. (2003).

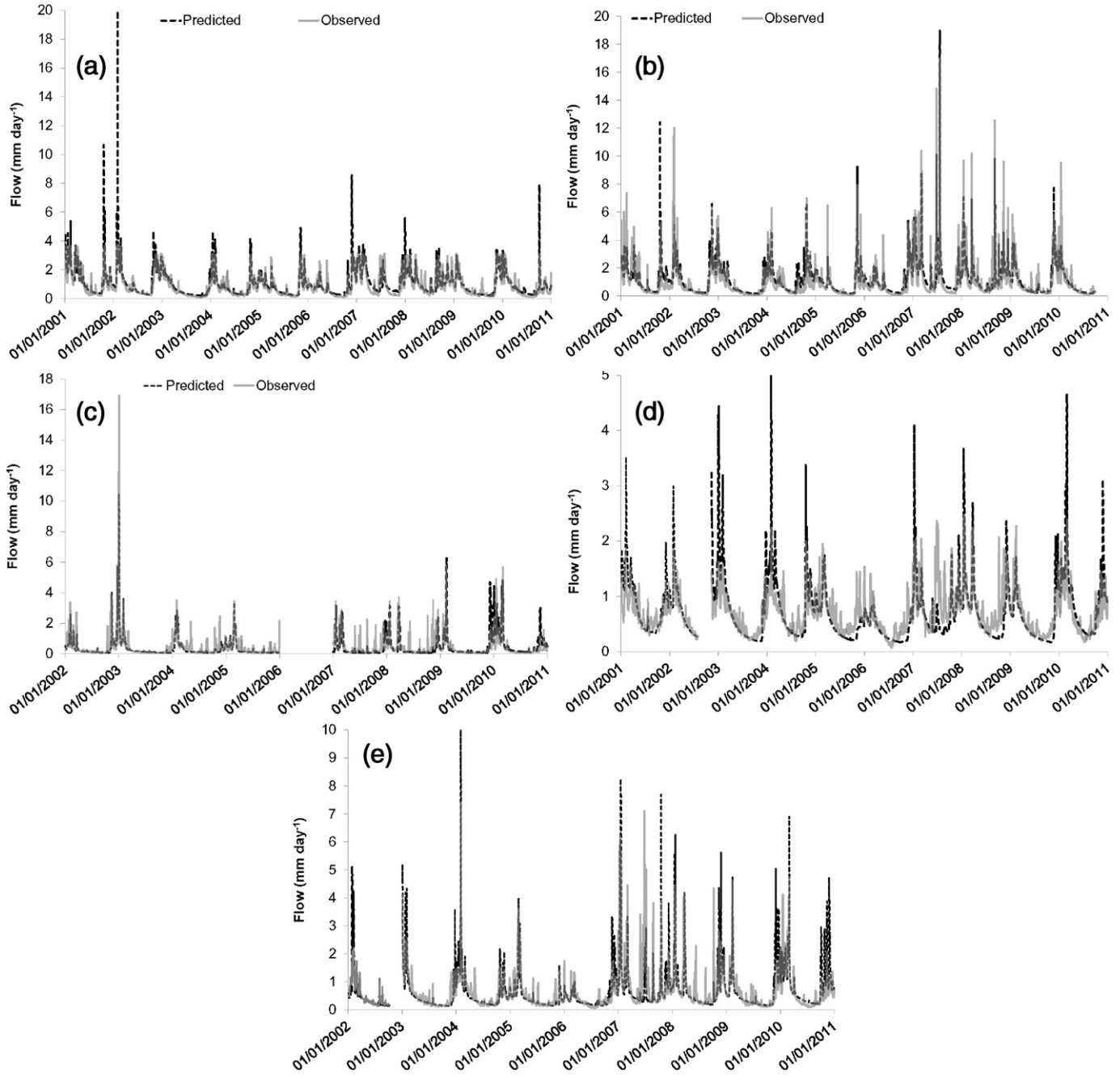


**Fig. 3.** Measured and predicted flow during the validation period in (a) the river Lugg at Lugwardine (b) the river Teme at Knightsford Bridge, (c) the river Waveney at Needham Mill (d) the river Wensum at Costessey Mill and (e) the river Yare at Colney.

larger catchments. Observed and predicted flows for the validation period are shown in Fig. 3. Model performance statistics for the calibration and validation periods are shown in Table 4. Observed and predicted flows for the calibration period and cumulative frequency distributions for pesticide concentrations are provided in the supplementary material.

In both the Lugg and the Teme catchments, IMPT reproduced both the timing and magnitude of peak flows reasonably well, particularly in the autumn and winter (Fig. 3a and b). In the Lugg validation period there was a slight over estimation of some peak events by the model (Fig. 3a), but these were generally above the rating curve limit of 3.13 mm $d^{-1}$ imposed in 2002.

In the Waveney catchment, model performance in the autumn and winter was also good for flow timing and magnitude. However, between May and September the measured flow was underpredicted in both the calibration and validation periods. Note that due to missing flow data in 2006 the results in Fig. 3c start from January 2007.

In the Yare catchment, model performance in the calibration period was good, but decreased in the validation period (Table 4; Fig. 3e). Overall, IMPT reproduced the timing of peak flows quite well and only missed a few peaks, principally in the summer periods. However, there was a slight tendency to over-predict peak flow events during the autumn and winter periods. This over-prediction could potentially affect the NSE as this metric is sensitive to extreme outliers due to the use of squared differences (Krause et al., 2005; Legates and McCabe, 1999; McCuen et al., 2006).

The Wensum is the only study catchment for which the model performed poorly in both the calibration and validation periods (Table 4). Typically the observed hydrograph was under predicted for long periods and peak flows were over-predicted for high magnitude events. In addition, the model failed to reproduce the timing of some events (Fig. 3d). The relatively poor model performance for the Wensum may be due to a failure to account for artificial influences in the catchment, such as water abstraction, effluent return flows and the influence of mill structures (and associated impoundments) which have been built along two-thirds of the main river course which can regulate the flow via sluices. This means that the river can behave more like a series of lakes (EA, 2010a). Another possible reason for poor model performance could be the use of an unrepresentative rainfall station.

### 4.3. Pesticide simulations in the five CSF catchments

The measured and predicted frequency of detections >0.1 μg $L^{-1}$ in the larger catchments are compared in Table 5. The range in predicted frequencies was derived considering the parameter envelope of best case and worst case $K_{OC}$ and $DT_{50}$ combinations. The measured frequency was captured by the model range in 17 out of the 40 pesticide/catchment combinations and was typically within a factor of three in all but three of the remaining combinations. In the East Anglian catchments (Waveney, Wensum and Yare) the predicted frequency of detections was typically less than the measured frequency but in the Lugg and the Teme frequencies were better predicted and, on occasion, over-predicted.

Spearman's rank correlation coefficients for the rank order of frequencies are also shown in Table 5. In three of the catchments (Lugg, Teme and Wensum), the correlation between measured and predicted ranks was significant ($p < 0.05$). In the Waveney and the Yare the correlation coefficient was positive and moderately high (but not significant) suggesting that predictions of the likelihood of challenging Drinking Water Directive compliance are uncertain.

As an example, the time-series of measured and predicted propyzamide concentrations are shown in Fig. 4 for all five catchments between September 2006 and September 2007. Results for other pesticides (2,4-D, carbetamide, chlorotoluron, clopyralid, isoproturon, MCPA and mecoprop) are presented in the supplementary material. In all five catchments, IMPT tends to predict peak concentrations greater than those typically observed in the measured data and earlier than those observed at the catchment outlet.

### 4.4. Discussion

Changes in pesticide concentrations in surface water often follow the hydrograph, increasing on the rising limb and falling during recession (Leu et al., 2004; Müller et al., 2003; Taghavi et al., 2010, 2011; Tediosi et al., 2012). Therefore, good hydrological predictions often underpin adequate predictions of pesticide exposure.

In the headwater sub-catchment of the upper Cherwell the drainflow hydrograph was well reproduced as were the peak concentrations of propyzamide and carbetamide. In the larger catchments hydrograph predictions from October to March, when autumn-applied herbicides are used were also generally very good for the Lugg, Teme, Waveney and Yare. For the Wensum, although the magnitude of peak events was not well simulated, the observed timing of the rising limb was usually identified, at least for the winter period.

Hydrograph discrepancies between IMPT predictions and observations could be due to inaccuracies and spatial variability in rainfall data and $ET_O$ estimations. For convenience, a single weather station was chosen for each catchment (Table 2) which is unlikely to be always

**Table 5**
Measured and modelled frequency of detections >0.1 μg $L^{-1}$ for each pesticide catchment combination.

| | Lugg | | Teme | | Waveney | | Wensum | | Yare | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Measured | Predicted[#] | Measured | Predicted[#] | Measured | Predicted[#] | Measured | Predicted[#] | Measured | Predicted[#] |
| 2,4–D | 0% | 0–3% | 0 % | 0–3% | 1 % | 0–0.4% | 1 % | 0–0.4% | 3 % | 0–0.2% |
| Carbetamide | 0.4% | 0.2–13% | 0.7 % | 0–14% | 21 % | 6–18% | 5 % | 2–19% | 11 % | 0–20% |
| Chlorotoluron | 9% | 6–20% | 7 % | 3–25% | 1 % | 10–13% | 3 % | 9–21% | 0.5 % | 10–22% |
| Clopyralid | 0% | 0–0.3% | 0.7 % | 0–0.1% | 9 % | 0–0.4% | 0.8 % | 0–0.5% | 4 % | 0–0.3% |
| Isoproturon | 10% | 18–29% | 15 % | 21–35% | 46 % | 11–13% | 27 % | 18–24% | 35 % | 20–26% |
| MCPA | 3% | 0.1–9% | 4 % | 0.2–11% | 10 % | 0.7–2% | 6 % | 0.2–4% | 8 % | 0.1–4% |
| Mecoprop | 3% | 13–25% | 7 % | 13–21% | 15 % | 11–13% | 7 % | 16–22% | 12 % | 18–23% |
| Propyzamide | 3% | 0–15% | 2 % | 0–19% | 15 % | 0.2–18% | 7 % | 0–20% | 10 % | 0–20% |
| R (Spearman) | | 0.80* | | 0.87* | | 0.60 | | 0.76* | | 0.61 |

Key: Green blocks are predicted ranges which span the measured frequency of con centrations greater than 0.1 μg $L^{-1}$, blue blocks are where the predicted frequency is greater than the measured frequency and orange blocks are where the predicted frequency is less than the measured frequency and orange blocks

[#] Range of predicted frequencies of detectionfor best case to worst case Koc and DT50 combinations.

* Significant at p<0.05

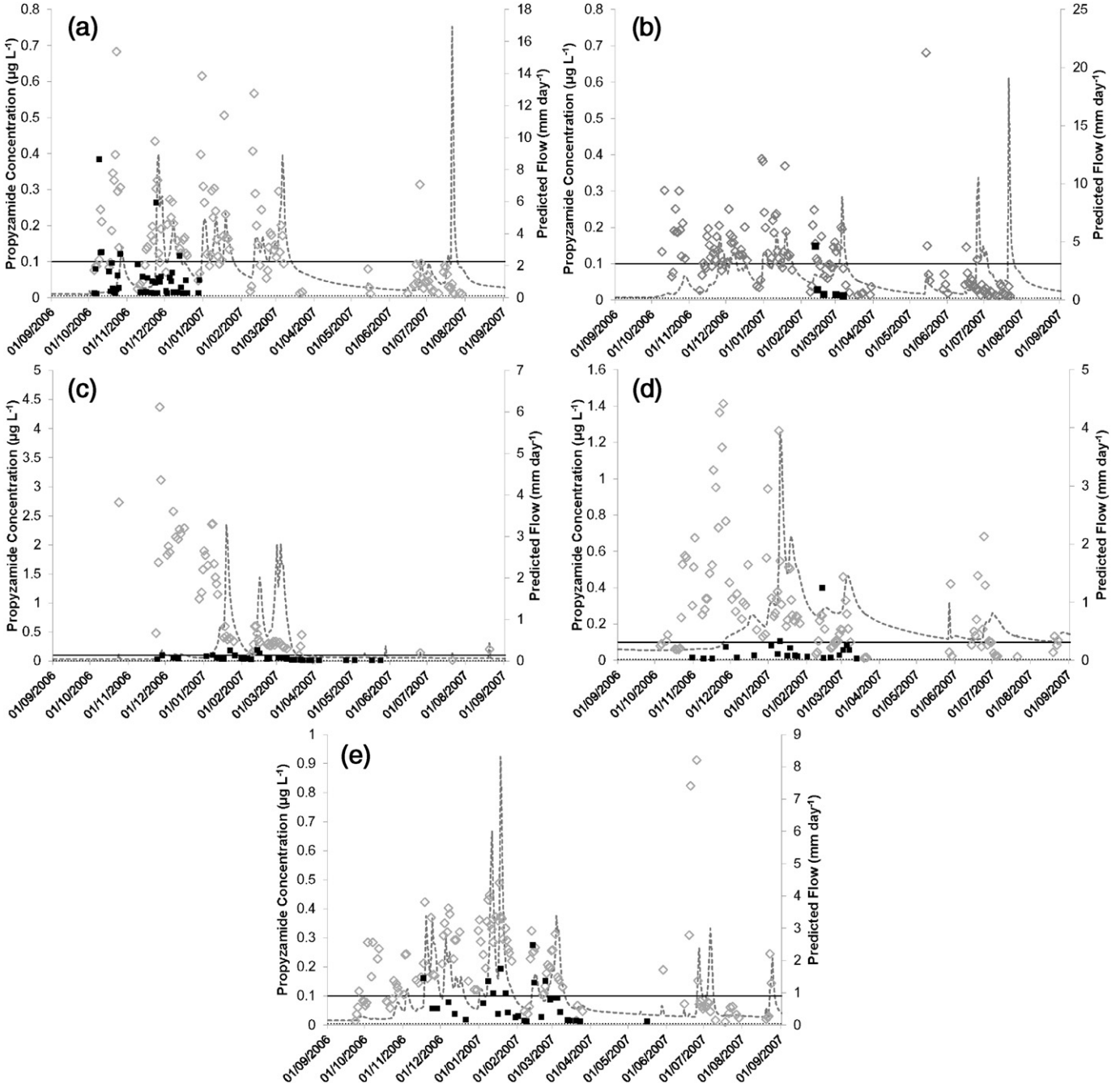


**Fig. 4.** Comparison of predicted and measured propyzamide concentrations and predicted flow between September 2006 and September 2007 in the (a) Lugg, (b) Teme, (c) Waveney, (d) Wensum and (e) Yare catchments. Note the different scales in different catchments.

representative of average conditions across the catchment over the whole period, particularly for rainfall. The estimation of $ET_O$ in IMPT was based on temperature using the Hargreaves method, which is known to be less accurate than the Penman-Monteith equation (e.g. López-Moreno et al., 2009).

The under-estimation of observed peak flows during the summer, in all five large catchments (Fig. 3) could (at least in part) be a result of an inadequate prediction of infiltration excess overland flow in the model due to the use of daily meteorological data. As a consequence the prediction of some spring-applied pesticide transfers could be underestimated if pesticide transport is predominantly via this pathway. Elsewhere, overland flow has been reported to contribute greater annual loads to surface water than tile drains for spring-applied herbicides such as MCPA between April and September (e.g. Logan et al., 1994) although the conditions occurring in this study (Ohio, USA) are probably not particularly representative of UK catchments. Other possible reasons for poorer summer performance of IMPT include failure to predict saturation excess overland flow from areas of topographic convergence, the possibility that macropore flow to field drains is not well simulated in summer (the field-scale test of the model was performed under winter conditions) and a poorer prediction of herbicide usage rates, particularly on grassland.

Some discrepancies between measured and modelled pesticide concentrations will certainly result from the low frequency of sampling (typically grab samples once every two weeks) which is unlikely to capture the highly episodic pattern of pesticide transfers reported for many surface water systems (e.g. Holvoet et al., 2007; Kreuger, 1998; Tediosi et al., 2012). Low sampling frequency for such pollutants often tends to

lead to an under-estimation of peak concentrations (Rabiet et al., 2010). Peak concentrations are typically highest in the first substantial rainfall event after application (e.g. Capel et al., 2001; Leu et al., 2004; Tediosi et al., 2012). In addition, point sources for pesticides such as spills on hard standings during fill up and washdown operations of spraying equipment could also contribute to exposure in the first subsequent storm event (Kreuger, 1998; Rose et al., 2001). This will not be captured by low frequency sampling but, equally, it will not be predicted by models such as IMPT. Similarly, pseudo-point-sources, such as the use of 2,4-D to treat Giant Hogweed (*Heracleum mantegazzianum*) on river banks (EA, 2010b) and the use of herbicides in urban areas and along roads and railways, could also lead to pesticide exposure which would not be predicted by the model.

Given the good model performance in the upper Cherwell, where application information was known and where samples were collected frequently, discrepancies between the measured and the modelled pesticide concentrations in the five larger catchments could also result from inadequacies in land management data (e.g. pesticide treated area, application rate and timing of application). The application window assigned to each crop/pesticide combination will not reflect year-to-year variations in actual application patterns, which will be influenced by factors such as crop rotation, disease and weed pressure, weather and ground conditions, crop growth stage and sprayer availability (HSE, 2009; Matthews, 2008; West et al., 2003).

The model described here only makes exposure predictions for surface waters (i.e. groundwater exposure is not included and shallow groundwater incursion into the soil is assumed to be pesticide free – Eq. (15)). Surface water contamination with pesticides is currently a more acute problem for most water supply companies in the UK than the contamination of groundwater. However, this is not to say that groundwater contamination is not a serious problem. Long residence times in both the vadose zone and in aquifers mean that where groundwater is contaminated, recovery times can be significant (several decades or more: e.g. Howden et al., 2011). It is possible to use IMPT for predicting groundwater contamination potential (Pullan, 2014) by moderating predicted leaching losses for sorption and dispersion below the base of the soil profile and by using a weighted average loss for recharge areas within source protection zones, if these have been defined. Predicting contamination levels at individual boreholes is, however, complicated by complex flow patterns in the saturated zone, which would require coupling IMPT predictions of pesticide inputs to the water table with a groundwater flow and contaminant transport model.

## 5. Conclusions

There is a clear need for catchment-scale modelling tools to predict pesticide exposure in surface waters, particularly when used for drinking water abstraction. Models used for assessing the risks of exposure in ground and surface water for pesticide registration are focussed on the propensity of a pesticide to leach rather than on the actual patterns of concentration which might result at a catchment scale from its operational application. These models are usually based on a mechanistic description of pesticide transport in one dimension. Although such a description can be used successfully to represent pesticide losses at the hillslope scale (Tediosi et al., 2013), its use in large catchments with a range of soil types, topography and land uses is more challenging, not least due to the high data requirements of many of these tools (e.g. Steffens et al., 2015). Here, we introduce a new model (IMPT) which captures the most important processes affecting pesticide fate and transport using data which are readily available at a national scale. The work described in this paper demonstrates that such an approach can generate acceptable reproductions of both hydrograph response and pesticide concentrations at scales ranging from the headwater (0.15 $km^2$) to the catchment (several hundred $km^2$). Predicted hydrological behaviour in drainflow in the upper Cherwell and at the outlets of the five larger catchments was generally reasonable in terms of NSE and PBIAS, suggesting that the representation of key hydrological pathways is adequate.

The predicted pesticide concentrations were also reasonable compared with the available observations, particularly at the headwater scale. In the five larger catchments, observed pesticide concentrations, with respect to frequency of detections >0.1 μg $L^{-1}$, were typically well predicted within the frequency envelope generated by uncertainties in $K_{OC}$ and $DT_{50}$. In the time-series comparison of concentrations in the larger catchments, the model tended to predict an exposure peak sooner than that seen in the measured data, which may reflect modelled inadequacies in land management data (particularly timing of application) as well as infrequent sampling.

Overall, the applications reported here suggest that IMPT is applicable across a range of catchment types and hydrogeological settings making it useful for identification and prioritisation of catchment-specific monitoring strategies, the spatial targeting of catchment management interventions and the prediction of the efficacy of different intervention options, as well as highlighting potential problems that could arise under future scenarios (e.g. climate and land use changes and shifts in pesticide usage).

## Acknowledgements

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.04.135.

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