

Exposure to sulfosulfuron in agricultural drainage ditches: field monitoring and scenario-based modelling

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Abstract: Field monitoring and scenario-based modelling were used to assess exposure of small ditches in the UK to the herbicide sulfosulfuron following transport via field drains. A site in central England on a high pH, clay soil was treated with sulfosulfuron, and concentrations were monitored in the single drain outfall and in the receiving ditch 1 km downstream. Drainflow in the nine months following application totalled 283 mm. Pesticide lost in the first 12.5 mm of flow was 99% of the total loading to drains (0.5% of applied). Significant dilution was observed in the receiving ditch and quantifiable residues were only detected in one sample ($0.06 \mu\text{g litre}^{-1}$). The MACRO model was evaluated against the field data with minimal calibration. The parameterisation over-estimated the importance of macropore flow at the site. As a consequence, the maximum concentration in drainflow ($2.3 \mu\text{g litre}^{-1}$) and the total loading to drains (0.76 g) were over-estimated by factors of 2.4 and 5, respectively. MACRO was then used to simulate long-term fate of the herbicide for each of 20 environmental scenarios. Resulting estimates for concentrations of sulfosulfuron in a receiving ditch were weighted according to the prevalence of each scenario to produce a probability distribution of daily exposure.

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1 INTRODUCTION

Pesticides present in surface waters may pose a risk to a range of aquatic organisms. The predominant routes of entry arising from diffuse applications of pesticide include spray drift, surface runoff and leaching to field drains. Less significant routes to surface water include groundwater seepage, sub-surface lateral flow and wet or dry deposition following longer range transport in air. Movement via field drains has been shown to be important in a number of countries including the UK^{1,2} and rapid transport of pesticide residues in drainflow has been demonstrated in several field experiments.^{3–5} Much research has focused on clay soils where the phenomenon of macropore flow through structural and/or biological voids accentuates transport to sub-surface drains. Loss of pesticide via field drains decreases with strength of sorption of the compound to soil^{3,6} and it is also strongly influenced by soil type, drain spacing and type and rainfall patterns shortly after application.¹ In the UK, total losses <0.1% of the applied amount have been reported for strongly sorbed compounds such as trifluralin and deltamethrin.^{4,7} Losses of the

moderately sorbed compound isoproturon have been reported to vary between approximately 0.1 and 0.5% in typical years.^{4,5} Transport of the weakly sorbed sulfonylurea herbicide triasulfuron from a heavy clay soil in southern England resulted in total losses to drains of approximately 5% of that applied.⁸ It has been demonstrated that much of the transport occurs during the first few drainage events after application,^{4,5} so that ecologically significant concentrations in the aquatic environment cannot be ruled out.

Evaluation of the potential adverse effects of pesticides on non-target aquatic organisms is a part of European registration procedures.⁹ Exposure concentrations estimated using agreed approaches are compared with ecotoxicological endpoints for indicator species representative of fish, invertebrates, algae and higher aquatic plants. Exposure has been most commonly calculated using look-up tables⁹ and/or simple formulae based on worst-case losses of pesticide from field experiments.¹⁰ A standardised modelling approach for the calculation of exposure has recently been established by FOCUS.¹¹ The tool combines mechanistic models with 10 standard

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environmental scenarios selected to represent the European agricultural area. Nevertheless, all current approaches are designed to produce a generalised expression of exposure whose conservatism derives from worst-case assumptions built into the calculation. There is no consensus on the approach to be adopted when a screening level assessment indicates a potential for impact on the aquatic environment.

Sulfosulfuron [1-(4,6-dimethoxyrimidin-2-yl)-3-(2-ethylsulfonylimadazo[1,2- α]pyridin-3-yl)sulfonyl-urea] is a sulfonylurea post-emergence herbicide for the control of couch and brome grasses, cleavers and other broad-leaved weeds in winter wheat. Sulfosulfuron is commercialised as a 800 g kg⁻¹ wettable powder formulation (Monitor™). The compound is acidic (pKa 3.5) as a result of ionisation of the urea bridge. Sorption is influenced by soil pH with a higher affinity for soil components under more acidic conditions. A single application of the product will typically be made in spring at a target rate of 20 g AI ha⁻¹.

As part of standard procedures for registering sulfosulfuron for use in the UK, a simple worst-case approach was adopted to estimate a predicted environmental concentration (PEC) for sulfosulfuron in a small ditch following entry via drainflow. Based on results from a long-term drainage experiment on a heavy clay soil in southern England,⁵ it was assumed that 1.9% of the total loading of sulfosulfuron to a 1-ha field would be transported in 10 mm of drainflow. It was further assumed that drainflow was subsequently diluted within a static ditch containing 30 000 litres of uncontaminated water. The resulting PEC (2.9 $\mu\text{g litre}^{-1}$) was compared with a 50% effect concentration (EC₅₀) for *Lemna gibba* (1.0 $\mu\text{g litre}^{-1}$) derived from a 14-day test in the laboratory. The ratio EC₅₀/PEC (0.34) was below the generally accepted threshold for higher aquatic plants (10), indicating that a potential for effects could not be ruled out when basing the risk assessment on these worst case assumptions. In response to these early results, a strategy combining experimental and modelling studies was devised to refine the assessment of risk for impact on higher aquatic plants. First, ecotoxicity tests were undertaken with three additional species of higher aquatic plant to establish their sensitivity relative to *L. gibba*.¹² Second, a field drainflow study was set up to investigate the potential for sulfosulfuron to be transferred to drainflow and receiving water bodies. Finally, mathematical modelling was undertaken to

assess likely levels of exposure for higher aquatic plants in the UK.

The present paper reports on the field drainflow study and the modelling exercise. Results originating from the drainflow study were simulated with minimal calibration using the macropore flow model MACRO¹³ in order to assess the ability of the model to simulate transport of sulfosulfuron via drains. The model was then used to extrapolate results based on a range of scenarios representative of environmental conditions within the use area for sulfosulfuron in the UK.

2 MATERIALS AND METHODS

2.1 Field drainflow study

A field drainflow study was undertaken to investigate the potential for movement of sulfosulfuron to drains and a receiving water body. The 7.7-ha field selected for the study was located in Maidwell, Northamptonshire, UK (52.2°N, 0.6°W). Annual average rainfall in the area is *ca* 660 mm. The soil at the site is a clay loam over clay of the Hanslope series (Table 1). This soil was considered relatively vulnerable to leaching of sulfosulfuron because (1) it was alkaline (pH 7.1–8.5); (2) it had a low organic carbon content in the topsoil (1.2%); and (3) it had a coarse structure likely to favour macropore flow. Vertical movement of water is strongly inhibited in subsoil layers at the site and artificial drainage had been installed in the form of plastic pipes (80 cm depth, 20 m apart) with gravel fill and a secondary mole drainage system (55 cm deep installed in 1994). Mole drains comprise a channel approximately 10 cm in diameter formed by pulling a metal bullet attached to a blade through a clay soil in a plastic condition. Water collected by the drains converged to a single outfall which was instrumented with a 90° V-notch weir to monitor flow, and an automated water sampler to collect sub-samples of drainflow for analysis. The drain outfall formed the start of a small ditch (30 cm wide at its base adjacent to the field site). A second V-notch weir and automatic sampler were installed *ca* 1000 m downstream. At the second monitoring site, the ditch was 100 cm wide at its base. Water originating from the field site combined with runoff from permanent pasture land, a main road, a small housing estate and a small tributary ditch. An automatic weather station recorded rainfall, air and soil temperatures,

Table 1. Properties of the Hanslope soil at the field site

Horizon	Depth (cm)	Particle size distribution			Total organic carbon (%)	pH in water	CEC (mEq 100 g ⁻¹)	Bulk density (g cm ⁻³)	Water content at -5 kPa (cm ³ cm ⁻³)
		0–2 μm (%)	2–63 μm (%)	63–2000 μm (%)					
Ap	0–30	27.6	34.5	37.9	1.2	7.1	24.4	1.50	39.7
Bw (g)	30–56	29.2	33.8	37.0	0.3	7.2	16.8	1.63	35.7
Bg	56–97	29.2	40.8	30.0	0.4	8.3	12.8	1.67	31.9
BCg	97–120	37.8	39.3	22.9	0.4	8.5	12.6	1.77	33.1

wind speed, humidity and solar radiation at an hourly time-step.

Sulfosulfuron was applied to winter wheat at Zadok's growth stage 37 (flag leaf just visible) on 16 May 2000 as a 800 g kg⁻¹ wettable powder formulation (Monitor) at a rate of 19.8 g AI ha⁻¹ in 200 litre water ha⁻¹. Flow was measured continuously at the two monitoring points following application. Water samples were collected between May 2000 and February 2001 in response to drainflow (drain outfall) or at intervals of 8 h (downstream site). Six neutron probe access tubes were installed in the field to a depth of 170 cm and soil moisture content was measured in 10-cm increments at intervals of one month and after heavy rainfall. Undisturbed soil cores (5 cm diameter, 30 cm long) were collected in acetate liners pre-treatment and at 0, 3, 7, 14, 28, 60 and 120 days after treatment (DAT). Twenty-one cores were taken along transects which were separated by 2 m for successive sampling occasions. The cores were divided into 10-cm increments and bulked by depth in batches of seven to give three replicate samples for analysis. Samples of soil and water were transported and stored at $-20\text{ }^\circ\text{C}$ prior to extraction and analysis.

Sulfosulfuron was extracted from drainage water by solid-phase extraction using Envi-18 SPE cartridges (500 mg, 3 ml) which were pre-conditioned with methanol (3 ml) and 1% acetic acid (2 × 3 ml). Each sample (100 ml) was acidified with acetic acid (1 ml) and drawn through the cartridge at *ca* two drops per second. The loaded cartridges were rinsed with 1% acetic acid (3 ml) before elution with acetonitrile + water (50 + 50 by volume; 5 ml). Sulfosulfuron was determined by reverse-phase HPLC-MS/MS with injection through a 50- μ l loop. Acetonitrile + water (50 + 50 by volume) was used to elute sample through a Hypersil HyPurity C-8 column (150 mm long) at 0.5 ml min⁻¹ with quantification by a Thermoquest Finnigan LCQ Duo with an electrospray ionization interface in positive ion mode. The limit of quantification (LOQ) was 0.05 μ g litre⁻¹ and recovery values were 106 (\pm 3)% and 92 (\pm 5)% at 0.05 and 3.00 μ g litre⁻¹, respectively.

Sulfosulfuron was extracted from soil by shaking subsamples (50 g) with acetone + water (2 + 1 by volume; 300 ml) for 1 h. The mixture was filtered through a glass microfibre filter. The filtrate (200 ml) was mixed with sodium chloride (20 g) and liquid-liquid partitioned with dichloromethane (100 ml). The organic phase was separated, dried with anhydrous sodium sulfate (20 g) and passed through a glass wool plug. The filtrate was evaporated to dryness, redissolved in cyclohexane + ethyl acetate (1 + 1 by volume; 5 ml) and cleaned up by passing through a gel permeation chromatography column (BioRad Bio-Beads S-X3; 50 g; mobile phase cyclohexane + ethyl acetate 1 + 1 by volume, at 5 ml min⁻¹) and then a deactivated silica gel column (silica gel 60; elution with dichloromethane + methanol 9 + 1 by volume; 3 × 5 ml). The eluant was evaporated to dryness

and resuspended in acetonitrile + water (30 + 70 by volume; 2 ml) with 1% acetic acid. Extracts were analysed for sulfosulfuron by HPLC-MS/MS as described above with a LOQ of 0.3 μ g kg⁻¹ and recovery values of 83 (\pm 3)% and 77 (\pm 1)% at 0.3 and 30 μ g kg⁻¹, respectively.

2.2 Model description and evaluation

The MACRO model¹³ (version 4.1) was selected for the modelling work as it can simulate both drainflow and macropore flow. MACRO is a physically based model with the soil porosity divided into two flow systems or domains (macropores and micropores), each characterised by a flow rate and solute concentration. Richards' equation and the convection-dispersion equation are used to simulate soil water flow and solute transport in the soil micropores, whilst a simplified capacitance-type approach is used to calculate fluxes in the macropores. Additional model assumptions include first-order kinetics for degradation in each of four 'pools' of pesticide in the soil (micropores and macropores, solid/liquid phases), together with an instantaneous sorption equilibrium in each pore domain described by a Freundlich isotherm.

MACRO has been evaluated against field data for the transport to drains of pesticides including bentazone, isoproturon and prochloraz.¹⁴⁻¹⁶ In general, the model demonstrates the ability to describe field behaviour following calibration. For the current exercise, MACRO was used to predict the behaviour of sulfosulfuron for environmental scenarios with no data to support calibration. In order to support this use of the model, data from the field drainflow study were first simulated with minimal calibration to evaluate model performance. Given the pattern of leaching observed in the field, it was considered essential to run the model using rainfall data recorded at an hourly rather than daily resolution. Hourly values were only available from the day before application, so initial soil moisture content was calibrated to match the volume (but not pattern) of drainflow in the first event after application (10 DAT).

Input parameters for MACRO were derived from measured data wherever possible. However, expert judgement based on previous application of the model to similar soils¹⁷ was used to establish the parameter value for water tension at the boundary between the two flow domains (CTEN), as this cannot readily be independently estimated. Values of -2.5 to -3.5 kPa were selected for the four horizons in the clay soil. The water content equivalent to this tension (XMPOR) and the pore size distribution index in the micropores (ZLAMB) were derived from measured water release data, whilst the conductivity at the boundary (KSM) was estimated using the equation given by Laliberte *et al.*¹⁸ Saturated conductivity (KSATMIN) was derived using a pedo-transfer function for clay and loam soils in England and Wales:

$$\text{KSATMIN} = 18.13 - 4.62\text{AC} + 0.538\text{AC}^2 \quad (1)$$

in which $KSATMIN$ is the saturated hydraulic conductivity ($mm\ h^{-1}$) and AC is the air capacity calculated as the difference between total porosity and water content at $-5\ kPa$ ($\% v/v$).

The aggregate half-width parameter ($ASCALE$) controls the movement of water and solute between the micropore and macropore domains. Values were selected from basic descriptions of soil structure using the rules proposed by Jarvis *et al.*¹⁹ The parameter describing the relative proportion of sorption sites in the macropore region ($FRACMAC$) was set to 0.02 (2% of sorption sites are situated in the macropores).

Sorption of sulfosulfuron in five soils with pH 5.3–7.9 was linearly related to pH ($P < 0.05$; $r^2 = 0.94$), with no discernible influence of soil organic matter content:

$$K_f = 2.09 - (0.26 * pH) \quad (2)$$

in which K_f is the Freundlich sorption constant. This equation was used to calculate partition coefficients to characterise sorption in the four horizons of the experimental soil. The pH of subsoil horizons in the Hanslope soil fell outside the range evaluated in sorption studies (Table 1) and negative values of K_f result from the use of eqn (2); K_f in these horizons was set to $0.01\ ml\ g^{-1}$. The average Freundlich exponent (0.93) from the five soils was used. The rate of degradation of sulfosulfuron in topsoil was calculated from sulfosulfuron residues measured during the field experiment. Corrections within the model for effect of soil temperature and moisture content on degradation were switched off. Subsoil rates were derived from that in topsoil using the equation of Jarvis *et al.*¹⁹ Interception of pesticide spray by the crop canopy was set to 79% to match initial soil residues measured immediately after application. Efficiency for subsequent wash-off of residues from plant surfaces was set at $2\%\ mm^{-1}$ (calibrated from a default value of $1\%\ mm^{-1}$). In the absence of measured data, rate of dissipation from plant surfaces was set to that measured in soil.

2.3 Scenario definition and modelling approach

The target area (wheat-growing land in England and Wales; *ca* 1.7×10^6 ha)²⁰ was divided into environmental scenarios comprising discrete classes of soil type and climate. The analysis was undertaken using the SEISMIC database,²⁰ a modelling support tool which allows climate, cropping and soil data to be overlaid and then provides basic environmental properties useful for deriving model input parameters. First of all, areas of wheat cultivation were overlaid onto those soils likely to be drained under arable cultivation to generate an estimate that 54% of the area cultivated with wheat in England and Wales is likely to be artificially drained. The soil series making up the drained wheat area were then divided into six broad classes (Table 2) based upon vulnerability for leaching of the acidic herbicide via drainflow. The division was made subjectively based on the relative mobility of sulfosulfuron (determined by soil pH) and the prevalence of rapid movement to drains via macropore flow (determined by clay content and structure). Drained soils with peaty topsoils were considered to have no vulnerability for leaching via drainflow because sorption of pesticides will be strong. Hence, only five of the six soil classes were considered within the modelling. A representative soil series was selected as lying at the vulnerable end of each of the five remaining classes (Table 2). For each representative series, profile information was extracted from SEISMIC (Table 3) and used to parameterise the model as described above. Soil parameter data within SEISMIC are held for 411 soil series. Data available for each characteristic layer under each of four different land uses (including arable) are depth, particle size distribution, organic carbon content, pH, bulk density, water retention curve, hydraulic conductivity at saturation and field capacity and van Genuchten's β and N .²⁰

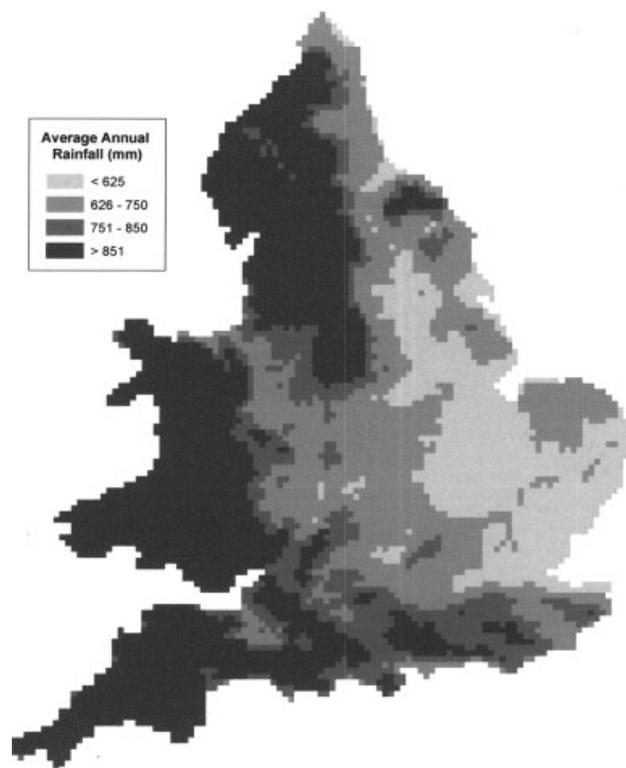
Areas of wheat cultivation in England and Wales were divided into four approximately equal climatic classes (Fig 1) designated 'dry' (<625 mm precipitation per annum), 'medium' (625–750 mm pa), 'wet' (750–850 mm pa) and 'very wet' (>850 mm pa). Four

Table 2. Division of the wheat-growing land in England and Wales into soil vulnerability classes

Representative soil series	Description of soil class	Proportion of wheat-growing land (%)
Denchworth	Clayey soils with a strong inhibition to downwards movement of water which have a soft impermeable layer within 100 cm of the soil surface and a gleyed layer within 70 cm depth	7.0
Hanslope	Soils with clayey upper layers	15.5
Brockhurst	Soils with clayey lower layers and lighter-textured upper layers	
Clifton	Medium loamy and silty soils	
Quorndon	Relatively permeable soils with a gleyed layer within 40 cm of the soil surface as a result of shallow groundwater	9.2
(None assigned)	Soils with humose or peaty layers	3.8
		3.5

Table 3. Selected properties of the five representative soil series selected for scenario-based modelling

	Depth interval (cm)	Organic carbon (%)	Sand (%)	Silt (%)	Clay (%)	Bulk density (g cm^{-3})	pH (1:2.5 in H_2O)
<i>Denchworth series</i>							
Horizon 1	0–20	2.9	17	40	43	1.17	6.3
Horizon 2	20–50	1.2	6	30	64	1.26	6.9
Horizon 3	50–70	0.8	5	31	64	1.31	7.0
Horizon 4	70–100	0.4	6	36	58	1.40	7.4
<i>Hanslope series</i>							
Horizon 1	0–25	2.9	30	32	38	1.18	7.7
Horizon 2	25–50	0.9	22	36	43	1.38	8.2
Horizon 3	50–65	0.5	20	33	47	1.45	8.3
Horizon 4	65–100	0.4	14	45	41	1.44	8.3
<i>Brockhurst series</i>							
Horizon 1	0–25	2.3	32	42	26	1.26	6.4
Horizon 2	25–45	0.6	30	44	26	1.49	6.4
Horizon 3	45–70	0.3	14	40	46	1.48	6.7
Horizon 4	70–100	0.2	7	48	45	1.51	7.5
<i>Clifton series</i>							
Horizon 1	0–25	3.1	50	30	20	1.20	5.9
Horizon 2	25–40	0.5	52	31	17	1.52	6.2
Horizon 3	40–75	0.4	38	32	30	1.55	6.8
Horizon 4	77–100	0.2	36	32	32	1.64	7.2
<i>Quorndon series</i>							
Horizon 1	0–30	2.7	60	25	15	1.25	7.1
Horizon 2	30–80	0.6	68	21	11	1.41	6.3
Horizon 3	80–120	0.3	73	18	9	1.43	6.3

**Figure 1.** Division of England and Wales into climatic classes based on average annual rainfall.

weather datasets were then selected from the SEISMIC database as representative of the four climatic classes. The datasets comprised 30 years of daily weather (precipitation, maximum and minimum air temperature, solar radiation) generated using the WGEN model.²¹ Weather data were generated on the basis of probability distribution coefficients derived from analysis of measured weather data at each site. A comparison of measured and generated data for a site in Cambridge showed that the model overestimated the number of days on which rainfall exceeded 0.25 mm by 17%. Rainfall volumes up to 20 mm day⁻¹ were well simulated on average, but extreme events were under-estimated (the generated and observed maximum daily rainfalls for the 30-year period were 35.4 and 43.2 mm, respectively). Average annual rainfalls for the four datasets were 588, 713, 815 and 1115 mm (Table 4). Potential evapotranspiration was calculated using Linacre's equation²² and adjusted using a fixed site-specific factor such that model simulations matched long-term averages for actual evapotranspiration.²³

The model was run for the 20 scenarios resulting from the combination of five soil and four climate classes and assuming annual applications of the test compound in the spring of each of 30 years. Degradation and sorption were simulated as described in Section 2.2 based on field dissipation, the regression for the sorption coefficient (eqn (2)) and the average value for the Freundlich coefficient. Average data on soil trafficability were used to select representative dates for application of 1 April to 1 May depending upon scenario. Application was delayed to the first subsequent dry day where rainfall exceeded 2 mm on the target application date or 7 mm on either of the next two days. Rainfall of 7 mm was considered an amount that could reasonably be forecast as heavy rainfall and where a farmer might delay application to protect efficacy. Aquatic organisms in receiving ditches and streams will not be exposed to raw drainflow. A simple approximation of dilution within a small receiving water body was considered on the basis of drainflow from a 1-ha field entering a ditch 100 m long, 1 m wide and with a water depth of 30 cm. It was assumed that the residence time of water in the ditch was 1 day, so that the daily input of drainflow and pesticide always entered the same volume of uncontaminated water. This assumption is conservative for areas with clay soils in the UK where residence time will frequently be less than 1 h.⁷ Given the relatively short residence time, no degradation of sulfosulfuron within the water column was considered in the calculation.

Cumulative distribution charts were constructed for maximum daily concentrations of sulfosulfuron in the water phase of the ditch. Maximum daily concentrations for each of 30 years simulated per scenario were extracted, resulting in a total of 600 annual maxima. The series of 30 values were then weighted according to the prevalence of

Table 4. Annual rainfall statistics (30 years) for the weather stations selected to represent the three climate scenarios (all values in mm)

Year	Cambridge (dry scenario)	Mylnefield (medium scenario)	Keele (wet scenario)	Rosemaund (very wet scenario)
30-year average	588	713	815	1115
Standard deviation	80	86	99	119
Minimum	447	526	614	858
Maximum	784	872	977	1361

the respective scenario across England and Wales (Table 5). Undrained and peaty soils, which represent 49.4% of the wheat-growing area in England and Wales, were attributed concentrations of zero and were included in the analysis in a similar way.

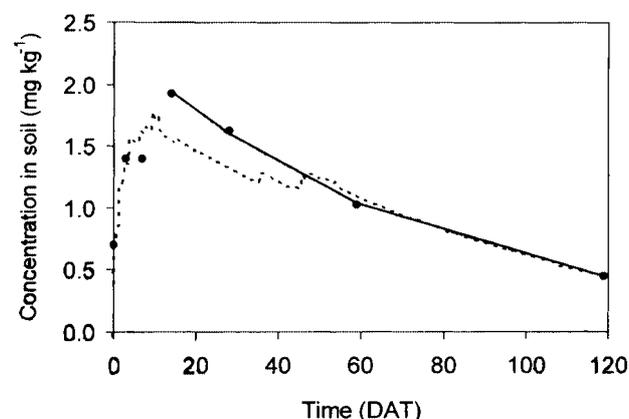
3 RESULTS

3.1 Concentrations in field drainflow

Concentrations of sulfosulfuron in the upper 20 cm of soil increased between 0 and 14 DAT to a maximum of $1.85 \mu\text{g kg}^{-1}$ (Fig 2). The increase was attributed to washoff of residues intercepted by plant surfaces in the 96.6 mm rainfall received during the period. All determinations at 20–30 cm depth were below the LOQ ($0.3 \mu\text{g kg}^{-1}$). Estimation of the field dissipation rate for sulfosulfuron in soil was therefore based on residues detected in the top 0- to 20-cm

Table 5. Proportion of the total wheat land in England and Wales accounted for by each scenario

Soil type	Extent of soil within each climatic scenario (%)				Total extent (%)
	Dry	Medium	Wet	Very wet	
Undrained	—	—	—	—	45.9
Peaty soils	—	—	—	—	3.5
Denchworth	2.7	3.0	0.8	0.5	7.0
Hanslope	9.0	5.6	0.5	0.4	15.5
Brockhurst	4.8	7.6	1.8	0.9	15.1
Clifton	1.5	5.2	1.6	0.9	9.2
Quorndon	2.4	0.9	0.3	0.2	3.8
Total	20.4	22.3	4.9	2.9	100.0

**Figure 2.** (O) Measured residues of sulfosulfuron in the top 20 cm of soil, (—) fit of a first-order dissipation curve from the maximum residue 14 DAT ($y = 2.36 - 0.0139x$; $r^2 = 1.00$) and (- - -) MACRO simulation of residues.

soil layers only and was calculated from the point of maximum accumulation. A first-order half-life of 49.8 days ($r^2 = 1.00$) was fitted to the observed pattern of dissipation from 14 DAT onwards.

Summary statistics for weather during the field experiment are provided in Table 6. Results for drainflow and associated losses of herbicide are summarised on a monthly basis in Table 7. Total drainflow was 283 mm (38% of rainfall), whilst at peak efficiency in February 2001, 65 mm flow was recorded (95% of rainfall). The 96.6 mm rain that fell in the first 14 DAT generated 12.5 mm drainflow. Subsequently, the drains did not run until September 2000, but there were then frequent drainage events throughout the winter of 2000/01.

Drainflow was measured on an hourly basis with the frequency of sampling for herbicide determined automatically according to rate of flow. Peak concentrations were short-lived, lasting only a few hours. Figure 3 shows drainflow and herbicide concentrations for the first event after application which commenced 10 DAT. The first sample collected in response to this drainflow event contained the largest concentration of sulfosulfuron ($2.3 \mu\text{g litre}^{-1}$), which is indicative of the importance of macropore flow phenomena for the transfer of pesticide to drains at the experimental site. The observed pattern of concentrations matches that recorded for a range of compounds applied to drained clay sites in the UK and elsewhere.^{3–5,7}

From June 2000 onwards, concentrations of sulfosulfuron in drainflow were much smaller and no concentrations above the LOQ ($0.05 \mu\text{g litre}^{-1}$) were detected from October 2000 onwards (Table 7). Almost 99% of the total loss of sulfosulfuron in drainflow (0.76 g) occurred during the first 14 DAT. It is considered that the early drainflow flushes pesticide immediately available for transport out of the soil and that remaining pesticide in the soil is then largely held away from the main flow pathways and is thus protected with respect to future drainflow events.² In the present instance, this effect was enhanced by the gap in drainflow between early June and September 2000. The loss to drains was 0.50% of the 153 g sulfosulfuron applied to the 7.7-ha site. This loss is an order of magnitude smaller than that reported for triasulfuron,⁸ primarily because sulfosulfuron was applied in spring and there was limited drainflow during the months immediately after application. The application date for sulfosulfuron of 16 May was a few weeks later than might normally be expected because

Table 6. Monthly rainfall and air temperatures at the field site (May 2000–April 2001)

Month	Rainfall (mm)	Rainfall in relation to the long-term mean (%)	Monthly average of minimum air temperature (°C)	Monthly average of maximum air temperature (°C)
May 2000	102.6	178	7.4	15.1
June 2000	35.0	66	10.4	18.2
July 2000	75.4	138	10.8	18.4
August 2000	49.8	74	11.7	21.0
September 2000	101.0	175	10.7	17.6
October 2000	102.8	186	7.0	12.4
November 2000	97.4	158	4.0	8.5
December 2000	75.2	134	3.1	6.5
January 2001	33.4	60	0.6	4.8
February 2001	69.0	157	1.6	6.8
Total	741.6	132	6.8	13.0

Table 7. Monthly rainfall and comparison between observed and simulated drainflow and associated losses of sulfosulfuron

Month	Rainfall (mm)	Observed drainflow (mm)	Simulated drainflow (mm)	Observed loss of sulfosulfuron in drainflow (g)	Simulated loss of sulfosulfuron in drainflow (g)
May 2000	102.6	12.5	11.4	0.75	3.83
June 2000	35.0	0.1	0	<0.01	0
July 2000	75.4	0	0	0	0
August 2000	49.8	0	0	0	0
September 2000	101.0	3.9	36.8	0.01	0.15
October 2000	102.8	40.2	72.6	— ^a	— ^b
November 2000	97.4	79.8	79.6	—	—
December 2000	75.2	55.5	54.0	—	—
January 2001	33.4	25.7	25.8	—	—
February 2001	69.0	65.3	49.7	—	—
Total	741.6	283.0	329.9	0.76	3.98

^a No observed residues above the limit of quantification ($0.05 \mu\text{g litre}^{-1}$) from October onwards.

^b Simulated residues in the range 0.06 – $0.16 \mu\text{g litre}^{-1}$ from October onwards.

of unfavourable ground conditions. Nevertheless, the heavy rainfall before and immediately after this date generated significant drainflow very soon after application.

Flow and concentrations of sulfosulfuron were also monitored regularly in the ditch receiving drainflow from the field. Total flow through the ditch over the whole experimental period ($7.4 \times 10^5 \text{ m}^3$) was approximately 35 times larger than cumulative drainflow from the experimental site for the same period. The compound was never detected at concentrations greater than the LOQ apart from a single sample collected 12 DAT which contained $0.06 \mu\text{g litre}^{-1}$.

3.2 Model evaluation

Figure 3 also compares observed and simulated drainflow and associated concentrations of sulfosulfuron for the first drainage event after application. As this 3-day event yielded almost 99% of the quantified loss of sulfosulfuron from the site, accurate representation by the model was critical. Measured drainflow and simulated output in Fig 3 have a 1-h resolution, whilst pesticide concentrations were measured once every 4 h for the period shown. Initial soil moisture contents were calibrated to ensure a match between

observed and simulated drainflow volume over the 3 days. Nevertheless, the model did not accurately describe observed behaviour, with the first peak in drainflow missed and the third peak significantly overestimated with respect to peak flow but not to total volume of flow (Fig 3a). Macropore flow is a highly stochastic process, and it is thus extremely difficult to simulate detailed behaviour over single events with great accuracy. Overall, the simulated hydrograph was more peaky than that observed, with a very rapid response to rainfall and decline from peak flows. The model parameterisation over-emphasised the influence of macropore flow on site hydrology over the course of the event. Only initial soil moisture content was adjusted within the model. It would have been possible to undertake a comprehensive calibration of the model to better simulate observed behaviour. However, the purpose of the evaluation was to investigate general accuracy of the model in simulating maximum concentrations of pesticide in drainflow. Further calibration was avoided as there was no potential to do this during the next step of extrapolating the model to representative soil scenarios.

MACRO did not simulate any concentrations of sulfosulfuron in drainflow 9–10 DAT when peak values were measured (Fig 3b) as the first peak in

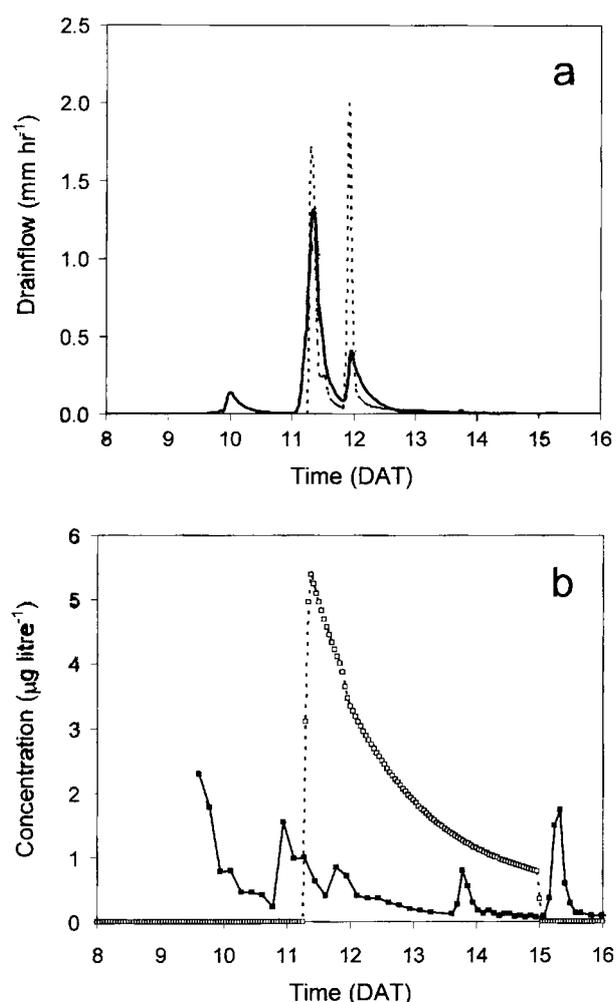


Figure 3. Evaluation of MACRO simulations for the first event after treatment: (a) (—) measured and (---) simulated drain discharge from the 7.7-ha site; (b) (■) measured and (□) simulated concentrations of sulfosulfuron in drainflow.

drainflow was not simulated. The pattern of largest concentrations of herbicide at the start of each peak in drainflow was well matched by the model for the peak 11 DAT. The maximum concentration over the event was over-predicted by a factor of 2.4. The decline in concentrations from the maximum was relatively well simulated by MACRO, although concentrations were consistently over-estimated throughout the event, and the influence of subsequent peaks in flow which resulted in a temporary increase in measured concentrations was not matched by the model. Whilst broad behaviour of the pesticide was well simulated by the model, the detailed pattern of the chemograph presented in Fig 3b is poorly described. The processes which control availability of pesticide for transfer into and transport by macropore flow are not well understood and cannot be completely simulated by current models.¹⁷ Most codes to date have adopted the dual porosity approach within deterministic models to describe macropore flow. There is an inconsistency in trying to simulate such a highly stochastic process using a deterministic model, but there are presently few alternatives. Grochulska and Kladvikova²⁴ combined a

two-region model with a transfer-function component and were able to fit the model to transport of bromide and two pesticides through small, intact cores of soil. However, the model was designed for calibration to interpret experimental results rather than for the predictive use that is required for current chemical regulatory systems. It is not clear how one could evaluate probabilistic model output against restricted experimental information such as that presented here.

Table 7 summarises measured and simulated drainflow and losses of sulfosulfuron to drains for the whole experiment. Monthly drainflow was well simulated, with the exception of September and October 2000, when the model over-predicted losses of water to drains. The trend for MACRO to over-estimate concentrations of sulfosulfuron in drainflow extended over the whole experimental period. The total loss of sulfosulfuron to drains was over-estimated by a factor of five for the period to September 2000 when quantifiable residues of sulfosulfuron were observed. There were no measured concentrations of sulfosulfuron above the LOQ ($0.05 \mu\text{g litre}^{-1}$) after the end of September, whereas MACRO simulated a continued low-level presence ($0.06\text{--}0.16 \mu\text{g litre}^{-1}$) through to the end of February 2001.

3.3 Scenario-based assessment of exposure

The model was run for the 20 scenarios (5 soil \times 4 climate classes) assuming annual applications of sulfosulfuron in each of 30 years. Daily concentrations of herbicide in the ditch are shown in Fig 4 for one of the most vulnerable scenarios (Denchworth clay soil in the wet climatic region). The pattern of concentrations was again indicative of macropore flow with a transient pulse of the chemical predicted to move to surface water in the first significant drainflow event after application. Residues in drainflow were then predicted to be much smaller for the remainder of the year. Concentrations and losses of sulfosulfuron were largest where drainflow was initiated soon after application in spring.

Table 8 provides comparative data on predictions for transport of sulfosulfuron to drains for the 20 scenarios. Losses and concentrations of the herbicide were greatest for the two clay soils (Denchworth and Hanslope) where macropore flow pathways can be expected to provide direct hydraulic connectivity between the soil surface and the secondary drainage system (mole channels).^{4,5} The Hanslope soil was the more vulnerable to leaching of this acidic compound because of the combination of high clay content and high pH. Losses and concentrations of sulfosulfuron generally increased the wetter the climate, as wetter conditions maximise the potential for drainflow soon after application. However, losses were generally slightly greater for the dry than for the medium climate scenario. This was attributed to the assumption that sulfosulfuron was applied somewhat earlier in the dry region because of more favourable ground conditions

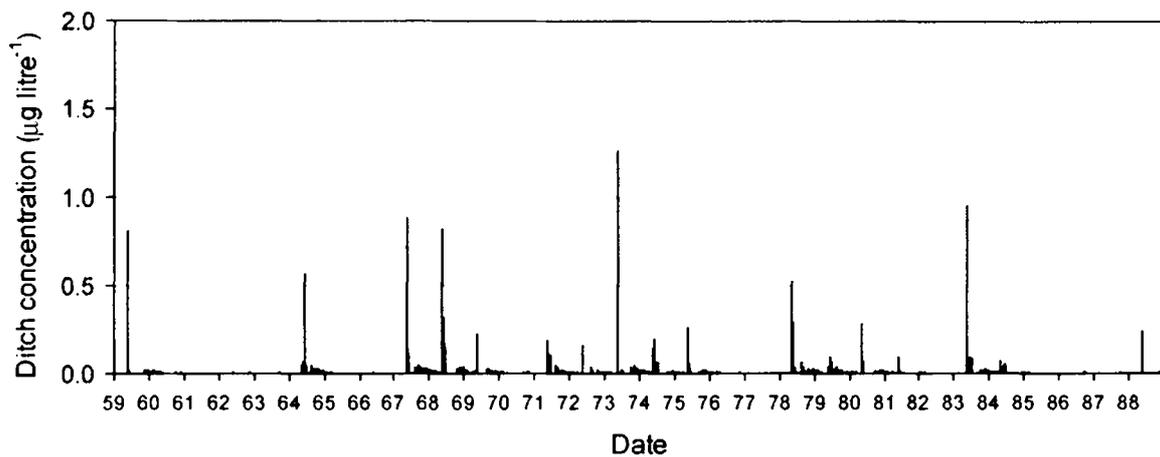


Figure 4. Predicted concentrations of sulfosulfuron in the receiving ditch following application to the Denchworth clay soil in the wet climatic zone.

in spring. Also, there were a number of years in the dry weather file with unusually wet conditions soon after application which resulted in large losses of the compound to drains.

The results presented in Table 8 do not provide any information about the relative likelihood of a particular outcome occurring. To quantify this, results must be weighted according to the relative abundance of the various scenarios within the landscape. A cumulative distribution chart was constructed using the maximum daily concentration in the water phase of the ditch for each simulation year (Fig 5). The chart shows the probability that the maximum daily concentration in a given year C is below a particular reference concentration, C_x . The chart gives a weighted distribution for the scenarios considered in the modelling. Taking the standard laboratory EC_{50} value for *Lemna gibba* as the measure of ecotoxicity, the probability that the maximum annual concentration will exceed $0.1 \mu\text{g litre}^{-1}$ (ie toxicity:exposure ratio <10) is 6.6%. The probability that the maximum annual concentration will exceed $1.0 \mu\text{g litre}^{-1}$ (ie toxicity:exposure ratio <1) is 0.5%. Davies *et al*¹² have reported that three higher aquatic plants tolerated exposure to sulfosulfuron at initial concentrations up to $3.33 \mu\text{g litre}^{-1}$ for up to 21 days. This tolerated concentration is the same as the maximum daily concentration predicted by MACRO for any scenario ($3.37 \mu\text{g litre}^{-1}$; Table 8).

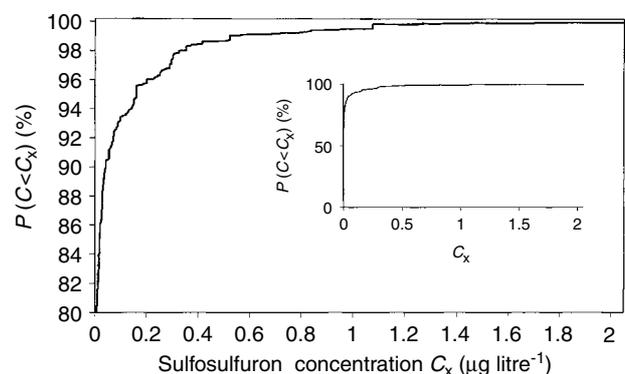


Figure 5. Cumulative distribution chart for concentrations of sulfosulfuron in the ditch. The y axis displays the probability that the maximum daily concentration in a given year C is below the reference concentration C_x . Inset shows the full distribution curve.

Finally, it is interesting to position results from the field study within the context of the broader prediction of sulfosulfuron behaviour from scenario-based modelling. Flow-weighted averages of measured residues of sulfosulfuron in samples taken over each day were calculated to derive the maximum daily concentration in raw drainflow from the field study. Concentration of sulfosulfuron was measured in samples taken every 4 h during drainage events; for the purposes of flow-weighting, that concentration was assumed to be constant for the 4 h following sample collection. The maximum daily concentration

Table 8. Summary results for scenario-based modelling of the transport of sulfosulfuron to drains (30-year simulation for each soil-climate combination)

Soil series	Average annual loss to drains (% of applied)				Maximum daily concentration in the receiving ditch ($\mu\text{g litre}^{-1}$)			
	Dry climate	Medium climate	Wet climate	Very wet climate	Dry climate	Medium climate	Wet climate	Very wet climate
Denchworth	0.21	0.08	0.73	1.20	0.84	0.26	1.27	2.14
Hanslope	0.34	0.24	1.74	2.66	1.07	0.42	1.99	3.37
Brockhurst	0.04	0.03	0.19	0.41	0.07	0.05	0.17	0.31
Clifton	0.01	0.01	0.09	0.22	0.01	0.01	0.10	0.14
Quorndon	0.01	<0.005	0.01	0.09	0.01	<0.005	<0.005	0.01

of sulfosulfuron in drainflow was calculated as $0.98 \mu\text{g litre}^{-1}$. To compare field results with the cumulative distribution chart for predicted behaviour (Fig 5), daily concentrations in field drainflow were diluted into an idealised receiving ditch as for the extrapolation exercise described above. The maximum daily concentration calculated for a ditch adjacent to the field site was $0.59 \mu\text{g litre}^{-1}$. This compares with a maximum value measured at any time during the experiment of $0.06 \mu\text{g litre}^{-1}$ and underlines the conservatism of the calculation of dilution in the ditch for the situation we studied. The calculated concentration of $0.59 \mu\text{g litre}^{-1}$ lies on the 99.1 percentile of Fig 5. Although the field site was not in a region with a very wet climate, an unusually large amount of rain was received very soon after application. In addition, the soil studied was particularly vulnerable to leaching of sulfosulfuron, as it combined a high pH with high clay content and strong soil structure.

4 DISCUSSION

There are established procedures in the EU for screening-level estimates of pesticide exposure for surface waters⁹ and these have been strengthened by the introduction of the FOCUS surface water scenarios.¹¹ However, there is no consensus on the approach to be adopted when a screening-level assessment indicates a potential for an impact on non-target organisms. The approach presented here combined measurement of concentrations of a herbicide in drainflow leaving a treated field with scenario-based modelling to assess the wider implications. Modelling scenarios were selected as representative of the issue at hand. A deterministic model was used to simulate pesticide exposure for combinations of soil type and climate. The model was able to simulate the broad behaviour of sulfosulfuron in the most vulnerable soil type. However, the fine detail of field results could not be matched exactly without more extensive calibration. Output was weighted according to scenario abundance to estimate the likelihood of exceeding a threshold concentration within the broader landscape. It would clearly be impractical to measure pesticide fate for the range of conditions considered here, and the limitations of using an imperfect model to extrapolate field behaviour need to be considered alongside the breadth of the assessment that the approach allows.

The environment into which pesticides are released is inherently variable both spatially and temporally, and techniques based on probabilistic modelling²⁵ and/or landscape analysis²⁶ have been proposed to express the variability within detailed exposure assessments. The modelling approach presented here is relatively simple and has low data and time requirements compared to more sophisticated approaches. Although the approach moves forward from a simple worst-case assessment to cover a realistic

range of conditions under which the herbicide is used, a number of worst-case assumptions are retained and provide an additional element of environmental protection. Most notably, simulated dilution of drainflow concentrations within the receiving ditch (almost always less than a factor of two) was conservative relative to that likely in the field. Recent research has demonstrated the importance of dissipation processes within surface waters following an input of pesticide,^{27,28} but many of the relevant processes are routinely ignored within assessments to support pesticide registration.

The main shortcoming of the approach is that it ignores much of the uncertainty associated with the modelling process. Uncertainties arise, for example, from spatial and temporal variability in the environment, from error associated with sampling and experimental measurement, from the selection of input parameters and definition of exposure scenarios, from subjectivity introduced by the modeller and from error associated with process descriptions within the model.²⁹ The uncertainty arising from variability may be addressed using probabilistic methods in combination with deterministic models.²⁵ A more robust solution will be the development and adoption of true stochastic models such as those based on the transfer function approach.^{24,30}

Model error has been defined as the failure of the model to represent reality accurately even when the input data are provided without error²⁹ and this can be a major source of uncertainty within any modelling exercise. Here, field data were generated for the chemical and one of the soils under consideration to allow a specific evaluation of model performance. Calibration of the model during the evaluation was restricted to those parameters considered essential to give a meaningful test of predictive accuracy for concentration of pesticide in drainflow. These were soil moisture contents immediately prior to application (as no pre-run of weather data was available), the use of a rate of dissipation from soil generated within the field study, and a calibrated simulation of interception by crop surfaces and subsequent wash-off. The evaluation of model performance was for concentrations of sulfosulfuron in drainflow leaving the site and optimisation of residues in topsoil over time was considered acceptable. The evaluation indicated the ability of the model to simulate behaviour in the most vulnerable soil type, but nothing can be deduced about performance for the other soils. In general, simulation of pesticide transport has proved easier for loamy soils than for heavy clays.¹⁷ A much larger evaluation dataset would ideally be required to support the scenario-based modelling.

The implication of the various approximations and uncertainties inherent in the approach we took is that the distribution of exposure concentrations presented in Fig 5 is itself uncertain. It is currently impractical to try to characterise all of the uncertainty because, for example, methods to incorporate model error are

lacking and there are insufficient experimental data to estimate many of the sources of uncertainty. A key question for regulation then becomes whether or not the predicted distribution for exposure is conservative. We believe this to be the case, primarily because of the conservatism introduced in the estimation of dilution within the ditch. As a result of the uncertainty, the risk assessment generated by comparing exposure with a measure of ecotoxicity does not give an absolute indication of risk. However, European regulation for pesticides is currently based on the application of uncertainty factors which are considered to address the uncertainty. By generating a distribution of estimates for one half of the ratio, the second question raised becomes at what level of probability should adherence to acceptable thresholds apply. This is a political rather than a scientific question. Probability levels of 90 or 95% have been proposed for the selection of environmental scenarios on which to base ecological risk assessment.^{9–11} Given that the distribution of risk is thought to be conservative and has an additional safety factor of either 10 or 100 according to the organism being protected, evaluation of toxicity–exposure ratios at one of these points in the distribution may be a pragmatic, if arbitrary, solution to the problem.

Although the method described here breaks the landscape down into representative scenarios, it takes no account of the intensity of occurrence of a particular scenario at a local scale. This could be overcome through the use of GIS technology to replace the national scenario statistics used here. True landscape analysis for pesticide risk assessment is in its infancy, but several exercises have now been reported.^{26,31} Maps of risk can be illustrated alongside the kind of cumulative distribution chart presented in this paper. The addition of a simple contagion matrix to quantify the amount of clumping and fragmentation of patches on a landscape³² could help to establish the extent to which the most vulnerable scenarios are concentrated within discrete locations.

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