

# Prediction of pesticide concentrations found in rivers in the UK

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**Abstract:** SWATCATCH is a distributed model combined with databases within a GIS as the POPPIE system to predict pesticide concentrations in rivers at the catchment outlet. The model was evaluated against a dataset of pesticide concentrations in rivers of England and Wales. More than 2000 individual analyses in each of the years 1995 and 1997 covered approximately 150 catchment–pesticide combinations drawn from 29 catchments and 16 pesticides, themselves selected to represent a range of characteristics and properties. SWATCATCH was better able to simulate maximum pesticide concentrations at any time during the year than the proportion of samples containing residues of a particular pesticide above the limit of quantification. The model simulated maximum pesticide concentrations in surface waters which were within a factor of 10 of those observed for 66–74% of catchment–pesticide–year combinations. Simulated and observed frequency of detection could not be differentiated using a  $\chi^2$  test for 54–67% of simulations. Time series analysis for seven of the 29 catchment–pesticide combinations indicated that measured and detected series of concentrations generally followed similar patterns. The evaluation supports the intended use of the model in assisting the construction of pesticide monitoring programmes.

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**Keywords:** model; evaluation; pesticide; GIS; catchment; monitoring data

## 1 INTRODUCTION

There is worldwide interest in quantifying and controlling pollution in surface waters, and pesticides rank amongst the potential contaminants of greatest concern.<sup>1</sup> Government agencies and water supply industries have statutory obligations to monitor water resources to demonstrate compliance with strict water quality criteria.<sup>2</sup> Increasingly, there are also statutory requirements to control contamination at source, as exemplified by the river basin management plans embodied in the European Union Water Framework Directive.<sup>3</sup> Appropriate design of monitoring programmes is essential to properly manage pesticides in the environment, and mathematical models can play an important role in their construction.

A number of approaches have been adopted to simulate pesticides in surface waters at the catchment scale.<sup>4</sup> Deterministic models differ in their treatment of spatial variability. Lumped models such as GLEAMS<sup>5</sup> and EPIC-PST<sup>6</sup> aggregate spatial variability into single input values at the small catchment level. Distributed models such as AGNPS,<sup>7</sup> SWAT<sup>8</sup> and SHETRAN<sup>9</sup> implicitly consider variability on the basis of cells or polygons. Intermediate approaches simulate on the basis of average parameters within discrete sub-catchments; examples include SWRRBWQ<sup>10</sup> and simulation with a fugacity model of a 400-km<sup>2</sup> river basin in Italy on the basis of 14 uniform geographical units.<sup>11</sup> Jolánkai *et al*<sup>12</sup> further

differentiate available models on the basis of the temporal scale of model simulations. They identify long-term, average loading models (steady-state models) which typically simulate annual loadings of contaminants, event-based models simulating the response of a drainage basin to a major precipitation event, and continuous application models which extend event-based capabilities to long-term simulations and have long computational time requirements. A common feature of the US water-quality models (eg EPIC-PST, AGNPS, SWRRBWQ) is their primary focus on runoff and erosion loadings to surface water. Pesticide concentrations in surface water are predicted for multiple points within the catchment, but fate of the pesticide within the receiving water is not considered. GLEAMS is the most highly developed in terms of description of pesticide processes, but the model contains no description of field drainage, and its scale of application is limited to a few fields. SHETRAN is a fully distributed, continuous application model (time step 15–120 min) with a comprehensive description of catchment and groundwater hydrology. The model requires a detailed set of input parameters, and this restricts its use to the study and management of highly characterised catchments.

SWATCATCH is a distributed model designed to simulate flow and pesticide concentrations at the catchment outlet.<sup>13</sup> Typical model runs cover several years, with input and output at a weekly resolution to

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simulate the effects of large flow events without the detail of event-based models. SWATCATCH has been packaged with databases and a GIS in a system called POPPIE (Prediction of Pesticide Pollution In the Environment) which has been developed by the Environment Agency of England and Wales to design and appropriately target pesticide monitoring programmes.<sup>14</sup>

Some of the models described above have been evaluated against data for pesticides in surface water at the field<sup>6</sup> or small catchment scale.<sup>15</sup> For example, GLEAMS was evaluated against data on atrazine runoff in field studies and watershed monitoring, and it was concluded that the model under-predicts concentrations by a factor of 2 to 5.<sup>15</sup> The work described here reports an evaluation of the POPPIE system against monitoring data for England and Wales.

## 2 EXPERIMENTAL

### 2.1 The model

The POPPIE system is based on a semi-empirical model, SWAT (Surface Water ATTenuation model), which simulates concentrations of agriculturally applied pesticides moving to surface waters.<sup>16</sup> The model builds upon an empirical link established in the UK between soil types and the amount of water moving rapidly to streams in response to rainfall.<sup>17</sup> SWAT combines pesticide losses via the hydrological pathways of overland flow, inter-layer flow (lateral transport within the soil profile) and drain flow. Soil series in the UK have been grouped into one of 29 classes that have been calibrated against measured flow characteristics for 800 catchments across the UK.<sup>17</sup> The two principal stream-flow coefficients in SWAT are the standard percentage runoff (that proportion of rainfall which causes a short-term increase in stream flow in the first 24-h period after a storm event) and the base flow index (that fraction of the long-term total stream volume which is represented by base flow).

Following application, pesticide is subject to leaching in any hydraulically effective rainfall (rainfall during periods of zero soil moisture deficit) with the mobile soil water fraction defined as the difference between the soil water content at  $-5$  and  $-200$  kPa. Decrease in concentrations in the soil water phase and re-distribution of pesticide within the soil profile as a result of degradation and sorption are described using attenuation ( $AF$ ) and partition ( $PF$ ) factors, respectively:<sup>18</sup>

$$AF = e^{-kt} \quad (1)$$

and

$$PF = \frac{1}{\{1 + (K_{dt} * \rho_b) + (C_a * K_H)\}} \quad (2)$$

where  $k$  is the first-order degradation rate constant ( $\text{day}^{-1}$ ),  $t$  is the time from application (days),  $\rho_b$  is the

bulk density of the topsoil,  $C_a$  is the air capacity fraction of the topsoil (the difference between volumetric water content at saturation and field capacity;  $\text{cm}^3 \text{cm}^{-3}$ ),  $K_H$  is Henry's constant for the pesticide ( $-$ ), and  $K_{dt}$  is a time-dependent partition coefficient between soil and water for the pesticide ( $\text{cm}^3 \text{g}^{-1}$ ) defined from the instantaneous partition coefficient,  $K_d$  as:

$$K_{dt} = K_d \{1 + (0.1 * t^{0.5})\} \quad (3)$$

Concentrations of pesticide in the rapid runoff to surface waters for a given rainfall event are calculated using a simple mixing and displacement of soil solution. A set volume of rainfall varying between 5 and 20 mm dependent on soil type<sup>16</sup> dilutes and displaces pesticide solution in the top 1 mm of soil. The resulting solution is transferred to surface waters minus a fraction of pesticide which is assumed to be repartitioned and which is obtained by applying the partition factor in eqn (2) above, but with  $K_{dt}$  replaced by  $K_d$ . The model does not account for transport in runoff of pesticide sorbed to sediment. Earlier research suggests that transport in solution is dominant for runoff in the UK, even for highly lipophilic compounds such as trifluralin.<sup>19</sup> In an evaluation of SWAT against field-scale experimental data from four sites, the model successfully simulated the transient peak concentrations of a wide range of pesticides during rapid movement of water to streams in response to rainfall.<sup>16</sup> Almost all simulated concentrations were within one order of magnitude of measured values.

SWATCATCH is the catchment scale version of the SWAT model which predicts weekly flow and associated concentrations of pesticide at the catchment outlet.<sup>13</sup> The hydrological basis of the model is a distributed system whereby a given catchment is spatially divided into a number of cells each  $2 \times 2$  km (or part thereof for cells at the catchment boundary). Rapid flow of water to the river and the associated concentrations of pesticides are calculated on a weekly basis for each soil type present. The proportion of the various soil types is then used to aggregate total flow to the river across the catchment and to calculate a flow-weighted mean pesticide concentration. The landscape position of a particular soil in relation to surface water is considered implicitly within the original regression analysis used to assign stream-flow coefficients to different soil classes. For example, a soil which is generally distant from surface water is likely to contribute relatively little to rapid movement of water and pesticide to rivers and will carry a relatively small coefficient for standard percentage runoff.

Volumes of water moving to groundwater are calculated as the product of the base flow index and hydraulically effective rainfall. Groundwater is considered to be at the base of the unsaturated zone or at the top of bedrock, and travel times are calculated using hydraulic conductivity of the different soil layers at field capacity. The mass of pesticide transferred to

groundwater in the leaching water is then calculated as for transport in the upper soil layers by applying attenuation and partition factors<sup>18</sup> (eqns (1) and (2)). A simple groundwater storage routine accounts for subsequent seepage of water and pesticide to the river. Initial groundwater storage,  $S_i$  is defined as:

$$S_i = AAHER * BFI * A \quad (4)$$

where *AAHER* is the long-term average annual hydraulically effective rainfall, *BFI* is the base flow index for the soil under consideration, and *A* is an empirical constant. Every week of the simulation, the storage receives inputs of water and pesticide as described above and loses a fixed percentage (*B*) of the stored volume of water and mass of pesticide to the river as base flow. In earlier work<sup>13</sup> calibrated values for *A* and *B* of 0.2 and 9.6, respectively, were obtained by comparing river flows simulated by SWATCATCH with weekly measured values collected over 3 years for 16 catchments in England and Wales. The catchments ranged in size from 60 to 4330 km<sup>2</sup> and covered a variety of hydrogeological conditions. Using the calibrated values for *A* and *B*, a linear regression of simulated against measured weekly flow (both in cumecs) yielded a line with a gradient of 1.0005 (standard error of slope 0.0077), an intercept of 0.27 and an *r*<sup>2</sup> value of 0.87.

The model does not account for residues in rivers arising from either non-agricultural use of pesticidal chemicals or point source contamination. As the true landscape position of inputs is not identified by the model, no account is taken of in-stream processes such as degradation or storage by the sediment. Similarly, the model relies upon the assumption that water abstractions have no effect on either volumes of water or amounts of pesticide within the catchment. Clearly, these assumptions each place limitations on the accuracy of the model and together limit the model's application to indicative simulation at the national scale. Detailed mechanistic modelling would be required to address specific issues within a given catchment.

The POPPIE system has been developed by the Environment Agency of England and Wales to predict pesticide concentrations in surface waters.<sup>14</sup> In turn, output is used in the targeting and refinement of pesticide monitoring programmes. The system combines the SWATCATCH model with a number of datasets within a GIS covering England and Wales. The databases incorporated into the system are: boundaries for the 903 catchments considered; soil series taken from a 100-m interpolation of a 1:250 000 scale soil map, and hydrological class and soil parameters by series and horizon; weekly rainfall and hydraulically effective rainfall (rainfall during periods of zero soil moisture deficit); pesticide loadings; and pesticide physico-chemical properties. All spatial data are at a 2 × 2 km resolution. Annual pesticide loadings at this scale were derived from regional survey data

using cropping statistics and were empirically interpolated to a weekly time-step from monthly totals. The approach was dictated by the temporal resolution of usage data, but it imposes clear limitations as the time from pesticide application to a rainfall event inducing runoff has been shown to be a very sensitive factor for chemical transport.<sup>20</sup> Hydrological output from POPPIE is base and total flow at the outlet of catchments throughout England and Wales at a weekly resolution. Pesticide concentrations are expressed as both peak and average weekly values with the former excluding dilution of rapid runoff by base flow.

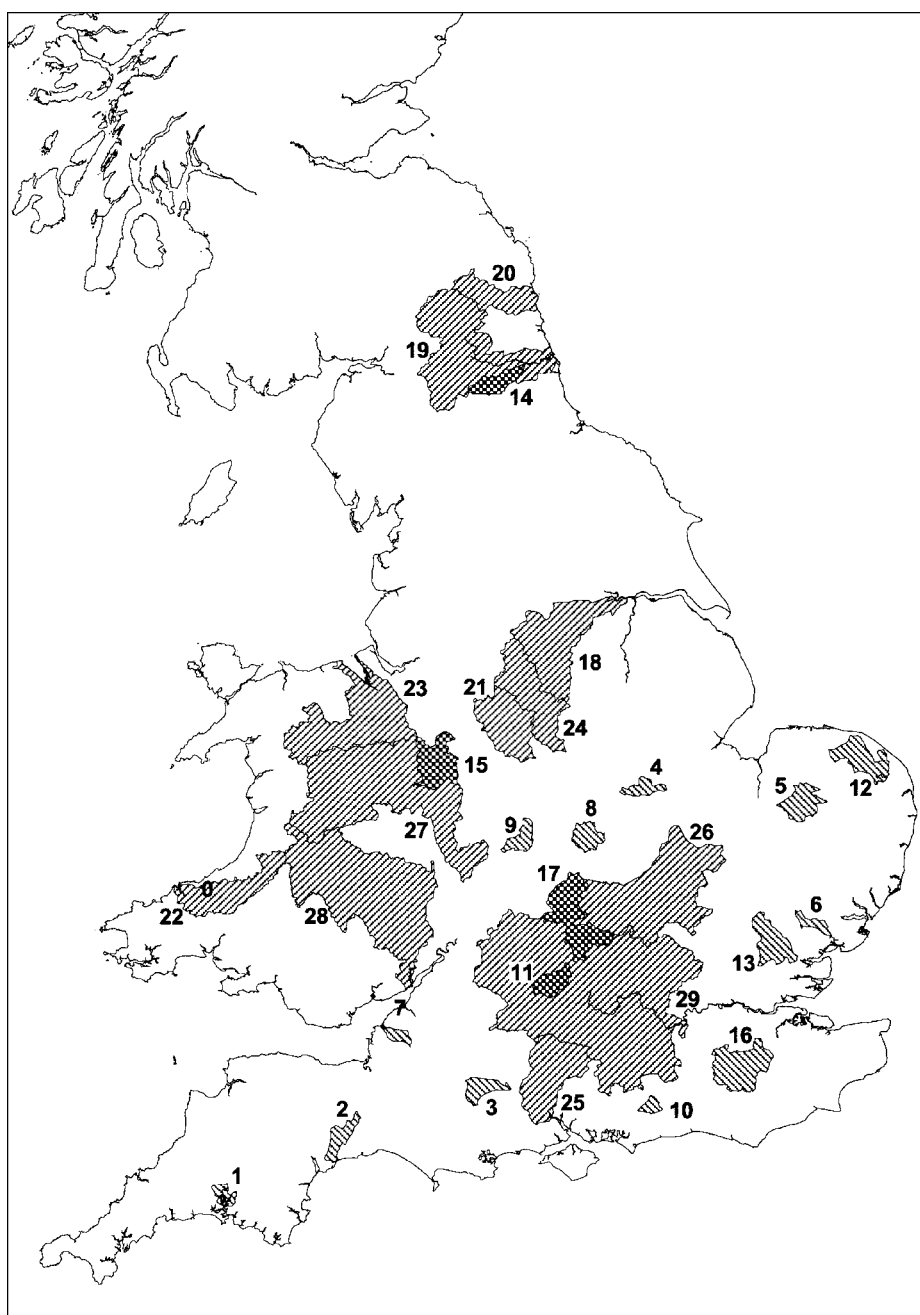
## 2.2 Sources of monitoring data

Two sources of data were accessed for model evaluation. The first was the Environment Agency's National Database of Pesticide Monitoring in the Environment,<sup>21</sup> which contains results from c 1 500 000 analyses of ground and surface water for 1992–1998. The monitoring is performed to fulfil a regulatory function and the dataset is thus generally unbiased, comprising controlled monitoring for a large number of pesticides (>160) at a large number of sites (>3500). Temporal resolution is relatively low, with typically 4–12 grab samples collected on a given date for each pesticide–site–year combination. These data are thus most appropriate for determining the relative frequency of occurrence of pesticides in catchments with differing properties.

Pesticide monitoring data with a higher temporal resolution were obtained from water companies. Industry data are used to demonstrate compliance with water quality standards and to optimise treatment of water to remove pesticides. They thus comprise high resolution monitoring for a more limited number of key pesticides and water sources. The maximum resolution in the data provided was 80 analyses for a single pesticide–site–year combination. Industry sampling is generally more intensive during times when pesticide pollution is expected (spring and/or autumn) and may thus provide a biased source of information. When expressed as a simple percentage of samples containing detectable residues of pesticides, results will tend to over-estimate actual presence of pesticides. However, sampling tends to be focused in response to key rainfall events in order to pick up peak concentrations of pesticides. As such, industry monitoring data are most appropriate for extracting peak concentrations of pesticides in rivers.

## 2.3 Selection of catchments for model evaluation

Twenty-nine catchments were selected (Fig 1) from the 903 identified within England and Wales. Choice of catchments was primarily constrained by the need to have plentiful monitoring data in a number of years and to avoid potential sources of point pollution (eg pesticide manufacturing plants). Wherever possible, catchments were included where routine Environment Agency monitoring, data were supplemented with results of more intensive monitoring by the water



**Figure 1.** The 29 catchments selected for model evaluation (checked areas indicate discrete sub-catchments contained within larger catchments).

industry. In addition, catchments were selected to obtain a spread of data with respect to size, hydrogeology, soils, geographical location and land use. The area of the catchments was 83–9386 km<sup>2</sup> and the proportion of each catchment overlying an aquifer was 21–99%. Dominant soils included free-draining permeable soils, clay-rich soils over impermeable substrates with strong inhibition to downwards movement of water, and peats. The extent of different land uses was: cereals 4–47%; vegetables 0–6%; potatoes/sugar beet/oilseed rape/maize 1–28%; fruit 0–2%; maintained grassland 6–68%; rough grazing 0–37%; and non-agricultural land 15–44%.

#### 2.4 Selection of pesticides for model evaluation

Sixteen pesticides were selected (Table 1) from more

than 160 monitored by the Environment Agency. Selection was made to give a range of properties and uses, but was strongly guided by those pesticides for which sufficient monitoring data were available. Detected compounds spanned a range of frequencies within the monitoring programme from frequent occurrences (eg atrazine and isoproturon; mean 42 and 25% positive detections, respectively, for the current dataset) to infrequent (eg triallate and trifluralin; mean 2 and 0% positive detections, respectively). The selection of compounds was biased towards herbicides (12 compounds) because the monitoring programme was dominated by these compounds and their physicochemical properties are often of the correct magnitude to enhance the propensity to be transported to surface waters. Three insecticides and

**Table 1.** Characteristics of the 16 pesticides selected for the model evaluation<sup>16,22,23</sup>

Common name	Soil sorption ( $K_{oc}$ ; $ml\ g^{-1}$ )	Soil half-life (days)	Vapour pressure (Pa)	Main uses in the UK
Aldicarb	30	30	$1.3 \times 10^{-2}$	Root vegetables
Atrazine	100	41	$3.9 \times 10^{-5}$	Maize, nursery, non-agricultural
Bentazone	42	12	$1.7 \times 10^{-4}$	Legumes
Bromoxynil	190 <sup>a</sup>	10	$6.3 \times 10^{-6}$	Cereals, maize
Chlorothalonil	1380	30	$7.6 \times 10^{-5}$	Cereals, vegetables, fruit
Dimethoate	20	7	$2.5 \times 10^{-4}$	Cereals, potatoes, sugar beet, vegetables, fruit, nursery, grassland
Ethofumesate	203	30	$3.9 \times 10^{-4}$	Sugar beet, fodder beet
Flutriafol	231 <sup>a</sup>	500 <sup>a</sup>	$7.1 \times 10^{-9}$	Cereals
Isoproturon	120	30	$3.2 \times 10^{-6}$	Cereals
Lindane	1100	400	$5.6 \times 10^{-3}$	Cereals, grassland, vegetables, fruit, storage and non-agricultural
Linuron	400	60	$5.1 \times 10^{-5}$	Cereals
MCPA	20	25	$2.3 \times 10^{-5}$	Cereals, grassland
Mecoprop	20	21	$3.1 \times 10^{-4}$	Cereals, grassland
Simazine	130	49	$1.6 \times 10^{-6}$	Maize, nursery, non-agricultural
Triallate	2400	82	$1.6 \times 10^{-2}$	Cereals, vegetables
Trifluralin	8000	60	$6.1 \times 10^{-3}$	Cereals, oilseed rape, sugar beet, vegetables

<sup>a</sup> KA Lewis, personal communication.

one fungicide were also included. The compounds covered a range of sorption and degradation behaviour in soil (Table 1).

## 2.5 Manipulation of monitoring data

A single monitoring site was selected for each of the 29 catchments to optimally fit four criteria: (1) located as close to the catchment outlet as possible (the primary output from the POPPIE system is pesticide concentration at the catchment outlet); (2) upstream of any major potential point source of contamination (where identified); (3) having the maximum amount of monitoring data for the 16 pesticides selected; and (4) coinciding as closely as possible with industry monitoring sites for those catchments with both Environment Agency and water industry data.

The resulting database for 29 monitoring points derived from the Environment Agency data was cleansed of non-routine monitoring by selecting only samples taken for routine monitoring and deleting all results arising from pollution incidents and investigations, effluent control and potential legal proceedings. The database contains a qualifier identifying the reason for sample collection. Environment Agency and water industry data were combined into a single database and resolved to a single limit of quantification (LOQ) selected as the most frequent within the run of data (these ranged from 1 to 100 ng litre<sup>-1</sup> for the different pesticides). Where an analysis carried a smaller LOQ, this was raised accordingly. Pesticide analyses with a larger LOQ were discarded. The resulting database contained 150 catchment–pesticide combinations with at least five monitoring data in each of two years (1995 and 1997). There were 2057 and 2282 individual analyses for 1995 and 1997, respectively. The percentage of positive detections for the 16 pesticides investigated ranged from 0 to 100% in 1995

and from 0 to 92% in 1997, whilst the median frequency of detection was 9% in both years.

## 2.6 Manipulation of output from POPPIE

The POPPIE system predicts pesticide concentrations as an uninterrupted value from zero upwards (in practice, values less than 0.001 ng litre<sup>-1</sup> are rare but not impossible). Since monitoring results are reported either as positive concentrations or as being less than the LOQ (ie either zero or in the range 0 to LOQ), POPPIE output was subjected to the same standardised LOQs derived for the monitoring data. All simulated concentrations less than the LOQ for a given catchment–pesticide combination were set to zero for consistency between simulated and monitored observations.

## 3 MODEL EVALUATION

The main constraints on the evaluation were: (1) monitoring data were dominated by values less than the limit of quantification; (2) the temporal resolution of model output and monitoring data were often markedly different (52 weekly simulated results per year compared with typically 4–12 monitoring observations per year, respectively); (3) monitoring samples were collected on a random basis and are likely to have missed absolute peaks in pesticide concentrations. Differences in temporal resolution are common when comparing pesticide models with experimental data because of the expense involved in analysis of pesticides. Non-parametric comparisons were used to evaluate the broad performance of the model (ability to simulate frequency of detection and maximum concentrations observed), whilst time series analysis examined patterns of concentrations for data series with a fine temporal resolution. Monitoring information for 1995–1997 was included within time

series analysis, whilst non-parametric evaluation focused on 1995 and 1997.

### 3.1 $\chi^2$ test

This tested whether the model could simulate the relative frequency of pesticide detection at the outlet of contrasting catchments. The  $\chi^2$  test allows unequal populations of data to be compared.<sup>24</sup> The test considered only the relative frequency of obtaining a detection of pesticide above the LOQ following a binary separation into detects and non-detects. A  $2 \times 2$  contingency table was drawn up for each catchment–pesticide combination and the hypothesis that frequency of detection was the same for measured and simulated data was tested at a 5% probability level ( $\chi^2 = 3.84$  with one degree of freedom). Catchment–pesticide combinations where measured and simulated frequency of detection could not be differentiated were deemed acceptable.  $\chi^2$  values could only be calculated where the simulated frequency of obtaining a residue above the LOQ exceeded zero. For catchment–pesticide combinations where POPPIE simulated no residues above the LOQ, model performance was said to be acceptable only if there were no measured residues of the compound above the LOQ.

### 3.2 Comparison of maximum concentrations

Peak concentrations of pesticides in rivers are particularly important for acute exposure determination and regulatory monitoring functions. Peak concentrations from monitoring data were compared to the largest of the weekly peak concentrations simulated by POPPIE for the equivalent period. A simple measure of acceptability was adopted with three levels of accuracy (Table 2). This approach is more readily assimilated by the end-users for the system than traditional statistics, as it clearly indicates margins of error likely to be associated with the output.

### 3.3 Time series analysis

Pesticide concentrations in surface water may show a distinct seasonal pattern or may be relatively uniform with time. The STATISTICA package (StatSoft Inc, Tulsa, OK, USA) was used to compare the form of observed and simulated series of pesticide concentrations. Monitoring data for 1995 to 1997 were compared with model output for the seven catchment–pesticide combinations which met the criteria of having at least 12 monitoring results per annum and

25% or more of both measured and simulated concentrations above the limit of quantification. Data were resolved to a four-week time-step for time series analysis as monitoring data for the seven combinations were on a monthly resolution or finer. Data for isoproturon in the Thames (catchment 29 in Fig 1) were numerous enough to permit a weekly time-step. Monitoring programmes undertaken by industry address compliance with water quality standards and thus attempt to intercept peak concentrations in rivers. They also show significant bias towards periods when pesticides are detectable in rivers. Thus, simulated data (apart from isoproturon in the Thames) were reduced to a four-week resolution by taking the largest of the four average weekly pesticide concentrations for each four-week period. As a small number of relatively large pesticide concentrations dominated the monitoring data, a natural logarithmic transformation was applied to both monitored and simulated data. An autocorrelation function was calculated for both sets of data and any seasonal effect was removed by differencing with a relevant lag (lags of 13, 26 and 52 weeks were investigated - see Table 5). Finally, a first-order autoregressive function was fitted to the transformed and differenced data. A process,  $X_t$  for timesteps  $t=1 \dots N$  is said to be a first-order autoregressive process if:

$$X_t = \rho[1] X_{t-1} + Z_t \quad (5)$$

where  $Z_t$  is a purely random process with zero mean and  $\rho[1]$  is the first-order autoregressive parameter. The significance of the resulting autoregressive function was tested using the residuals from the fitted function, which are random and close to zero if the fit is good. The autocorrelations of these residuals were also examined (particularly for lags 1 and 2) and were assessed for significant differences from zero using the crude limits of  $\pm 2/\sqrt{N}$  where  $N$  is the number of points in the time series.<sup>25</sup>

## 4 RESULTS AND DISCUSSION

### 4.1 Model performance with respect to frequency of detection

It is important to know whether the model can predict those pesticides that may be present in surface water in different catchment types. From comparisons for  $c$  150 catchment–pesticide combinations, 67 and

**Table 2.** Acceptability criteria relevant to the comparison of observed and simulated maximum concentrations of pesticides

Under-estimation	Residues above the LOQ detected but not simulated by the model	or	Detected peak concentration $>X$ times the simulated peak <sup>a</sup>
Acceptable	No residues above the LOQ simulated or detected	or	Simulated peak concentration within a factor of $X$ of the detected peak <sup>a</sup>
Over-estimation	Residues above the LOQ simulated by the model but not detected	or	Simulated peak concentration $>X$ times the detected peak <sup>a</sup>

<sup>a</sup> where  $X=2, 5$  or  $10$ .

**Table 3.** Model performance with respect to frequency of detection sorted by catchment size (summary of individual tests on c 150 catchment-pesticide combinations per annum)

Year	Catchment size (km <sup>2</sup> )	Combinations where $\chi^2$ calculated			Combinations where $\chi^2$ not calculated		
		Total number	Percentage acceptable	Percentage not acceptable	Total number	Percentage acceptable	Percentage not acceptable
1995	0–300	28	64	36	12	58	42
	300–1000	18	67	33	3	100	0
	1000–3000	21	52	48	41	76	24
	3000–10 000	12	75	25	12	58	42
	All	79	63	37	68	71	29
1997	0–300	32	44	56	12	80	50
	300–1000	12	67	33	4	25	75
	1000–3000	22	41	59	41	68	32
	3000–10 000	14	57	43	12	58	42
	All	80	49	51	69	61	39

54% of simulations were classified as ‘acceptable’ for years 1995 and 1997, respectively (Table 3). For instances where  $\chi^2$  could be calculated, levels of acceptability ranged from 49 to 63%, whilst 61 to 71% of comparisons were acceptable for catchment-pesticide combinations where  $\chi^2$  could not be derived. The model was thus better able to simulate total absence of pesticide residues than the frequency of detection where residues were intermittently present. There was no overall trend of the model performing better for a particular catchment size. However, simulations for the very large Thames receiving area (9386 km<sup>2</sup>; catchment 29 in Fig 1) were generally poor (data not shown) and this might be attributed to both the size of the area and the extensive abstractions along the length of the Thames. The evaluation for the four comparison types ( $\chi^2$  calculated/not calculated, acceptable/not acceptable) was not biased with respect to frequency of monitoring.

#### 4.2 Model performance with respect to simulation of maximum concentrations

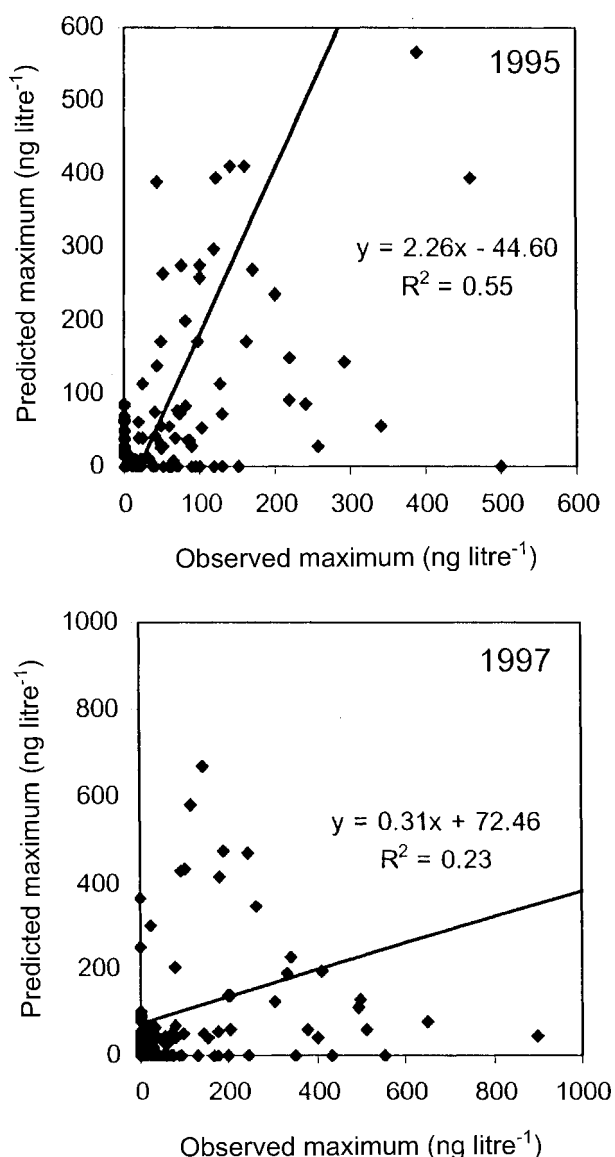
Generally, model simulations within a factor of 10 of observed values might be considered acceptable for policy and regulatory applications, particularly given the many constraints on simulating pesticide transport at the catchment scale.<sup>4</sup> At this level of accuracy, acceptable simulations were obtained for 74 and 66% of combinations in 1995 and 1997, respectively (Table 4). Model performance deteriorated little when the

acceptability factor was set to 5, but declined markedly when the factor was reduced to 2. Linear regression analyses of simulated against observed peak concentrations for 1995 and 1997 had gradients of 2.26 (over-estimation) and 0.31 (under-estimation), respectively (Fig 2). However, there was large variability in the two fits ( $P < 0.001$ ,  $r^2 = 0.55$ , standard error of the slope = 0.17 for 1995;  $P < 0.001$ ,  $r^2 = 0.23$ , standard error of the slope = 0.05 for 1997). The difference in model behaviour for the two years might be attributable to a number of factors, including a failure to adequately describe the effects of different weather conditions. In general, observed maxima were larger in 1997 and in part this may reflect monitoring (particularly by the water industry) which was better targeted on periods with likely contamination. The progressive targeting of monitoring over time would have no impact on model output and may partly explain the change from over- to under-estimation.

Separation of simulations for individual pesticides showed that maximum concentrations of strongly sorbed compounds (linuron, triallate, trifluralin) were well simulated, whilst those of more mobile pesticides (bromoxynil, isoproturon, mecoprop) were often over-estimated. The model assumes that, as the front of pesticide moves down the soil profile over time, the compound is evenly distributed between the soil surface and the depth of the front. For more mobile pesticides, the immediate surface layers may be leached of chemical. The assumption will thus tend

Year	Simulations within a factor of	Under-estimations (%)	Acceptable simulations (%)	Over-estimations (%)
1995	2	17	52	31
	5	11	71	18
	10	10	74	16
1997	2	30	42	28
	5	19	61	20
	10	16	66	18

**Table 4.** Model performance with respect to simulation of peak concentrations detected (values are percentages of c 150 comparisons)



**Figure 2.** Linear regression analyses of observed and simulated maximum concentrations for *c* 150 catchment-pesticide combinations in each of two years.

to over-estimate concentrations of more mobile pesticides in soil water in the mixing zone and will lead to an over-estimation of concentrations entering surface water. A more realistic description of the redistribution of pesticide down the soil profile would overcome this problem.

#### 4.3 Time series analysis

Measured and simulated concentrations resolved to a one- or four-week timestep are provided in Fig 3 and results of the time series analysis for each of the seven pesticide-catchment combinations meeting the minimum data criteria are summarised in Table 5 (numbers in parentheses refer to the catchment number in Fig 1). A purely visual comparison of the data in Fig 3 suggests that POPPIE output gave a reasonable match to patterns of detected concentrations for lindane in the Ock, isoproturon in the Ock, Thames and West Rother and atrazine in the Test.

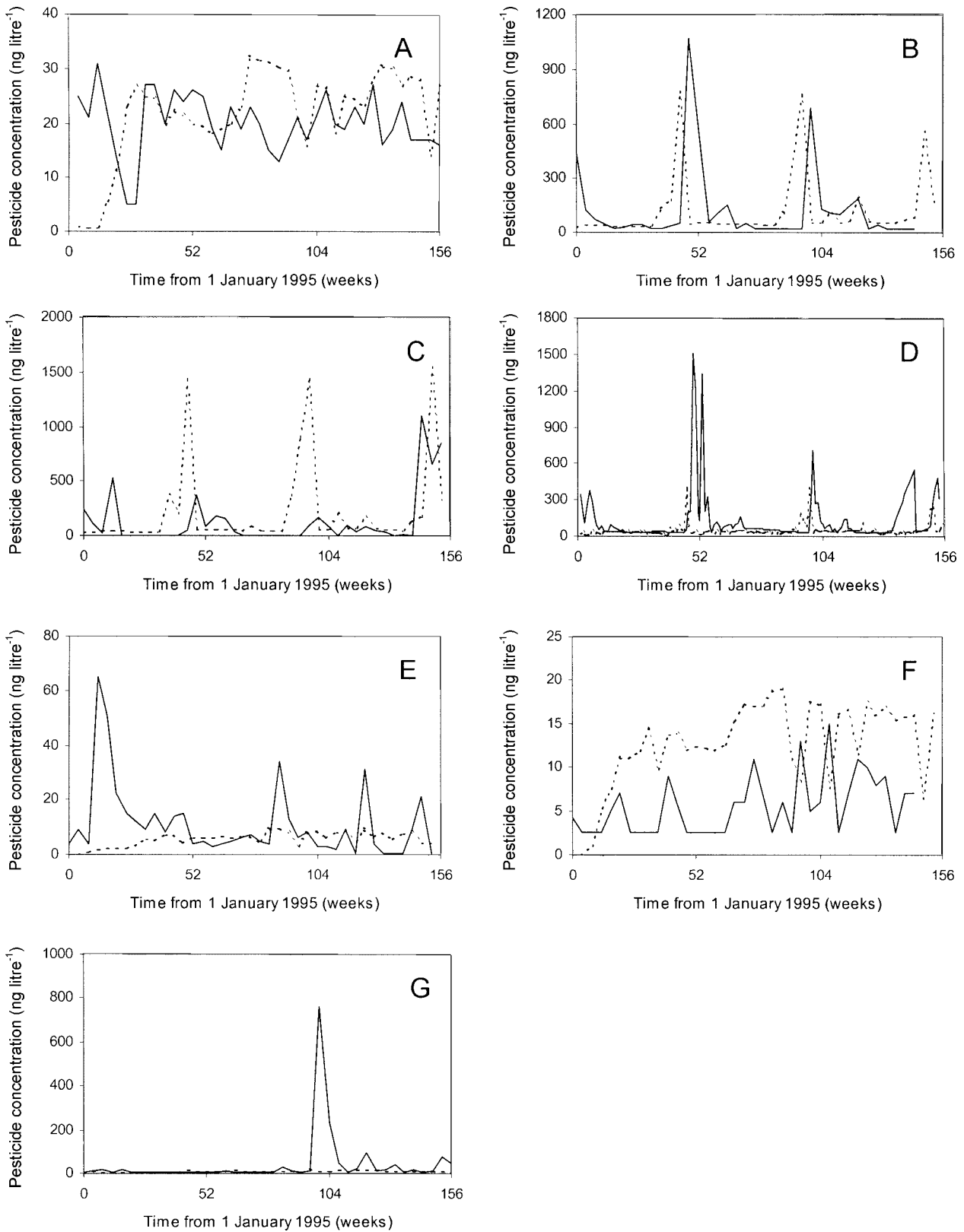
However, peak concentrations of isoproturon were always under-estimated. The resolution of pesticide usage data was monthly and the slight temporal shift in peak concentrations of isoproturon (Fig 3B, C and D) is attributable to the empirical division of pesticide applications between weeks making up any given month. Measured concentrations of simazine in the West Rother and lindane in the Don were not well matched by the model.

In all analyses involving isoproturon, the simulated data followed an autoregressive function when transformed and differenced over one year. Where there were enough measured data, these also followed an autoregressive function whose parameter was not significantly different from the simulated data function. Measured and simulated data followed the same form, dominated by the usage pattern for the compound, with applications occurring mainly in autumn each year. It should be noted, however, that the confidence intervals around the autoregressive parameter were particularly broad (Table 5). The results indicate that movement to surface waters occurs soon after application. Previous research in the UK has shown that drainflow can be an important route of entry into surface waters for autumn-applied herbicides such as isoproturon and that losses are greatest in the first event after application.<sup>19,20</sup> Losses in spray drift during application or runoff from farmyards following tank-filling operations are further processes which could contribute to the seasonal pattern of concentrations in rivers.

For other pesticides, the simulated data sometimes followed an autoregressive function, although the autoregressive parameter was close to unity, indicating that the autoregression may be unreliable. As the data were produced by a model, it is unlikely that they were purely random. Measured data for the other pesticides considered (atrazine, lindane and simazine) appeared to follow a purely random pattern. In part, this may be explained by disparate uses for all three compounds, which follow a less marked seasonal pattern than isoproturon, a herbicide used only on cereals. Aerial deposition of lindane has been shown to be widespread at low levels and may have resulted in a background presence of this compound in surface water.<sup>26</sup>

## 5 CONCLUSIONS

The evaluation of the SWATCATCH model reported here was rigorous in that: (1) it included data for contrasting chemicals and environmental conditions; (2) there was no potential for calibration of the model; and (3) the evaluation dataset was not used in the development of the program. The model performed relatively well in simulating both the identity of pesticides which would be detected at each catchment outlet and the maximum concentration for most catchment-pesticide combinations. The model has been designed and tested at the scale of application for which it was developed. Results indicate that



**Figure 3.** Measured and simulated concentrations for seven catchment–pesticide combinations; (A) atrazine in the Test; (B) isotopuron in the Ock; (C) isotopuron in the West Rother; (D) isotopuron in the Thames; (E) lindane in the Don; (F) lindane in the Ock; (G) simazine in the West Rother; (—) measured; (-----) simulated.

SWATCATCH can assist in the construction of pesticide monitoring programmes. The main shortcomings of the model are that it does not account for residues in rivers arising from either non-agricultural

use of pesticides (eg use on hard surfaces) or point source contamination from farmyard activities and spills. Both of these routes of entry have been shown to be important,<sup>27,28</sup> but to date there are no catchment-

**Table 5.** Time series analyses for seven catchment–pesticide combinations

Pesticide–catchment combination <sup>a</sup>	Measured data		Simulated data	
	Period of any significant seasonal effect	Fitting of autoregressive function after differencing to remove seasonal effect <sup>b</sup>	Period of any significant seasonal effect	Fitting of autoregressive function after differencing to remove seasonal effect
Atrazine in the Test (catchment 25)	No seasonal effect	First-order function with ( $p[1]=0.989;95\%CI=0.933,1.044$ )	No seasonal effect	First-order function with ( $p[1]=0.999;95\%CI=0.951,1.048$ )
Isoproturon in the Ock (catchment 11)	No seasonal effect	Random pattern only	1 year	First-order function with ( $p[1]=0.490$ )
Isoproturon in the Thames (catchment 29)	1 year	First-order function with ( $p[1]=0.610;95\%CI=0.456,0.759$ )	1 year	First-order function with ( $p[1]=0.368;95\%CI=0.219,0.516$ )
Isoproturon in the West Rother (catchment 10)	1 year	First-order function with ( $p[1]=0.352;95\%CI=0.034,0.675$ )	1 year	First-order function with ( $p[1]=0.524;95\%CI=0.231,0.817$ )
Lindane in the Don (catchment 18)	No seasonal effect	Random pattern only	No seasonal effect	First-order function with ( $p[1]=0.985$ )
Lindane in the Ock (catchment 11)	No seasonal effect	Random pattern only	No seasonal effect	First-order function with ( $p[1]=0.960$ )
Simazine in the West Rother (catchment 10)	No seasonal effect	Random pattern only	No seasonal effect	Random pattern only

<sup>a</sup> Value in parentheses refers to the catchment number on Fig 1.

<sup>b</sup>  $p[1]$ =first-order autoregressive parameter; 95% CI=95th percentile confidence intervals.

scale pesticide models which account for either process.

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