Uncertainty and sensitivity analysis of the HardSPEC environmental exposure model for pesticide regulatory assessments

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Sensitivity and uncertainty analysis of the HardSPEC model

HardSPEC is a realistic but worst-case environmental exposure model used by HSE in regulatory risk assessment of pesticides. It predicts concentrations of pesticides in surface and groundwater following pesticide use for weed control on areas like pavements and roads. The concentrations predicted by the model are used to help determine whether the risk posed by the pesticide use is acceptable.

The model is important in decisions on the authorisation of some pesticide uses. Applicants for pesticide uses sometimes ask HSE to consider a change to the properties of the substance or a change in the model, so the assessment is more appropriate for the use scenarios. HSE wanted to explore how sensitive the model is to changes in the assumptions used in the model. HSE also wanted to understand the uncertainties associated with such changes. In addition, HSE wanted to write the model into a different computer language to enable future development of a more easily maintained model.

The project found that HardSPEC output was most sensitive to substance properties and usage details. Output was also sensitive to a number of parameters built into the standard exposure scenarios within the model. This will help HSE understand the significance of changes requested by applicants.

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Key Messages

HardSPEC is an environmental fate model that predicts concentrations of pesticides in surface and groundwater following application on hard surfaces, such as roads, pavements and railway tracks, and a subsequent series of rainfall events; such pesticide use is typically of herbicides used for weed control. HardSPEC is used by HSE to assess the risk of, and take decisions related to, herbicide application. The model contains over a hundred parameters that relate to herbicide properties, herbicide application, and the environment of four application scenarios. While HardSPEC predictions are consistent with measurements in available monitoring data, HSE would like to measure the sensitivity of the model, i.e. how much the predicted concentrations vary when the values of specific parameters are changed, to understand the effect of potential changes to the model and help assess the model validity. Such sensitivity analysis typically involves making thousands of predictions using different parameter values. However, the model is implemented in a spreadsheet that only allows manual changes to the values of a small set of parameters, making sensitivity analysis impractical.

In this project we implemented the model in Matlab, a scientific programming language, and verified that the results precisely matched the results from the spreadsheet implementation. We developed a sensitivity analysis framework that varies the values of any of the parameters automatically and records the predicted concentrations.

The code implementation and verification led to a number of changes to the model, although the effect on predicted peak concentrations was minimal. The sensitivity analysis found that across the application scenarios, peak concentration in surface water was most sensitive to

- Application rate and the fraction of areas treated
- Herbicide solubility
- The substance partition coefficient for concrete, Kp
- The soil-water partition co-efficient normalised for soil organic carbon content, Koc

The sensitivity framework also allows the volume of the first rainfall event to be varied. The effect on peak concentration was found to depend on both herbicide and scenario.

The sensitivity framework and analysis allow HSE to assess potential changes to the model formulation, changes to values of herbicide properties, changes to application scenarios, and changes to the rainfall sequence. Implementation of the model in a programming language enables future development of a more easily maintained model.

Executive Summary

Background

HardSPEC is a generic tier one exposure model, originally developed at Cranfield University, for estimating surface water and groundwater exposure resulting from herbicides applied to hard surfaces such as roads, pavements and railway tracks. Any regulatory submission for authorisation of a Plant Protection Product (PPP) use on hard surfaces is assessed using HardSPEC. The model provides estimates of herbicide substance concentrations in surface water sources following application of the herbicide and a sequence of rainfall events over a 73-day period for four different use scenarios: urban, major road, railway and domestic (home & garden). The model additionally provides predictions of the concentration of the herbicide in groundwater (arising from use on railways) at a well head over a 1500-day period for three aquifer types: chalk, limestone, and sandstone.

HardSPEC has ten primary input parameters, which relate to the specific physical and chemical properties of the substance, and are based on measurements from the pesticide’s dossier. The model also contains an additional 33 calibrated parameters (relating to coded relationships within the HardSPEC model), 90 fixed scenario-specific parameters and 40 task-based parameters that relate to the use of the herbicide under particular circumstances. Default values for these latter 40 parameters are available in the model although these can in principle be modified by a user. The model is currently implemented in an MS Excel workbook which can be downloaded from the HSE website: https://www.hse.gov.uk/pesticides/pesticides-registration/data-requirements-handbook/fate/hardspec.htm.

Although available monitoring data indicate that predictions from HardSPEC are consistent with measurements, only limited validation of the model has been undertaken. Through varying the task-based parameters and sequence of rainfall events in the HardSPEC model a range of estimates of chemical concentrations can, in principle, be generated. However, the spreadsheet implementation does not allow automation of parameter variation, so a rigorous study of the variability in HardSPEC predictions has not been previously undertaken.

Aims and objectives

This project aimed to

- Recode the HardSPEC model in a scientific programming language
- Verify the code and improve the spreadsheet implementation
- Conduct sensitivity analysis to identify the parameters that have the greatest impact on predicted pesticide concentration
- Propose opportunities for model refinement

Methods

The HardSPEC model was implemented in Matlab, a scientific programming language, to allow parameter variation to be automated. To verify that the Matlab implementation exactly replicated the spreadsheet implementation, six herbicides and an additional hypothetical substance were used as input to both implementations. The test substances were chosen to cover a large range of herbicide parameter values. Predicted concentrations as well as the values of over ten thousand interim calculations from Matlab were compared to the equivalent values in the spreadsheet. In the verified model, all values agreed to ten significant figures. This phase of work led to a number of model refinements, although the effect on peak concentrations was minimal. The Excel implementation of the updated model has since been made available on the HSE website.

A sensitivity analysis framework for the Matlab implementation was developed, allowing an uncertainty and sensitivity analysis of the HardSPEC model to be undertaken, in conjunction with the original model developers, to identify areas of the HardSPEC model where further refinements might lead to a more precise estimation of chemical concentrations.

Results

The sensitivity analysis indicated that across the urban, domestic and road application scenarios, the largest main effects on peak concentration in surface water were due to

- Application rate and the fraction of areas treated
- Herbicide solubility
- The substance partition coefficient for concrete, Kp

and in the railway scenario the largest main effects were due to

- The soil-water partition coefficient normalised for soil organic carbon content, Koc
- Application rate

For the contribution from application day spray drift, the largest main effect in the urban, domestic and road application scenarios was application rate, whereas for the railway scenario it was the distance from the railway cess (i.e. the area between the track and the edge of the embankment) to the water body.

The findings reflect the large ranges of application rate and herbicide property values needed to cover the test substances that the model was verified on. Focussing on a narrower range of values, consistent with a single class of pesticide, may, in the future, allow more precise investigation of the sensitivity to exposure scenario parameters.

The effect of the volume of the first rainfall event on peak concentration depended on both herbicide and scenario.

Conclusions

The development work undertaken in this project has led to a number of improvements to the HardSPEC model that have been made to the Excel implementation, available to download from the HSE website for use by stakeholders. The code implementation enables future development and maintenance of the model, and allows exploration of sensitivity of the model predictions to changes in parameter values.

Contents

1 Introduction

1.1 Background

Herbicides are commonly used for weed control on non-agricultural surfaces such as footpaths, road edges and railway track beds. In contrast to the fate of pesticides applied in the soil-based agricultural environment, there is little information on the dissipation and re-distribution of herbicides used in ‘hard surface’ environments and any associated contamination of receiving waters. Prior to 2004, in the absence of such information, the UK Pesticides Safety Directorate (now known as the Chemicals Regulation Directorate (CRD)) used a crude exposure assessment that assumed all of the herbicide applied on hard surfaces ‘not intended to bear vegetation’ was lost to surface waters in a volume equivalent to 25mm of rainfall.

To redress the paucity of information about the transfer of herbicides from hard surfaces to water a programme of experimental research was conducted between 1997 and 2004 to investigate and model the losses of herbicides from a variety of relevant man-made surfaces. The ultimate objective of this research programme was to develop a conceptual (mathematical) model that could provide estimates of herbicide concentrations in various water-bodies following the application of herbicides to hard surfaces and subsequent rainfall events. The first-tier model for estimating surface- and ground-water exposure that resulted from this research is described in Hollis et al. (2004). The model itself was implemented in an Excel-based program known as HardSPEC. An update of the technical guidance, which accompanied version 1.4.3.2 of the HardSPEC model, has been published (Hollis et al., 2017).

The HardSPEC model has three basic uses: assessing surface water and (for use of herbicides on railways) groundwater contamination from ‘typical’ professional use on hard surfaces; use on hard surfaces by amateurs (in a domestic setting); exclusive use on railways. Herbicides are applied to hard surfaces in urban, suburban and rural locations but the amounts of herbicide applied and methods of application will differ depending on the application scenario and the surface types involved (Hollis et al., 2017). The model is therefore built around six exposure scenarios, which cover a range of circumstances under which herbicide may be applied. Each exposure scenario is designed to represent reasonable worst case conditions under which herbicide may be applied in a particular situation. The exposure scenarios are briefly described below:

> Major Road Stream. A surface water stream receiving surface drainage from a major road in a rural setting where the hard surface areas drain via gully pots. The stream also receives drainage from an adjacent 1ha agricultural field.
> Urban Stream. A surface water stream receiving surface drainage from an urban catchment within which the hard surface areas drain via gully pots.

Urban Pond. A pond receiving surface drainage waters from an urban catchment within which the hard surface areas drain via gully pots. This scenario is intended to represent the use of collecting ponds within Sustainable Urban Drainage Systems (SUDS).

Railway Groundwater. The abstraction point of a local groundwater body that receives herbicide leached from a double railway track which crosses the groundwater catchment.

Railway Ditch. A ditch adjacent to a railway embankment receiving water which has leached through railway ballast.

Suburban (domestic use) Stream. A surface water stream receiving surface drainage from a suburban catchment within which herbicides are applied to some hard surface areas on domestic properties.

Further technical detail on scenarios and the underpinning assumptions are described in Hollis et al. (2017). The guidance document, supporting experimental studies which underpin the model and the software are available from the HSE website https://www.hse.gov.uk/pesticides/pesticides-registration/data-requirements-handbook/fate/hardspec.htm

As input the HardSPEC model takes ten primary input parameters which relate to the specific chemical. For most of these parameters the model input is based on measurements documented in the pesticide's dossier and the proposed application details. However, two parameters are not routinely presented within the dossier: these can be calculated from available properties of the pesticide or derived from experimental wash-off studies using a calibration module of HardSPEC. The HardSPEC model also contains an additional 33 calibrated parameters (relating to coded relationships with the HardSPEC model), 90 fixed scenario-specific parameters and 40 task-based parameters that relate to the use of the herbicide under particular circumstances. Default values for these latter 40 parameters are available in the model although these can in principle be modified by a user – such changes would, however, require a solid evidence base.

Based upon user input (and default values for other model parameters), the model subsequently calculates estimates of chemical concentrations in surface water sources following application of the herbicide and a sequence of rainfall events over a 73 day period for the different application scenarios described above. The model additionally calculates predictions of the concentration of the herbicide in groundwater (arising from use on railways) at a well head over a 1500 day period for three aquifer types (chalk, limestone and sandstone). Predictions are returned for acute predicted environmental concentrations (PECs) of the chemical in surface water (water phase (μg L^{-1}) and sediment phase (μg kg^{-1})) for urban stream, urban pond, major road stream, domestic stream, railway ditch leaching and railway ditch run-off scenarios. For all except the domestic stream, PEC resulting from application day spray drift is also returned. Furthermore, concentrations in groundwater are estimated for the railway over groundwater scenario for chalk, limestone and sandstone aquifers.

Example HardSPEC output under the default ‘Atrazine’ scenario that is pre-coded in the HardSPEC download is shown in Table 1 and Table 2.

Table 1: Example HardSPEC spreadsheet output for surface water bodies corresponding to the default herbicide properties (corresponding to ‘atrazine’)

	Acute (24 hrs) concentration		Application day PECsw from spray drift (mg L^{-1})
Application scenario	Water phase (µg L^{-1})	Sediment phase (µg kg^{-1})	
Urban stream	326.69	326.455	27.52
Urban pond	30.052	34.776	0.173
Major road stream	173.713	173.713	19.549
Domestic stream	87.029	87.029	0
Railway ditch leaching	15.67	15.67	7.881
Railway ditch runoff	45.068	45.068	7.881

Table 2: Example HardSPEC spreadsheet output for railway over groundwater application using the default herbicide properties (corresponding to ‘atrazine’)

Average annual concentration at the base of the railway formation (mg L^{-1})	9.7

Exposure at the abstraction well-head	Chalk	Limestone	Sandstone
Maximum concentration in well (µg L^{-1})	5.7843	1.6616	1.6706
Period when plume > 0.1 µg L^{-1} in well (days)	119	97	97

Calculations associated with the model outputs demonstrated in Table 1 and Table 2 are made over several thousand cells within multiple linked Excel worksheets.

Whilst the current version of HardSPEC has to date satisfied regulatory requirements and has proved popular with users of the model the current Excel implementation has a number of short-comings:

- Calculations are not transparent. Within the model, calculations are based upon cell references within spreadsheets and these cannot be easily linked to equations within the guidance document. Changes to the model require developer expertise, therefore HSE lack the in-house expertise to maintain the HardSPEC model.
- Coding errors are easily made and difficult to identify since a model built in Excel does not lend itself to conventional software testing programme. Formulae have to be checked on a cell-by-cell basis. Each release of HardSPEC has identified and fixed a small number of coding errors and whilst model outputs are judged to be fairly insensitive to any remaining errors following release version 1.4.3.2 of HardSPEC, an error free version of the model is desirable.
- The model cannot be easily modified. A task such as varying the rainfall sequence would be a major effort and prone to further coding errors.
- The Excel implementation of HardSPEC does not lend itself to batch processing operations. Modern techniques for uncertainty and sensitivity analysis require

thousands of parameter sets to be run through a model in order to thoroughly test the performance of the model. Whilst available monitoring data indicates that predictions from HardSPEC are consistent with measurements (Hollis et al*.,* 2004), a more rigorous testing of the mathematical model is clearly desirable to identify its sensitivity and uncertainty to parameter variation.

A new version of the HardSPEC model developed in collaboration with the original authors of the model and implemented in a modern programming language is therefore required. Whilst the ultimate aim of the project is to develop an updated version 2.0 of the HardSPEC model with a similar look and feel and some enhanced capabilities, the aims of the current phase of the project described in this report were twofold:

1. Development of a transparently coded error free HardSPEC code which would form the bedrock of a new software application. In the interim a final certified error free version of the Excel implementation would result from this phase of work.
2. Identify suitable (lower and upper) limits for varying parameters in the HardSPEC model and conduct uncertainty and sensitivity analyses of the model, based upon these limits. This would facilitate a more rigorous testing of the underpinning mathematical model, provide new insights into the model and its key interdependencies between parameters, and identify areas where research into future model refinement might be directed.

2 Methods

2.1 Recoding of HardSPEC

2.1.1 Choice of software programming language

Several programming languages are commonly used for scientific computational modelling, including Python, R and Matlab. These languages are well-suited to rapid code development on small to medium sized projects: they do not require time-consuming compilation and they have integrated development environments that include debugging functionality and allow easy examination and visualization of data. While any of these languages would be well suited to implement HardSPEC, Matlab was chosen on the basis of maintainability and in-house coding expertise. Matlab is commercially supported, ensuring ongoing maintenance and reliability.

Use of the Matlab software development environment requires payment of a licence fee. However, Matlab code and executable software generated from the code can be freely distributed, allowing the Matlab implementation of HardSPEC to be run without payment of a licence fee, but limiting development of the code to individuals or organizations that hold a Matlab licence. For future flexibility regarding distribution and development of the HardSPEC model code, coding features were restricted as far as possible to use just those operations and features that are available in most common programming languages (i.e. Matlab libraries which are specific to the software were not utilised). Thus the code was designed to be easily translatable to other programming languages.

2.1.2 Software design and maintainability

We used consistent code formatting to make the code easier to maintain. For example, camel-case formatting was used for variable names (e.g. `SpecificGravity`) whereas underscores were used in function names (e.g. `get_rainfall_sequence`) allowing the two to be easily distinguished. Furthermore, variable and function names were made explicit (e.g. the amount of herbicide intercepted by plants was recorded in a variable called `AmountInterceptedByPlants`) allowing equations in the code to be easily interpreted and compared with those in the HardSPEC documentation and other literature. Future developments to the model should thus be easier to implement in the code.

The code was written in a modular design, following the Excel implementation of HardSPEC as closely as possible. Each Excel tab was implemented by one Matlab function (i.e. a file containing a block of code) with the exception of the losses_AR tab, which was encoded in three functions corresponding to sections of the worksheet that perform different calculations (Appendix A, Table A1). These functions are run in sequence from a top-level `hardspec` function. Each function returns the results of its calculations to the main `hardspec` function, which passes the results on to one or more subsequent functions (Appendix A, FigureA1). Within each function the calculations were broken down into smaller sub-functions which perform a series of simple calculations: often these sub-functions correspond to a single row or single column of an Excel tab. The same calculation is typically performed for each material, scenario and rainfall sequence time-step, differing only in the material and scenario parameters. Re-using the sub-functions improves maintainability: an error in the function will affect all outputs, making it more likely to be observed, easy to locate, and, moreover, making it simple to correct with a single edit.

Excel version 1.4.3.2 of HardSPEC contains a number of unlabelled parameters and constants. The origins of these values were located in the documentation (Hollis et al., 2017) to determine their meaning. In the Matlab implementation these constants were replaced by variables (e.g. `LitresPerCubicMetre = 1000`, `NonSolubleLossZPower.Constant.Asphalt = 1.1387`). Thus, the Matlab implementation is more transparent and the values of these constants can be easily changed. The only hardwired value retained in the model is 100, used to convert from percentages to fractions: the parameters being converted include '`Percent`' or '`Pct`' in their name, so the meaning of the constant is apparent.

Some parameters in the model are calculated from the values of other parameters. All dependencies were located by the model authors, and the Matlab implementation was adapted such that only independent parameters were assigned values; all dependent parameters are calculated from the values of their independent precedents (Appendix A, figure A2). As well as improving maintainability (by removing the need to manually update the values of dependent variables and check their consistency with regard to the values of independent variables), this separation of parameter value assignment and calculation was needed to build a software framework for the uncertainty and sensitivity analyses. The HardSPEC code was run repeatedly from a wrapper function, `sensitivity_run`, which overwrites the default values of specified independent variables, passes the independent variables to the `hardspec` function , and subsequently receives and saves the model outputs (Appendix A, Figure A3).

2.1.3 Verification

To verify the code implementation of HardSPEC, the results of the Matlab calculations corresponding to all the cells in the Excel implementation tabs 'mass lost per 0.5mm rain', 'losses_AR', 'Groundwater model' and 'Railway_surface_water' (with the exception of cells that are not used in subsequent calculations) were written to spreadsheets in corresponding cell locations. For each cell the Matlab output was subtracted from the Excel output, and the numerical precision needed to represent the difference was calculated, e.g. if outputs were identical to the 13th decimal place but differed at the 14th decimal place the precision needed is 14. Excel and Matlab comply to the IEEE 754 floating-point standard, with precision of variables limited to 15 significant figures, although calculations may result in lower precision due to rounding error and truncation. To allow for this, the code implementation was accepted if the maximum difference was at the 11th significant figure. The verification procedure was conducted seven times using herbicide parameters for atrazine, diuron, glyphosate, isoxaben, oryzalin, oxadiazon and a hypothetical herbicide with parameter values suggested by the model authors.

The cell-by-cell comparison allowed any significant difference in the final output (e.g. maximum concentration in sediment in the major road scenario) of the two implementations to be traced to the first calculation that differed by more than machine precision. Furthermore, intermediate calculations which differed, but did not affect the final output (e.g. they only affected concentrations at times after the maximum concentration was reached) could easily be located and investigated. Errors in either the Excel or Matlab implementation were rectified and the verification spreadsheets were recalculated iteratively until the differences were below the acceptance threshold of 11 significant figures.

2.2 Sensitivity analysis

2.2.1 Theoretical background

HardSPEC is an example of a deterministic computer model, where the term *computer model* describes a mathematical model implemented within a computer code. The model is deterministic since if it is run repeatedly for the same set of inputs, the results from each calculation are identical (this contrasts with a stochastic model where a code returns different outputs resulting from repeated runs of the model). Whilst HardSPEC does not require numerical methods to solve the equations, due to the many parameters required to define scenarios and the discontinuities in a number of the equations, the model is, nevertheless, non-transparent in its behaviour.

For mathematical models where the outputs can be expressed as simple functions of their parameters/inputs, and the model takes only a small vector of inputs, it is a trivial process to study how model outputs change in response to perturbations to the model inputs. In contrast, it is a non-trivial process to study the behaviour of a *computer model.* Specific tools have therefore been developed to aid the efficient study of the dependency of the model outputs from computer models on model inputs (Iooss and Saltelli, 2017).

Uncertainty analysis is the study of the variability in the output(s) from deterministic computer models that result as a consequence of uncertainty in model inputs. Global sensitivity analysis goes a step further in ascribing the variation in model outputs to individual parameters or interactions between parameters. Uncertainty analysis and sensitivity analysis require different computational tools as described in 2.2.4 and 2.2.5.

2.2.2 Computational framework

A process known as decoupling was adopted to facilitate the batch running of the HardSPEC model in Matlab (MATLAB, 2014a) and the subsequent post-processing of model output using R (R Core Team, 2014). This process involved initially generating a design matrix, using functions in the R Sensitivity package (Pujol and Iooss, 2015). Each row of the matrix is a *design point,* comprising a set of HardSPEC model parameter values that will be used when running the model. Each column of the design gives the full set of values for a single model parameter within the design.

In the second phase the design matrix was read into Matlab. For each row of the design matrix in turn, the default values of model parameters corresponding to the columns of the design matrix were over-written by the design point, and the HardSPEC model was executed. For each scenario studied, the PEC calculated by the HardSPEC model was recorded, generating a vector of HardSPEC output of the same length as the design. These model outputs were subsequently written to .csv files and analysed within R using functions in the R Sensitivity package (Pujol and Iooss, 2015). Further detail is given in sections 2.2.4 and 2.2.5.

2.2.3 Parameters

The HardSPEC model takes ten primary input parameters. A further 145 independent parameters within the model were identified for further study. In some cases these independent parameters did not directly correspond to HardSPEC model parameters. For these cases, hyper-parameters (for which sensitivity ranges could be more easily specified) were defined, and HardSPEC parameters were subsequently derived from these hyper-parameters.

Suitable ranges for all parameters under study were determined by the model developers. The reason for the choice of range and origin of the default value were recorded. Table B1 in Appendix B gives this information for the herbicide parameters, and a spreadsheet giving the corresponding information for all the independent parameters of the model can be downloaded from the HSE website https://www.hse.gov.uk/pesticides/pesticides-registration/data-requirements-handbook/fate/parameter_details.htm

Based upon specified limits probability distributions were ascribed to parameters. Uniform distributions were assumed for all parameters except those with a range in excess of three orders of magnitude (i.e. an upper limit in excess of 1000). For the subset of parameters with a very large range (Kp asphalt, Soil Koc, Solubility and Application rate) log-uniform distributions were instead assumed – under this distribution sampling is disproportionately focussed on the lower end of the parameter range.

The generation of design points, described in section 2.2.2, was based upon the limits and subsequently assumed probability distributions described above.

2.2.4 Uncertainty analysis

Uncertainty analysis was performed in order to assess the qualitative behaviour of the HardSPEC model in response to changes in parameters. A 2000 point maxi-min Latin Hypercube Design (LHD) was generated using the DiceDesign package in R and the HardSPEC model was run at each design point. The predictions of pesticide concentrations over time (days after application) for the 2000 model runs (i.e. one run per design point) were studied for each of the model outputs of interest. The relatively simple technique employed in this work was devised to efficiently study the qualitative behaviour of the model over the specified parameter ranges and was principally employed to check that unusual concentration-time predictions were not generated: i.e. as a test of the robustness of the model in response to changes in parameters.

2.2.5 Sensitivity analysis

A one-at-a-time (OAT) sensitivity analysis was initially undertaken with only the 10 herbicide (primary user input) parameters studied. In this analysis a three step process was implemented: 1) set herbicide parameters to those of a test substance; 2) vary one parameter over its range while keeping others at their baseline values, recording responses (PEC values for each use scenario); 3) reset the parameter to baseline and repeat step 2) for each parameter in turn. The process outlined above was conducted with baseline parameters corresponding to the test substances of atrazine, diuron, glyphosate, isoxaben, oryzalin, oxadiazon, and a hypothetical herbicide. Table 3 gives the range and distribution of parameters used in the OAT analysis.

Table 3. Parameter ranges used in OAT analysis.

Parameter	Lower	Upper	Distribution
% of applied herbicide impacting on the surface water body as spray drift in Urban & Major Road scenarios	0	10	linear
% of domestic households spot spraying hard surfaces in the 'worst case' scenario	1	50	linear
Measured Kp asphalt (mg/m^2)	1	5000	log
Measured Kp concrete (mg/m^2)	1	55	linear
Soil Koc (mL/g)	1	10000	log
Solubility (mg/L)	0.1	100000	log
Specific Gravity	0.1	2.5	linear
DT50 in soil (days)	1	500	linear
DT50 on hard surfaces (days)	1	500	linear
DT50 in sediment (days)	1	500	linear
DT50 in water (days)	1	500	linear
Application rate (g/ha)	10	5000	log
Fraction of 774.7 m^2 railway track target area actually sprayed	0.2	1	linear
Run-off attenuation factor applied to leached load from ballast	0.2	1	linear
Railway scenario hand-held sprayer % of applied amount impacting as spray drift	0	10	linear
Fraction of 100m^2 target area spot sprayed	0.2	1	linear

Whilst the OAT analysis is simplistic, the results can be analysed using simple graphical techniques and allow the behaviour of the model around realistic parameter settings to be investigated; in particular unintended features of the model may be identified. Results are sensitive to the baseline values assumed for parameters and furthermore, interactions cannot be studied through the OAT for any one test substance. However, by repeating the analysis with the baseline values centred on different herbicides, a first impression of the overall behaviour of the model and the importance of interactions between parameters may be established.

Sensitivity analysis of the entire set of HardSPEC parameters was implemented using a more formal framework: following the OAT analysis the ranges of the log-distributed parameters in Table 3 were reduced to the ranges given in Appendix B Table B1. Due to the large number of parameters the two-stage analysis proposed by Campalongo et al. (1999) was implemented. In the first phase a screening approach using elementary effects, commonly known as the Morris Test (Morris, 1991), was applied. The Morris test is a compromise between depth of information provided by the analysis and computational efficiency – it required less than 1000 runs of the model in total. The Morris Test computes two measures for each parameter, μ^*, which is a measure of the average effect of a parameter on model output and σ, which quantifies both the degree of non-linearity of effect and/or degree to which a parameter interacts with other parameters within the model. Through a plot of μ^* against σ a subset of important parameters that should be taken forward to a second phase of analysis can be visualised – in simple terms the parameters with large μ^* and σ relative to other parameters are those within the greatest influence on model output. For each model output under study, those parameters with μ^* in excess of 5% of the maximum value of μ^* were taken forward to the second phase.

The second phase of sensitivity analysis was undertaken using a variance–based sensitivity analysis for the subset of retained parameters following the screening approach. Variance-based methods (Chan et al., 2000; Prieur and Tarantola ,2017) aim to quantify the proportion of variance[1] that may be ascribed to particular parameters or interactions between parameters. The variance-based analysis computes two measures per parameter, the *main effect* and the *total effect* sensitivity indices. The main effect sensitivity index is the proportion of variance that can be accounted for by a particular parameter. The total effect sensitivity index is the proportion of variance accounted for by an individual parameter *and* interactions between it and all other parameters. The total effect sensitivity index does not quantify the effect of individual interactions between pairs of parameters; however results from sensitivity analysis in conjunction with expert knowledge of the HardSPEC model (i.e. knowledge of developers) may provide insights into specific interactions.

Various methods are available for computing main and total effects (Campalogo and Saltelli, 1997; Chan et al., 2000; Saltelli et al., 1999; Prieur and Tarantola, 2017). The extended Fourier amplitude sensitivity test (eFAST) (Saltelli et al. 1999) was initially applied due to its computational efficiency relative to other methods; however the method proved to be unreliable due to the discontinuities within the model. The method of Owen

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[1] Variance is a single number summary of the overall variability in a particular model output, which occurs as a consequence of varying model inputs over the ranges specified by their respective probability distributions. In simple terms larger variance indicates that a model output changes substantially dependent upon changes to inputs.

(2013) was ultimately applied due to its ability to calculate confidence intervals for main and total effects and the accuracy of the method in quantifying small main/total effects.

Between 9 and 17 parameters were studied for the different outputs, with the differences resulting from the screening analysis applied in the first phase. In this analysis 30,000 runs of the model per varying parameter were used (requiring between 270,000 and 510,000 evaluations of the HardSPEC model).

2.3 Rainfall Analysis

The HardSPEC model generates predictions of pesticide concentrations based upon a specific sequence of rainfall events over a 73 day period. The sensitivity of the model to perturbations in this sequence has not been previously investigated – this would have been a major task requiring significant modifications to the Excel implementation of HardSPEC. In comparison, the vectorised calculations in the Matlab version allow changes to the rainfall sequence to be easily implemented.

The sensitivity analysis framework was adapted to allow the hardspec code to be run repeatedly using a different rainfall sequence for each run of the model. While there are innumerable possible rainfall sequences, the theory underpinning the HardSPEC model suggest that the amount of rainfall on the first day after herbicide application is likely to be the most influential; the default rain sequence has 5 mm of rain on the first day after application. Hence the default rainfall sequence was used in this study with only the rainfall on the first day varied.

A rainfall of between 0.5 and 20 mm was considered (in steps of 0.5 mm). The acute concentration in water and sediment was recorded for the six surface water scenarios using the six test substances, with all other parameters taking default values.

2.4 Distance from railway cess to water body

The distance from the cess[2] to the water body in the railway leaching and railway runoff exposure scenarios affects the distance from each section of the sprayed railway area to the water body. This distance is an important factor in the calculations of pesticide entry into the water body via spray drift. The default value in the model is for a distance of 2.9 m and represents a reasonable worst case estimate. However, this distance may differ substantially from the assumed value in the model over different sections of railway. The sensitivity analysis framework was therefore adapted to allow the hardspec code to be run repeatedly using a different distance between the railway cess and ditch for each run. The distance was varied from the default value of 2.9 m up to a maximum of 170 m (in the global sensitivity analysis the range was 2.9 m to 169 m). The acute concentration in water and sediment, and the application day spray drift was recorded for the railway leaching and

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[2] A cess is the area to the side of railway tracks, between the track and the edge of the embankment.

runoff models. The analysis was run for all six test substances but excluded the hypothetical substance.

3 Results

3.1 Recoding

A new implementation of the HardSPEC model was successfully coded in Matlab based upon available documentation and the existing Excel version (1.4.3.2) with the Matlab version developed using the software development conventions described in section 2.1.

During coding a small number of differences between constants/relationships in the HardSPEC documentation and in the Excel implementation were identified, along with a mismatch between the rainfall sequences encoded in different Excel worksheets. The verification procedure highlighted several erroneous cell references and internal inconsistencies, typically when the same calculation should be performed across multiple materials, scenarios, etc. but the Excel spreadsheet included variants of the calculation. For example, in the railway surface water leaching model the variation of groundwater velocity with distance to the water body was only implemented for the first one metre section of track, whereas the Matlab code repeats the calculation over the second to the eighth one metre section.

These differences were addressed over a few software development cycles: the changes were made by the model authors in the Excel implementation (detailed in Hollis *et al*, 2020), and then the Matlab implementation was updated as necessary and verified against the new Excel implementation. The final version of the model implemented in Matlab for the sensitivity analysis corresponds to a development version of the Excel implementation (v 1.5.2-3.1, which has never been released on the HSE website) which contained changes that have been implemented in the more recent releases of HardSPEC. None of the updates had a significant impact on the main outputs of the model: for the test substances the maximum concentration decreased only marginally, and still occurred on the first day after application.

3.2 Sensitivity Analysis

3.2.1 Uncertainty analysis

In each of the six surface water scenarios (urban stream, urban pond, major road, domestic use, railway leaching and railway runoff) concentration-time relationships were studied for the acute concentration of herbicide in the water phase, the acute concentration in the sediment phase and the contribution of application day spray drift. Analysis demonstrated that the behaviour of the concentration-time profiles, corresponding to the 2000 HardSPEC runs, was credible for each of the scenarios, indicating that the underlying model was robust to perturbations in the model parameters. Detailed results on this analysis are not presented.

3.2.2 One-at-a-time analysis

The sensitivity of 18 outputs with respect to the herbicide parameters were analysed using seven sets of baseline parameters, corresponding to the test substances. For each of the six surface water scenarios (urban stream, urban pond, major road, domestic use, railway leaching and railway runoff) the acute concentration of herbicide in the water phase, the acute concentration in the sediment phase and the contribution of application day spray drift were plotted against the standardized value of the parameter being varied (i.e. the value is scaled from zero to unity).

Figure 1 to Figure 4 each show results for water and sediment phases for urban stream, urban pond, domestic and railway leaching scenarios respectively. The baseline parameters corresponding to these plots relate to the test substance atrazine. The five parameters that generated the largest range of output values are indicated in each legend. A comparison of the changes in the various model outputs as each parameter is systematically varied from its minimum to maximum value gives an indication of the relative importance of parameters, subject to the limitations of local sensitivity analysis mentioned earlier (section 2.2.5). As expected, application rate and soil Koc have a strong influence on the model output. Furthermore, the figures indicate the range of values over which abrupt changes take place and the form of the changes. Variation of specific gravity gives discontinuous variation in the predicted acute concentration in both the water and sediment phases, whilst solubility gives a non-monotonic output with discontinuities in the gradient – these changes reflect the coded relationships for the properties in the HardSPEC model which are modelled by different equations over different ranges of specific gravity and solubility respectively, rather than a single (smooth) coded relationship.

Figure 5 shows the model output for the urban stream scenario when oryzalin and isoxaben are the baseline substances. Compared with atrazine, these substances show differences in the absolute concentration, and differences in the relative sensitivity to changes in different parameters. A particularly large change in the concentration can be seen at the midpoint of specific gravity for the analysis based upon oryzalin: the minimum concentration in both water and sediment occurs near to the mid-point of the specific gravity range.

Variation in the concentration due to spray drift on application day depends only on the parameters related to the quantity of herbicide applied that contribute to spray; hence the concentration is independent of the physico-chemical parameters, as indicated by the flat response in Figure 6. Whilst the absolute level depends on scenario specific parameters, these are not varied in OAT analysis. Spray is modelled using the same parameters and relationships in the urban stream, urban pond and major road scenarios. Likewise the railway leaching and railway runoff models use the same parameter and formulation as one another. In the domestic scenario the stream is enclosed in a culvert and hence does not receive any contribution from spray drift.

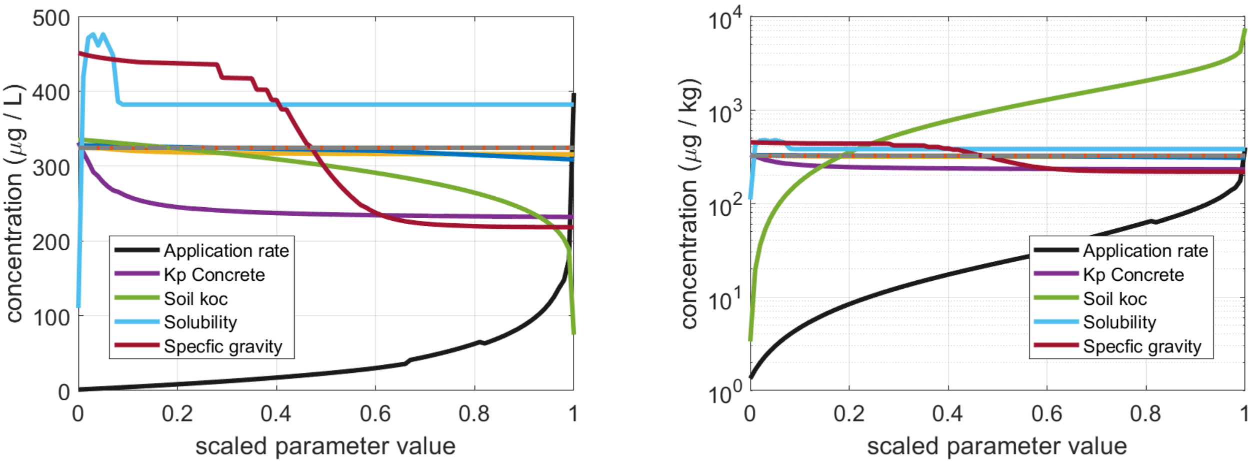

Figure 1 Acute concentration in water (left) and sediment (right) in the urban stream scenario, when atrazine is the baseline substance. Note that concentration in sediment is displayed using a log scale.

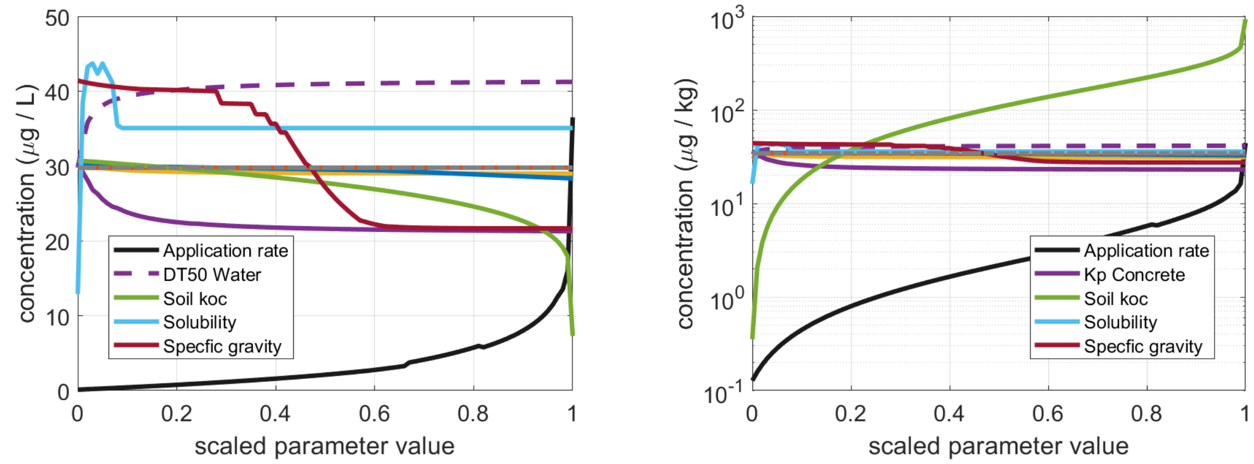

Figure 2 Acute concentration in water (left) and sediment (right) in the urban pond scenario, when atrazine is the baseline substance.

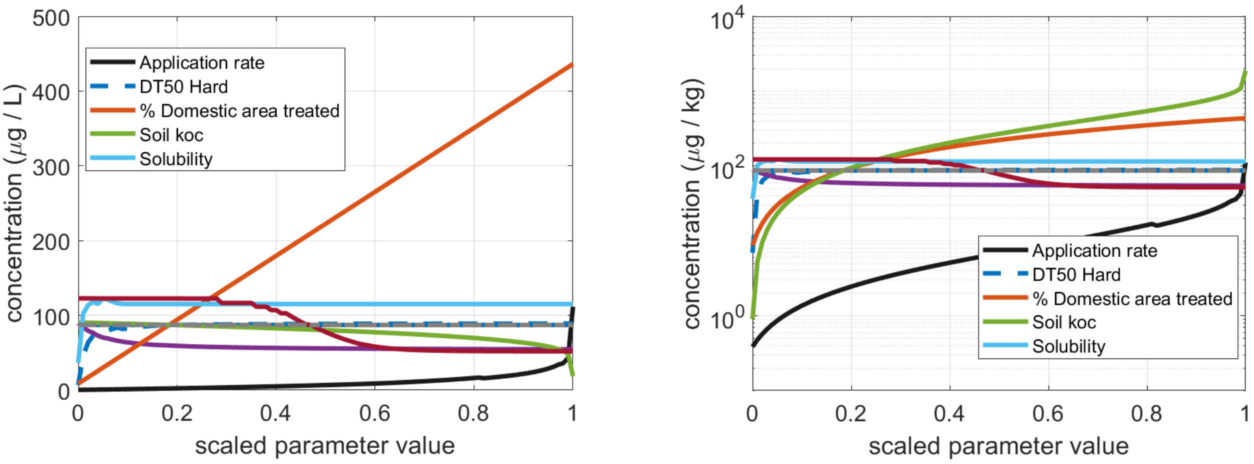

Figure 3 Acute concentration in water (left) and sediment (right) in the domestic use (home and garden) scenario, when atrazine is the baseline substance.

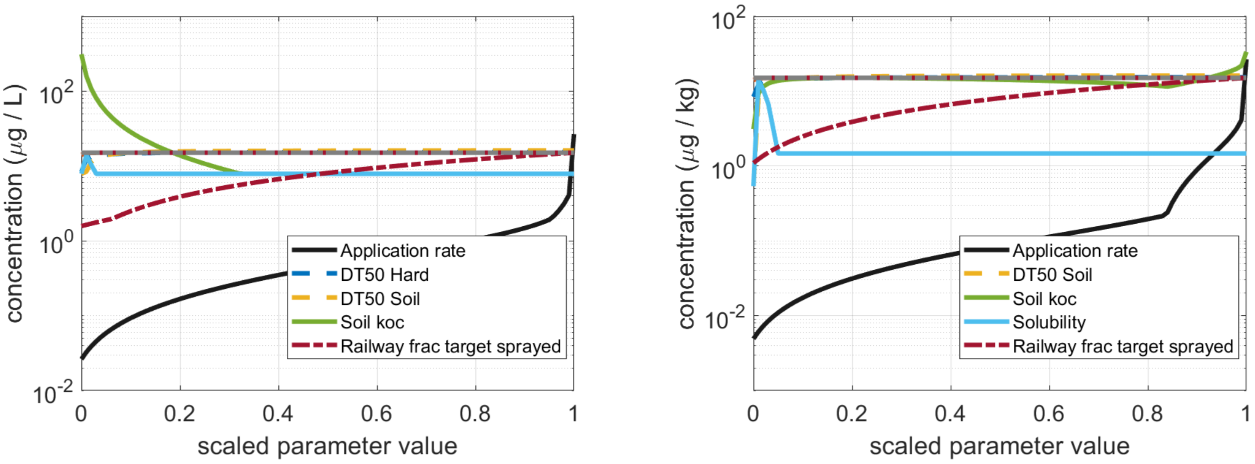

Figure 4 Acute concentration in water (left) and sediment (right) in the railway leaching scenario, when atrazine is the baseline substance.

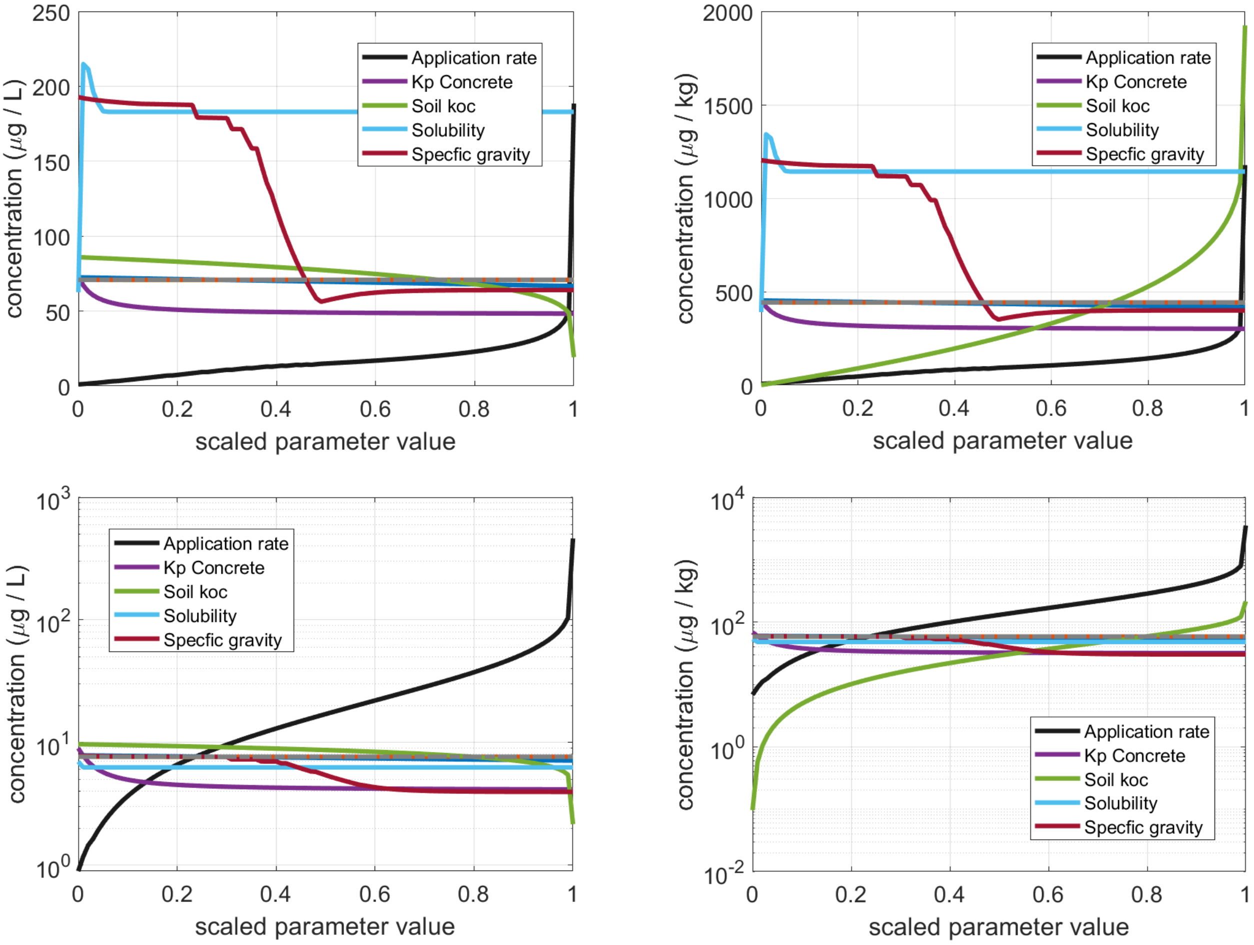

Figure 5 Acute concentration in water (left) and sediment (right) in the urban stream scenario, when oryzalin (top) and isoxaben (bottom) are the baseline substances.

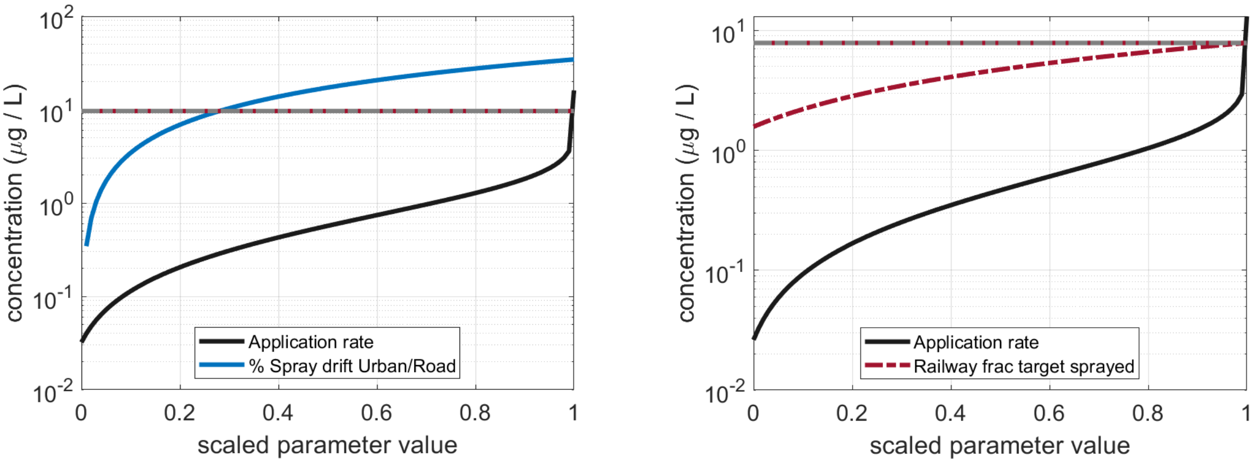

Figure 6 Concentration of atrazine due to spray drift on application day in the urban stream (left) and railway leaching (right) scenarios.

The discontinuities in PEC as a function of specific gravity for atrazine (Figure 1), the increase in PEC for oryzalin initiated at the mid-point in the specific gravity range (Figure 5), and the non-monotonic changes related to solubility, were investigated by the model authors. These anomalies were found to be the result of errors in the application of the model’s solubility and specific gravity components of the surface wash-off algorithms in the “Masses lost per 0.5mm Rain” worksheet. These errors were corrected in the Excel implementation of the model and using this version (version 1.5.2-4) it was confirmed that the anomalous patterns were eliminated (Hollis *et al.*, 2020). None of the corrections had a significant impact on the main outputs of the model: for the test substances the maximum concentration decreased only marginally, and still occurred on the first day after application.

3.2.3 Sensitivity – Morris Test

Whilst the initial OAT analysis focussed mainly on the chemical specific parameters, this second phase studied a much larger number of parameters. A more rigorous sensitivity analysis framework was applied to study the important parameters and interactions between parameters for each of the scenarios. The two stage-approach described in section 2.2.5 was applied.

Each of the exposure scenarios coded in HardSPEC is modelled using approximately 60 parameters, many of which (such as herbicide properties) are common across scenarios. Parameters describing the stream (or pond) were excluded from the global sensitivity analysis (as these features are unlikely to be changed by the regulator, and volume changes are expected to have predictable effects on concentration) reducing the number of parameters of interest to approximately 50 per scenario.

The computationally efficient Morris test was conducted to identify a sub-set of sensitive parameters to be taken forward into the second phase of analysis. The Morris test was applied for each of 19 model outputs: acute concentration in the water and sediment phases of the six surface water scenarios, spray drift contribution in five of the surface water scenarios, the maximum concentration at the source well-head in the groundwater model with a chalk aquifer, and the duration that the concentration at the well-head was above 10% of the peak value. Although the HardSPEC output gives the duration above 0.1 μg/L, for many combinations of parameters the concentration never reaches this value, hence the threshold was set to 10% of peak value as this will always return a non-zero duration and hence be informative regarding sensitivity.

For all model outputs σ was highly correlated with μ* (Figure 7 gives typical results), and hence selection was based on μ* alone. For each output, the number of parameters above 5% of the maximum μ* is given in

	Acute conc. water phase	Acute conc. sediment	Spray Drift	Max conc. at well-head	Duration above 10% of max at well-head
Urban Stream	17	16	4		
Urban Pond	11	11	4		
Domestic use	14	11			
Major Road	9	11	4		
Railway Leaching	11	5	3		
Railway Runoff	15	7	3		

	Acute conc. water phase	Acute conc. sediment	Spray Drift	Max conc. at well-head	Duration above 10% of max at well-head
Groundwater (chalk)				14	9

Table 4. However, global sensitivity analysis was not conducted for the acute concentration in sediment due to time constraints: the concentration in water is usually the more onerous consideration from a regulatory perspective and hence sensitivity of this output is more important for analysis.

	Acute conc. water phase	Acute conc. sediment	Spray Drift	Max conc. at well-head	Duration above 10% of max at well-head
Urban Stream	17	16	4		
Urban Pond	11	11	4		
Domestic use	14	11			
Major Road	9	11	4		
Railway Leaching	11	5	3		
Railway Runoff	15	7	3		
Groundwater (chalk)				14	9

Table 4 Number of parameters selected by Morris screening for each output.

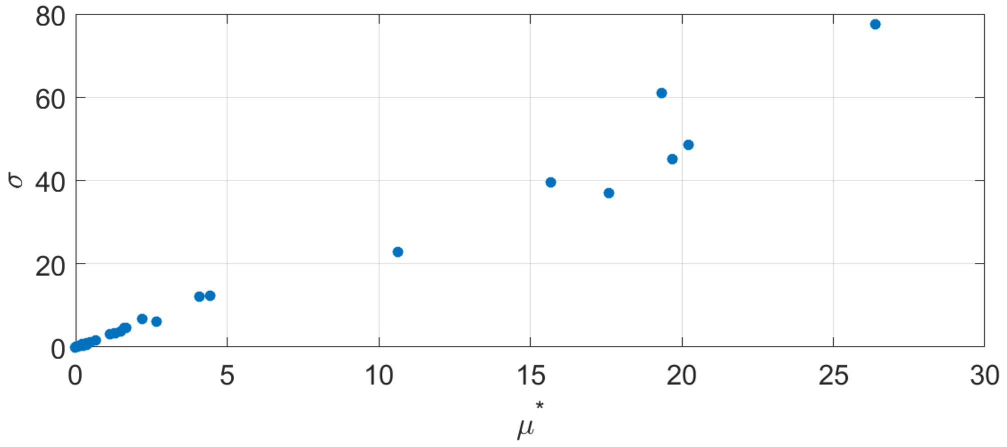

Figure 7 Morris screening results for the 53 parameters used to model acute concentration in water in the domestic use scenario: each point shows σ and μ* for one parameter.

3.2.4 Sensitivity – Variance-based analysis

Detailed results from global sensitivity analysis are given in Figure C1 to Figure C7 in Appendix C. In these plots main and total effects are plotted for only those parameters for which the main effect is greater than 1% of the total variance, and/or the total effects are greater than 2.5%. A summary of these results is made below.

The ranks of the parameters having three largest main effects on the acute concentration in the water phase are given for each scenario in

Table **5**. The application rate was dominant for the acute water concentration in the urban stream, urban pond and road scenarios, with the main effect accounting for approximately 50% of variance in these scenarios. Solubility and Kp concrete were also identified as having large main effects (

Table **5**). There were significant interactions between application rate and other parameters in all of these scenarios – the interaction between application rate and herbicide solubility was the most notable of these.

For the domestic scenario a larger number of parameters were identified as being of some importance for this scenario. Application rate was the dominant main effect for acute water concentration, although only accounted for approximately 20% of variance. Solubility, the % of areas treated and Kp concrete were other parameters having notable main effects. The interactions between parameters were particularly notable for this scenario. Of the 14 parameters plotted in Figure C4, 8 had negligible main effects but non negligible interactions. Whilst it is clear that the application rate significantly interacts with other parameters the overall results are difficult to interpret due to the large number of parameters and complex interactions (involving more than two parameters).

For the railway leaching scenario the acute water concentration – main effects of the application rate and Koc were relatively small, accounting for approximately 5% of variance – the interaction between these two parameters was substantial accounting for the vast majority of variance. For the railway run-off scenario the acute water concentration was sensitive to a larger number of parameters although only the soil Koc and application rate had significant main effects (each accounting for approximately 10% of variance). The majority of variance was accounted for by interactions for this scenario – the interactions between soil Koc, solubility and the application rate appear to be the most significant (Figure C6).

The ranks of the three largest main effects on the concentration due to spray drift on application day are given for each scenario in Table 6. Spray drift was sensitive to a smaller group of parameters. For the urban stream, urban pond and road scenarios two parameters - the application rate and % applied impacting as spray, urban & road - accounted for approximately 50% and 20% of variance respectively through their respective main effects in each of these three scenarios. The interaction between these two parameters was also significant and accounted for the majority of remaining variance.

Parameter rankings for the two railway scenarios are also given in Table 6. The distance from cess to the water body accounted for approximately 40% of variance through its main effect and application rate accounted for 10% of variance in both scenarios. A substantial interaction between these two parameters accounted for the majority fraction of variance not already explained by the main effects. The behaviour of the HardSPEC model is substantially simpler for calculations of spray drift, driven by two /three parameters.

Results from the railway over groundwater scenarios, max concentration in the well and duration above 10% of the peak concentration are shown in Figure C7 – results relate to chalk in both cases. The peak concentration was most sensitive to the application rate, soil Koc and solubility parameters. All three main effects were small however the interactions between these three parameters accounted for a large fraction of variance. In contrast the duration above 10% of the peak concentration – a measure of the persistence in groundwater- was sensitive to a larger pool of seven parameters. A decay rate constant was the most sensitive parameter accounting for approximately 50% of variance (Figure C7).

Table 5 Parameters responsible for the three largest main effects on acute concentration in the water phase.

	Urban				Railway	
	Stream	Pond	Domestic	Road	Leaching	Runoff
Herbicide: Application rate	1	1	1	1	2	2
Herbicide: Solubility	2	3		2		3
Herbicide: Kp concrete	3		3	3		
Urban: hard surfaces as % of catchment		2				
Herbicide: % domestic areas treated			2			
Herbicide: Soil Koc					1	1
Railway: distance from cess to water body					3	

Table 6 Parameters responsible for the three largest main effects for application day spray drift contribution.

	Urban			Railway	
	Stream	Pond	Road	Leaching	Runoff
Herbicide: Application rate	1	1	1	2	2
Herbicide: % applied impacting as spray, urban & road	2	2	2		
Urban: width asphalt/concrete area strip sprayed	3	3			
Railway: distance from cess to water body				1	1
Herbicide: Uncertainty, fraction 774.7m^2 railway area sprayed				3	3

3.3 Rainfall Analysis

The acute concentration in water and sediment was recorded for the six surface water scenarios using the pesticide properties corresponding to the six test substances and with all other parameters set at their default values. Only the rainfall on the first day after application was varied in this analysis with rainfall of between 0.5 and 20mm considered in 0.5 mm steps. The default value in HardSPEC is 5 mm.

A plot of acute concentration in water as a function of rainfall is shown for the six surface water scenarios in Figure 8. The six response curves shown in each plot correspond to the six test substances.

The responses are generally non-monotonic and unimodal due to the opposing effects of increased wash-off (resulting in greater mass, tending to increase concentration) and increased volume of the water body (tending to decrease concentration) which have different dependencies on the rainfall. The discontinuity of the effect of solubility also affects the shape of the response curves. For the urban stream and domestic scenarios a higher peak concentration was reached at a rainfall below the default 5mm in the HardSPEC model, whereas for the urban pond and the Roadside scenarios it is reached at a rainfall above the default 5mm: the first day rainfall that gives the maximum concentration and the increase in concentration relative to the baseline at 5mm rainfall both depend on chemical properties.

The response curves for the urban pond scenario show non-smooth variation up to about 3mm of rainfall. This was investigated by the model authors and found to be caused by errors in the calculation of non-soluble losses on asphalt algorithms, combined with the dynamics of partitioning in the pond. The errors have been corrected in the more recent versions of the Excel implementation (Hollis *et al* (2020)).

The railway scenarios use a fixed volume ditch, hence there is no dilution effect: as a consequence the peak concentration is unaffected by rainfall where it is the result of application day drift (lines with zero slope for glyphosate, isoxaben, oryzalin and oxadiazon in Figure 8). For atrazine and diuron however, increasing amounts of day 1 rainfall result in increasing PEC, at least for events greater than about 3mm. For rainfall events up to about 3mm however, there is a decrease in PEC. This occurs in both Runoff and Leaching scenarios, although for the latter, the decrease is more modest. This pattern results from the dynamics between leaching for small, but increasing volumes of rainfall on day 1, followed by larger volumes of rainfall on subsequent days (Hollis *et al* , 2020).

The acute concentration in sediment is proportional to that in water, so the curves have identical shapes: the ratio between the phases depends on the herbicide properties (Figure 9).

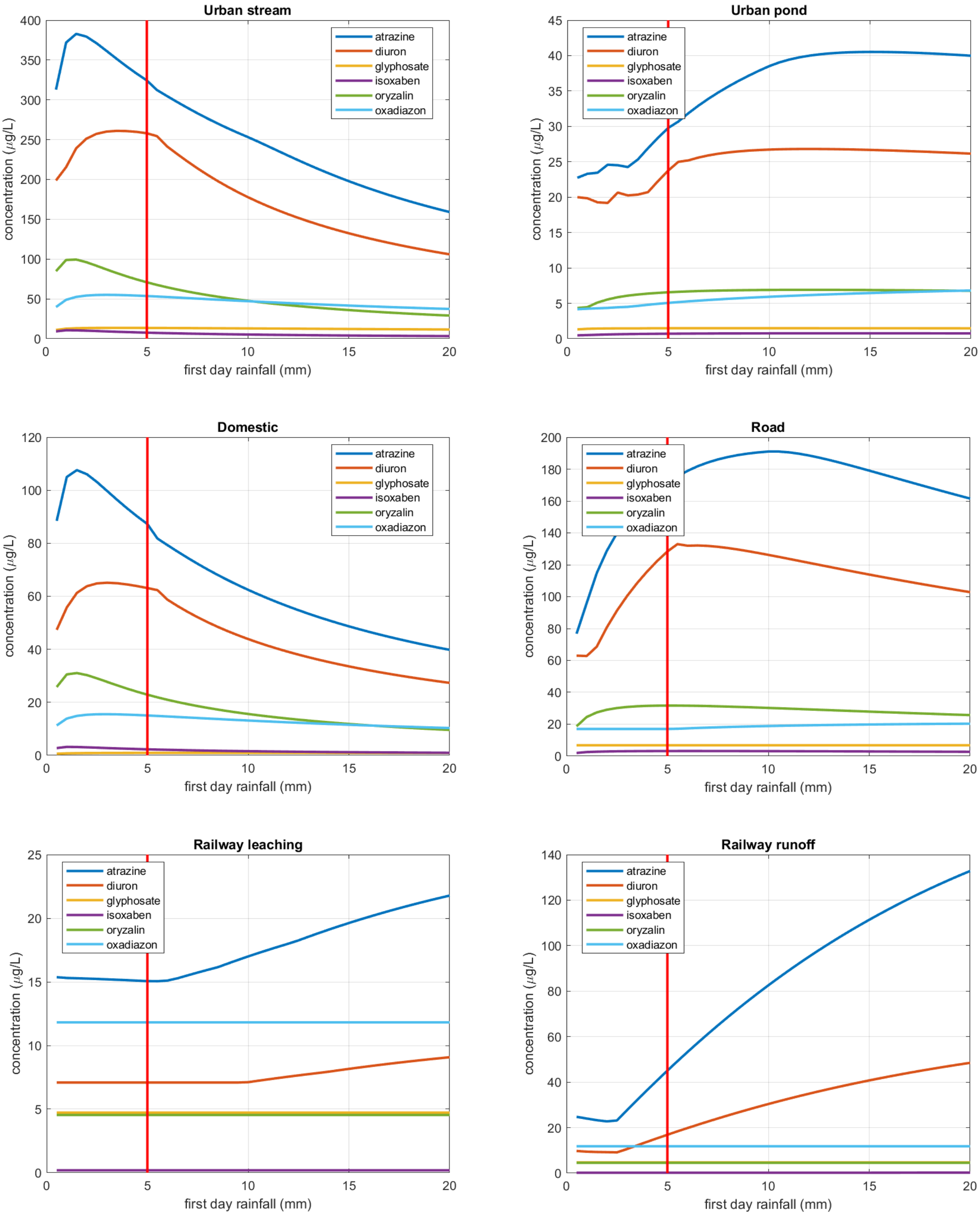

Figure 8 Response of the acute concentration in water to rainfall on the first day after application for each surface water scenario. The red line indicates the level used in the default rainfall sequence: 5mm.

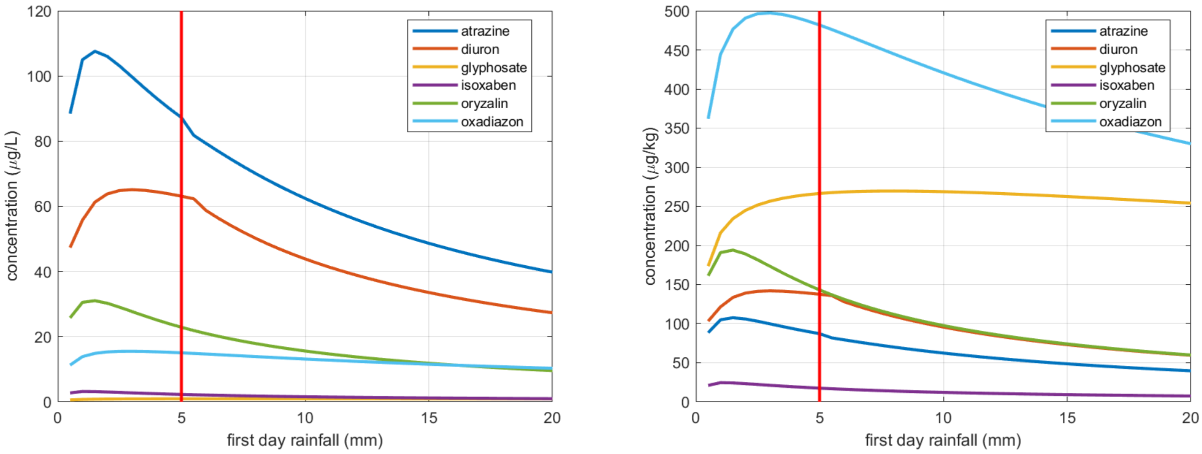

Figure 9 Comparison of the response of the water phase (left) with the sediment phase (right) to rainfall on the first day after application for the domestic use scenario.

3.4 Distance from railway cess to water body

The acute concentration in water and sediment, and the application day spray drift was recorded for the railway leaching (Figure 10) and runoff (Figure 11, left) models over a range of distances between the railway cess and the ditch. The analysis was run for six test substances. The application day spray drift curves are identical for the runoff and leaching models (Figure 11, right), and furthermore the shapes are identical for the different substances, with variations in magnitude only, depending on the application rate.

The acute maximum concentrations in water of glyphosate, isoxaben, oryzalin and oxadiazon for the leaching and runoff scenarios (Figure 10, left plot) are the result of application day spray drift over a large range of distances. The response curves of the concentrations are identical to those for application day spray drift (Figure 11, right plot) up to the distance where the drift becomes insignificant and leaching or runoff determines the maximum concentration. For atrazine and diuron, acute concentration responses are not controlled by application day spray drift but depend on the dynamics of leaching through the railway ballast and, for the leaching scenario, the underlying embankment material and lateral transport through the local groundwater. The latter varies with distance from the cess to the ditch, and the response curves reflect interactions between the leaching dynamics and transport distance changes. For the Railway runoff scenario atrazine and diuron acute concentration response depends solely on leaching dynamics through the railway ballast and then direct input to the stream via runoff. This means that acute concentrations are not affected by the distance from the cess to the stream (Figure 11, left plot). The practical implication is that the Railway runoff scenario is only relevant to surface water ditches directly adjacent to the embankment. If the model were to be amended such that the ditch is no longer directly adjacent to the embankment, the impact of this change should be assessed using the leaching scenario.

Results from this analysis indicated that increasing the distance to the water body had the effect of reducing the concentration – depending upon the properties of the substance this decrease could be quite sharp. The default value of 2.9 m for this distance could substantially overestimate the pesticide concentration for sections of track where the distance from the cess to the water body is substantially (or even modestly) greater than 2.9 m – this parameter therefore encodes a conservatism that might in principle be eliminated through utilising local information on the section of track.

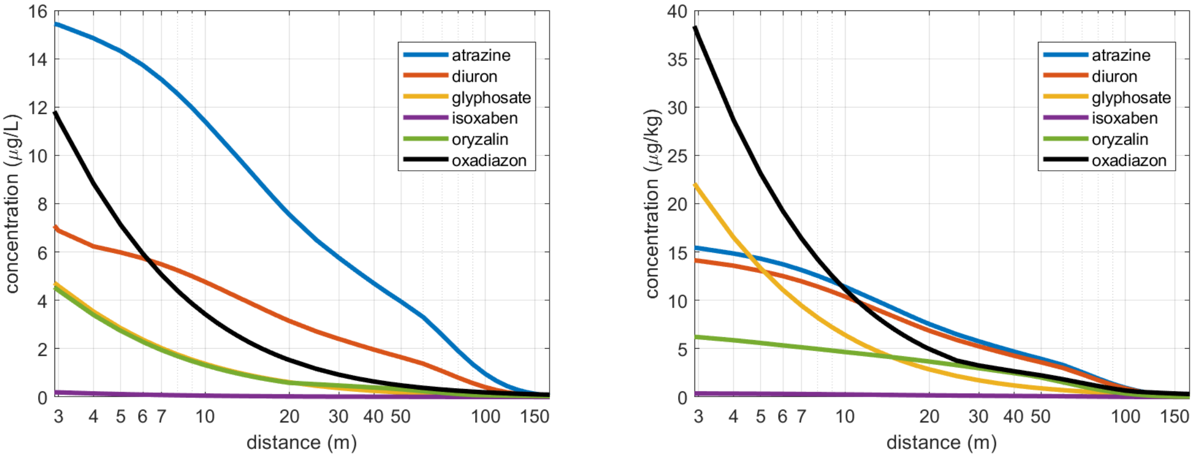

Figure 10 Acute concentration in the water phase (left) and the sediment phase (right) in the railway ditch resulting from leaching shown as a function of the distance from the cess to the ditch.

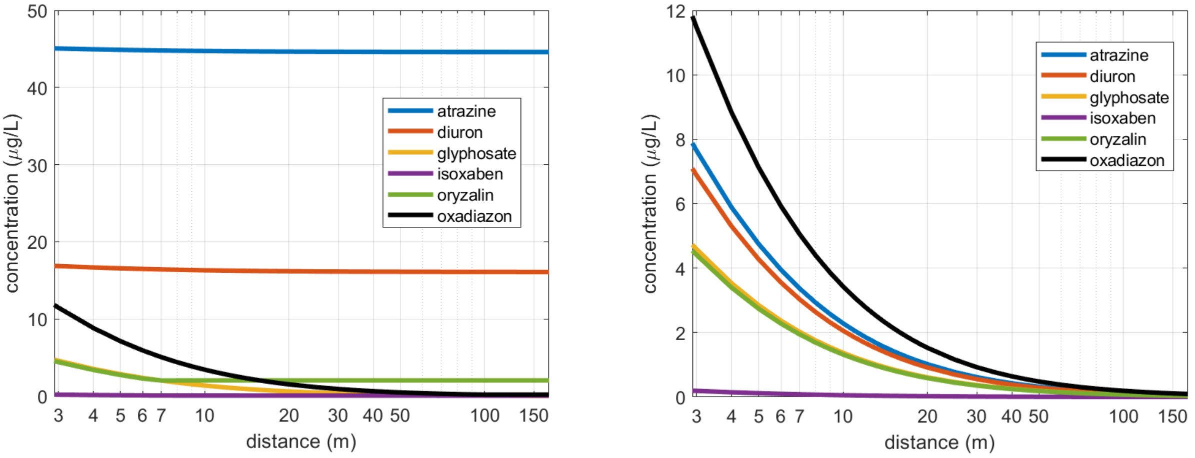

Figure 11 Left: acute concentration in the water phase in the railway ditch resulting from either runoff down the embankment or from spray drift on the day of application. Right: The concentration in water in the railway ditch due to just spray drift on the day of application.

4 Discussion

In the introduction to the report four specific shortcomings of the Excel implementation of the HardSPEC model were identified. Specifically:

- calculations were not transparent and could not be easily linked to equations within the guidance document;
- the model contained a number of un-identified coding errors;
- the model could not be easily modified;
- the form of the model did not lend itself to batch processing operations.

The first aim of this work was to develop a transparently coded error free HardSPEC model which could ultimately form the bedrock of a new software application. A new implementation of the HardSPEC model was successfully coded in Matlab. Standard software development conventions were followed in producing a robust, transparent and error free implementation of the model. Calculations in this new version of HardSPEC are vectorised where appropriate which allows efficient model development and minimises the risk of coding errors. Variable names were chosen to be consistent with equations in the guidance document (Hollis et al., 2017). Changes and refinements to the Matlab model can be easily made; one such change investigated in current work was of perturbations to the rainfall sequence in the days following application, which would have been a major undertaking (and prone to error) in the Excel implementation.

A small number of errors in the Excel implementation were identified as a consequence of the recoding. Errors were resolved in conjunction with the original authors of the HardSPEC model and the Matlab and the updated Excel developmental version 1.5.2-3.1 of HardSPEC return fully consistent estimates of PECs and all intermediate calculations. None of the identified coding errors were of high consequence. A further set of improvements to the model in response to the findings of sensitivity analysis (using the one-at-a time method) will be made during the second phase of the project – these are conceptual changes rather than coding errors and improve the conceptual basis of the model.

As a further consequence of the recoding of HardSPEC in Matlab, batch processing operations could be executed, with HardSPEC repeatedly executed at the command line. The techniques for uncertainty and sensitivity analysis used in this work required many thousands of model evaluations to be made at different parameter values: without batch processing and efficient handling of model inputs and outputs this would not have been computationally feasible.

Sensitivity analysis of the HardSPEC model proved to be difficult with the approach of Owen (2013) ultimately used for the quantitative variance-based sensitivity analysis. The sample sizes used in this work were a factor of ten in excess of usual computational requirements for variance-based sensitivity analysis. The higher computational burden for accurate results appears to be as a consequence of a number of discontinuities in the HardSPEC code, which sensitivity analysis algorithms struggled with. The discontinuities occur as a consequence of several equations, which operate over different functional range of parameter space (i.e., three different equations might be applied for a model parameter over the ranges 0-0.3, 0.3-0.7 and 0.7-1), being used to model the behaviour of particular processes. It is important to note this is a problem with the various algorithms for variance-based sensitivity analysis and does not imply a problem in the HardSPEC model.

Results from the variance-based sensitivity analysis were dependent upon the scenario with some notable differences between the urban/road scenarios and the two rail scenarios. The HardSPEC model was most sensitive to the herbicide properties and application details: application rate, Kp concrete, herbicide solubility and % applied impacting as spray drift for the urban/road scenarios, and application rate, solubility, soil Koc and uncertainty fraction 774.7 m^2 railway area sprayed for the railway scenarios. However, the various PECs were also sensitive to a subset of scenario specific parameters. The domination of the herbicide properties reflects the large ranges ascribed to these parameters, which cover the properties and use characteristics of all the test substances. A sensitivity analysis that focussed on a narrower range of herbicide properties (consistent with a class of pesticide) or for a given named herbicide with known and fixed properties, would allow a more precise investigation of the sensitivity of the PEC to the various parameters which define the exposure scenarios. This would be a useful extension to current work and could be rapidly applied using the codes developed for this work.

A potential further use of batch processing is a probabilistic risk assessment of herbicide usage. Preliminary analysis of rainfall indicates that for some herbicides such as atrazine across realistic levels of rainfall on the day after application, the water-phase PEC could be significantly higher than that calculated using the current fixed rainfall sequence with 5mm of rain on the day after application. By running the model with hundreds of different rainfall sequences taken from historical meteorological records the regulator could compare, say the 90th percentile of PEC (as a ‘realistic worst-case’) with a threshold. Risk assessment could hence be based on whether the chance of exceeding the threshold is greater or less than 10%.

In a later phase of this project it is intended to develop a new software application that replaces the current Excel implementation of HardSPEC. The bedrock of the application, a functional Matlab implementation of the HardSPEC model is already available; therefore a user friendly interface that interacts with the Matlab model is the primary requirement. The user interface, documentation and additional functionality of this version of the HardSPEC model will be developed in conjunction with members of the Hard Surfaces Steering Committee.

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6 Appendix A: Code Implementation Schema

Table A1 Matlab functions (run from the hardspec function) and their equivalent Excel worksheets.

Excel tab	Matlab function	Matlab output structures
Herb_props	get_herbicide_properties	Herbicide
-	get_stream_par	StreamPar
Calibration_module	calibration_module	CalibratedPar
-	get_all_scenario_parameters	ScenarioPar
Urban_scenario	get_urban_scenario	ScenarioPar.Urban
Domestic_Use_scenario	get_domestic_use_scenario	ScenarioPar.Domestic
Major_scenario	get_road_scenario	ScenarioPar.Road
Railway_scenario	get_railway_scenario	ScenarioPar.Railway
Goundwater_model	get_groundwater_scenario	ScenarioPar.Groundwater
-	get_rainfall_sequence	RainfallPerDayRounded
Masses lost per 0.5mm rain	calc_loss_per_half_mm_rain	LossPerDay
losses_AR	calc_loss_after_rainfall	ConcentrationStream and ConcentrationPond
losses_AR	calc_loss_railway_base	RailwayMassLoss
losses_AR	calc_railway_leaching_and_runoff	ConcentrationRailwayDitch
Railway_surface_water	calc_railway_surface_water	Load
Goundwater model	calc_groundwater	LoadGroundwater
OUTPUT	make_report	-

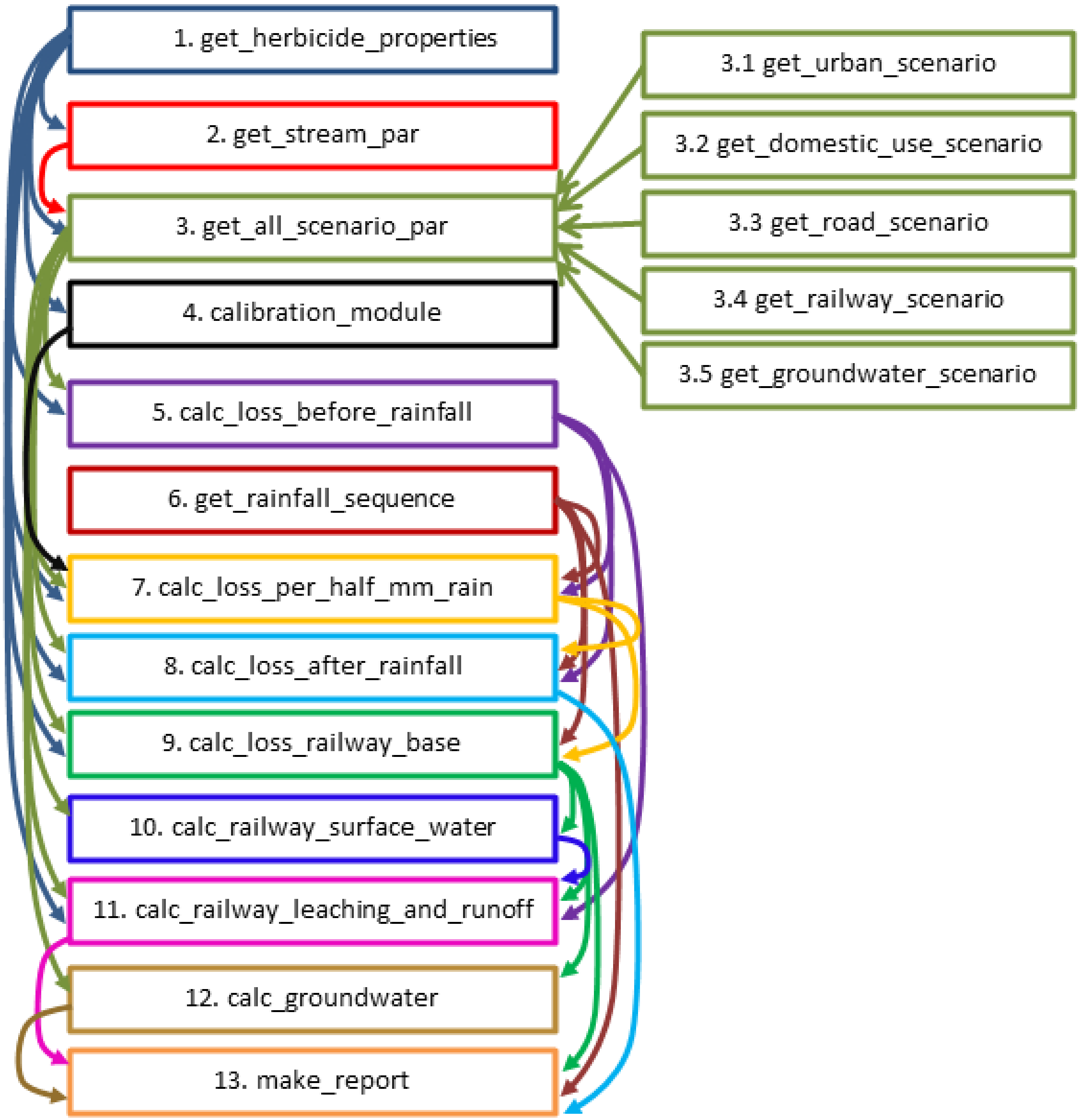


Figure A1 Sequence of Matlab functions run in the top level `hardspec` function and their dependencies. Numbers indicate the order in which functions are run and arrows indicate which functions use the output structures of a previous function.

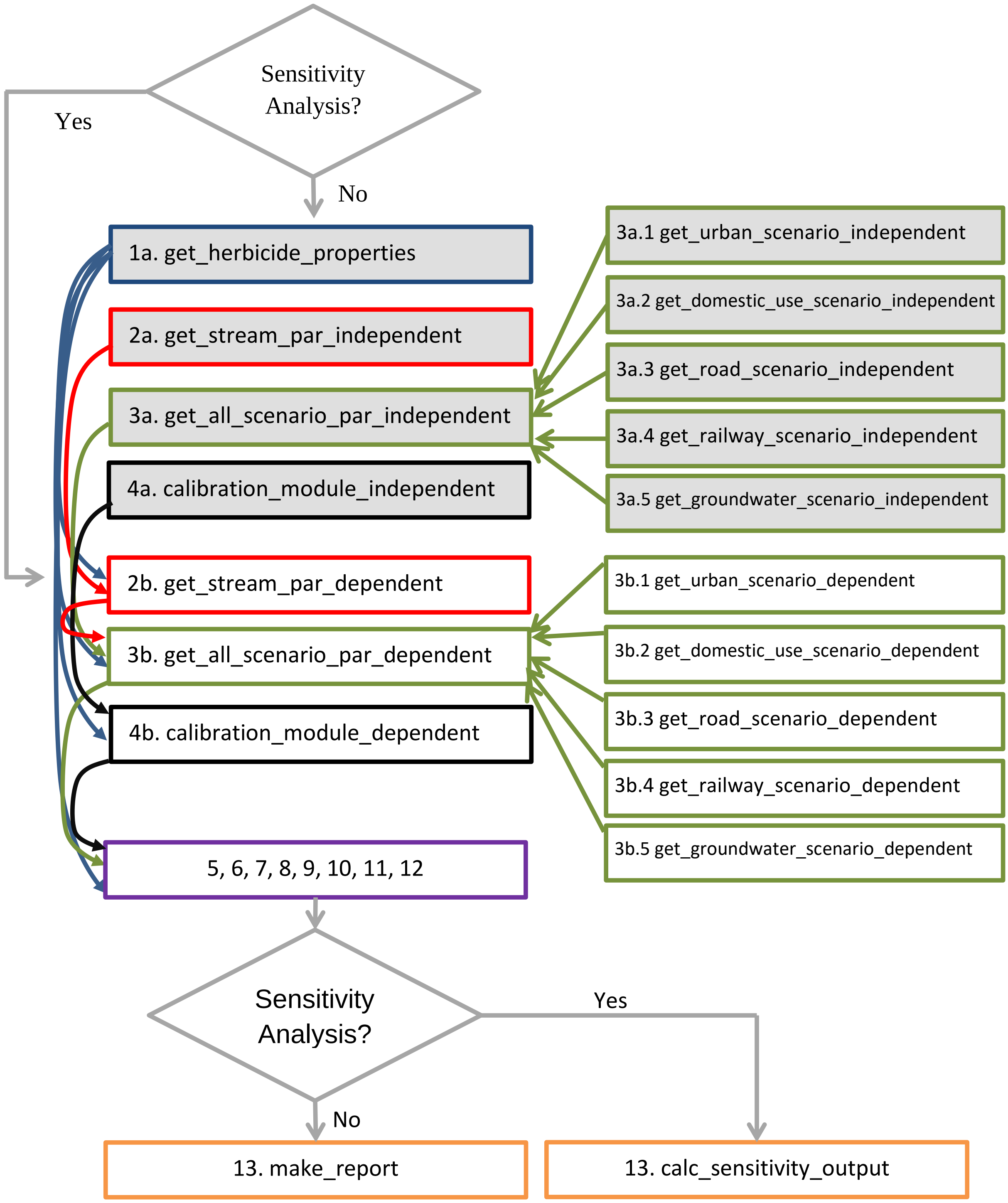


Figure A2 Matlab `hardspec` function adapted from the design in Figure A1 to calculate dependent variables from specified independent variables, adding functionality needed for sensitivity analysis. Arrows connected to diamonds indicate the order of program flow rather than function outputs: if sensitivity analysis is conducted, independent parameters taken from the design matrix are passed into the `hardspec` function. Functions numbered 5,…,12 are identical to those shown in Figure A1.

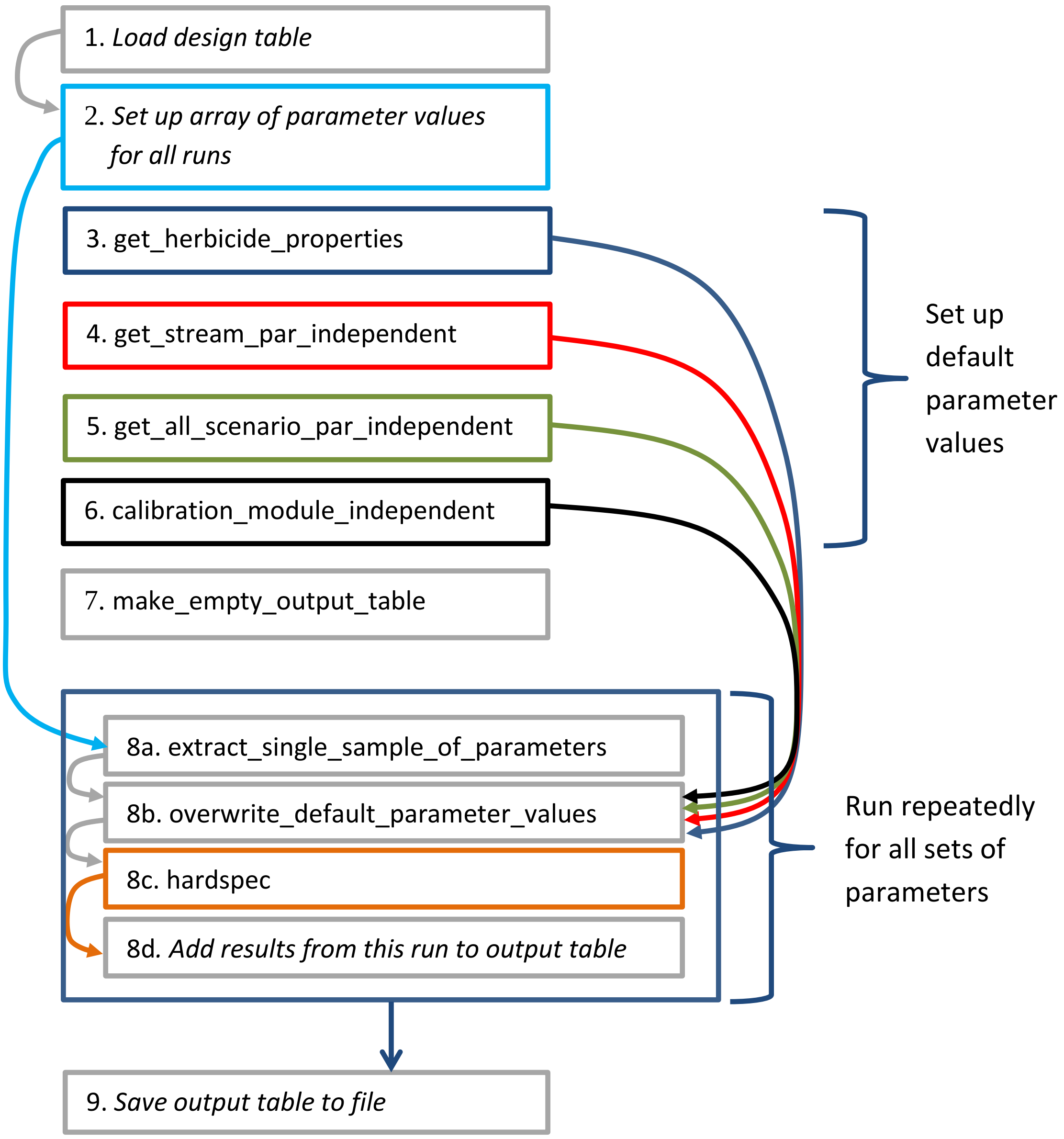


Figure A3 Schematic of the Matlab function `sensitivity_run` which runs HardSPEC repeatedly for sensitivity analysis. Italics denote simple operations that do not require a separate function. The functions 3,…,6 are the same as those used within the HardSPEC function (see Figure A2)

7 Appendix B: Model parameters

Table B1 Parameter defaults and sensitivity ranges

Parameter [Description] {Origin of Default}	Default	Bounds
Properties.PctAppliedSprayDriftUrbanAndRoad [% of applied herbicide impacting on the surface water body as spray drift. Urban & Major Road] {Taken from the FOCUS Surface Water Scenario drift calculator and is based on a hand held application for a crop < 50 cm high and at a distance of 1 m from the edge of the 'crop' to the start of the water body.}	2.8	0, 10
Properties.PctDomesticAreasTreated [% of domestic households spot spraying hard surfaces in the 'worst case' scenario] {Based on confidential EPOS monthly sales information, supported by data from a study of domestic usage within a small suburban catchment in York (Ramwell & Kah, 2010)}	10	1, 50
Properties.MeasuredKpAsphalt [Measured Kp asphalt (mg m-2)] {Not normally known unless specifically measured. Where not known, calculated from a relationship with soil Koc}	none	1, 200
Properties.MeasuredKpConcrete [Measured Kp concrete (mg m-2)] {Not normally known unless specifically measured. Where not known, calculated from a relationship with soil Koc}	none	1, 55
Properties.SoilKoc [soil Koc (mL g-1)] {Input based on measurements from the Pesticide Dossier}	none	1, 4000†
Properties.Solubility [solubility (mg L-1)] {Input based on measurements from the Pesticide Dossier}	none	0.1, 1000†
Properties.SpecificGravity [Specific Gravity] {Input based on measurements from the Pesticide Dossier}	none	0.1, 2.5
Properties.DT50Soil [DT50 in soil (days)] {Input based on measurements from the Pesticide Dossier}	none	1, 500
Properties.DT50HardSurfaces [DT50 on hard surfaces (days)] {Not known, assumed to be 2 x DT50 in soil}	none	1, 500
Properties.DT50Sediment [DT50 in sediment (days)] {Input based on measurements from the Pesticide Dossier}	none	1, 500
Properties.DT50Water [DT50 in water (days)] {Input based on measurements from the Pesticide Dossier}	none	1, 500

Table B1 (continued) Parameter defaults and sensitivity ranges

Parameter [Description] {Origin of Default}	Default	Bounds
ApplicationRate [Application rate (g/ha)] {Input based on measurements from the Pesticide Dossier}	none	10, 3000†
Uncertainty.Fraction774pt7m2RailwayAreaSprayed [Fraction of 774.7 m^2 railway track target area actually sprayed] {Assumes application via Radiarc nozzles to the whole track}	1	0.2, 1
Uncertainty.RunoffAttenuationLeachedLoadFromBallast [Run-off attenuation factor applied to leached load from ballast]	1	0.2, 1
RailwayDitchHandSpray.PctAppliedSprayDrift [Railway scenario hand-held sprayer % of applied amount impacting as spray drift.]	2.8	0, 10
RailwayDitchHandSpray.Fraction100m2SpotSprayed [Fraction of 100m^2 target area spot sprayed]	1	0.2, 1

† Values transformed to non-linear scale for sensitivity analysis

8 Appendix C: Global Sensitivity Analysis

Results from Global Sensitivity Analysis are given for 13 model outputs in Figure C1 to Figure C7. For each plot the solid bar represents the main effect and clear bar the total effect for the parameter (main effect in addition to interactions involving the parameter). Note that total effects are summed over interactions which may include the same parameter multiple times without accounting for double counting, and hence they could sum to over 1.0 (i.e. 100%), although in the current analysis this did not occur . Effect sizes are estimates derived from a numerical routine and as a consequence the calculated total effects may sometimes be lower than the main effect for a given parameter: the upper bound of the 95% confidence interval on the total effect is indicated in the figures by an error bar.

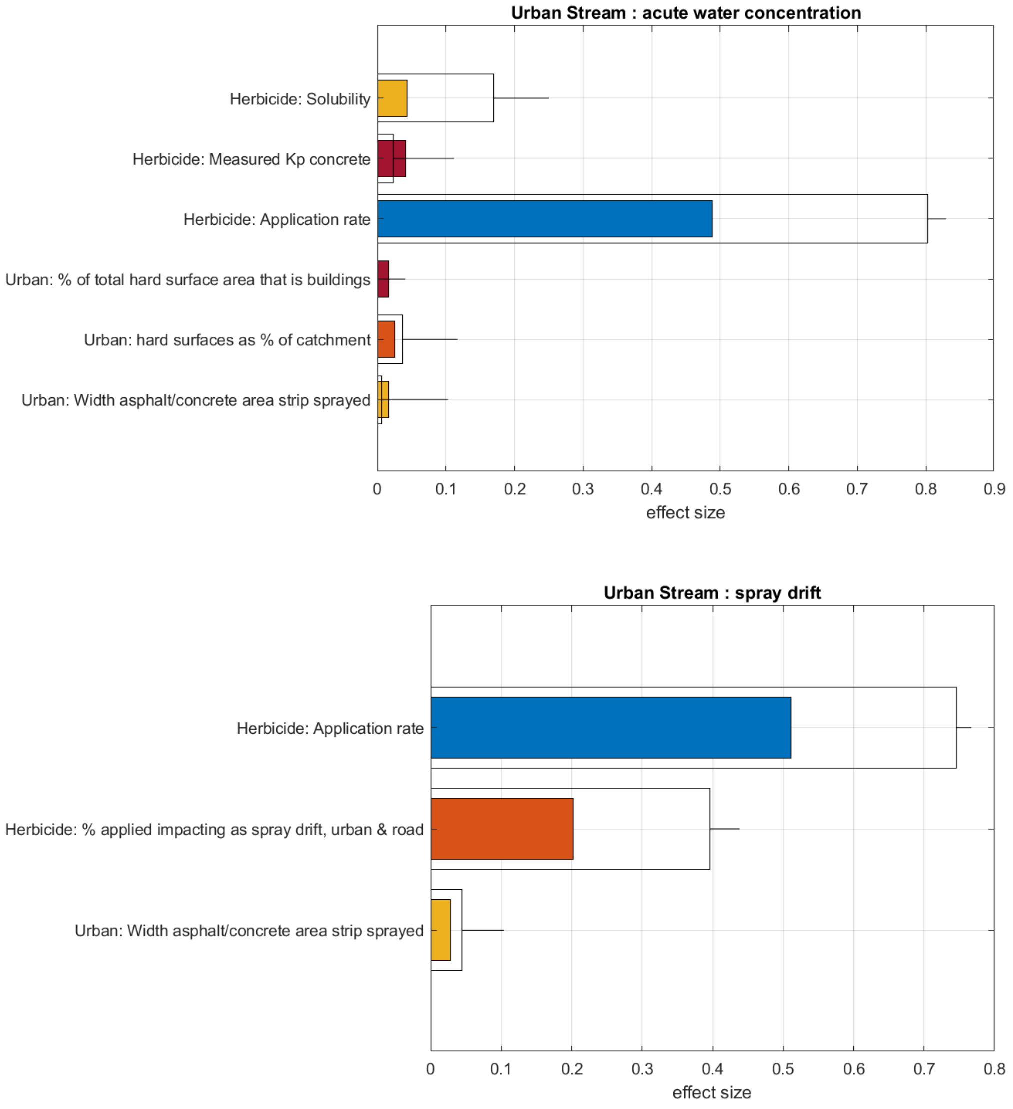
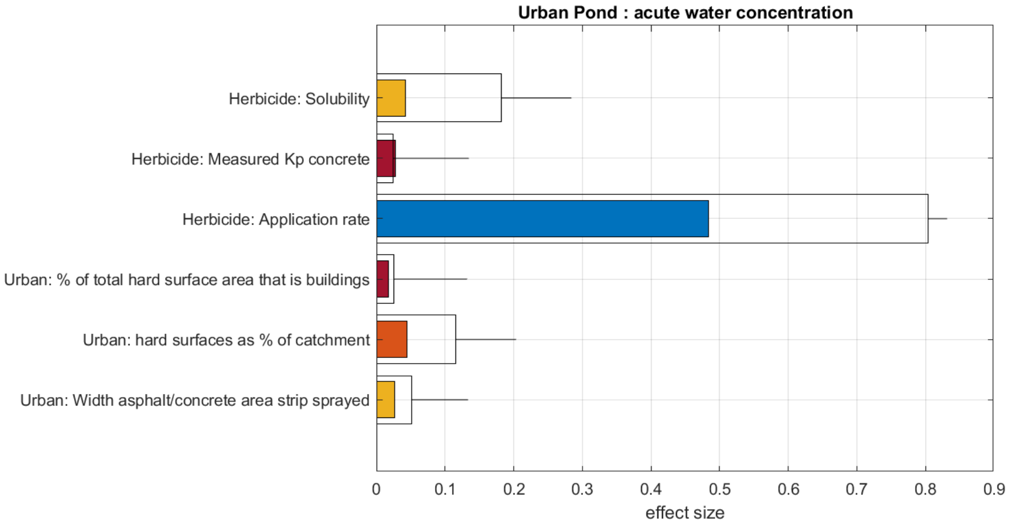


Figure C1: Main effects (solid bars), total effects (clear bars) and upper bounds on the total effects (error bars) for the most influential parameters in the urban stream scenario.



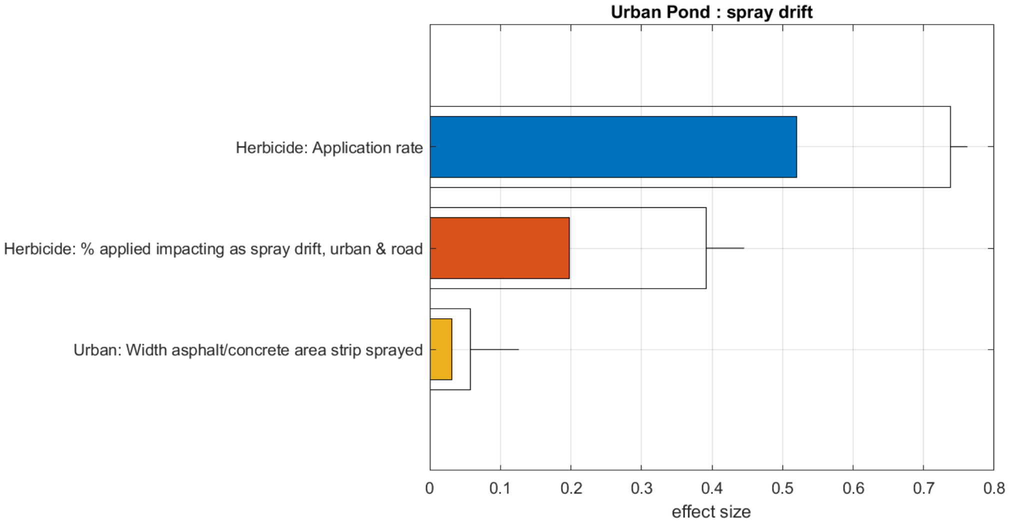
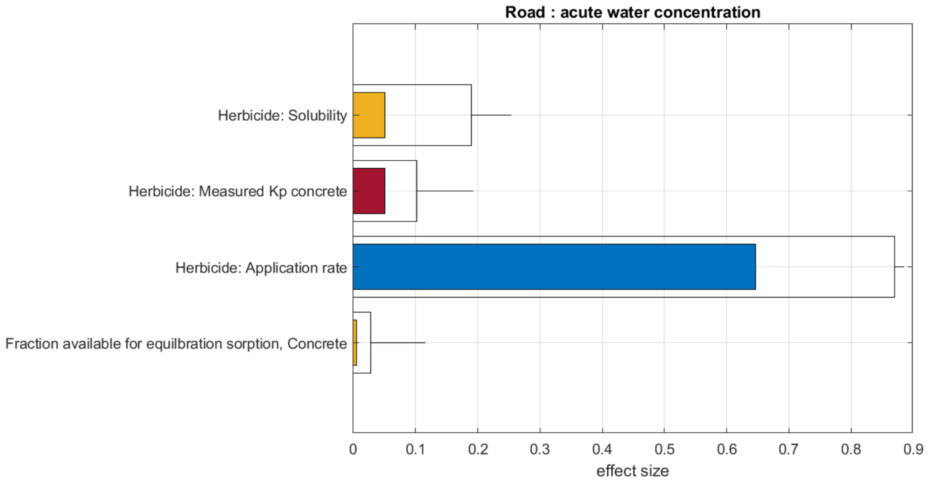


Figure C2: Main effects (solid bars), total effects (clear bars) and upper bounds on the total effects (error bars) for the most influential parameters in the urban pond scenario.



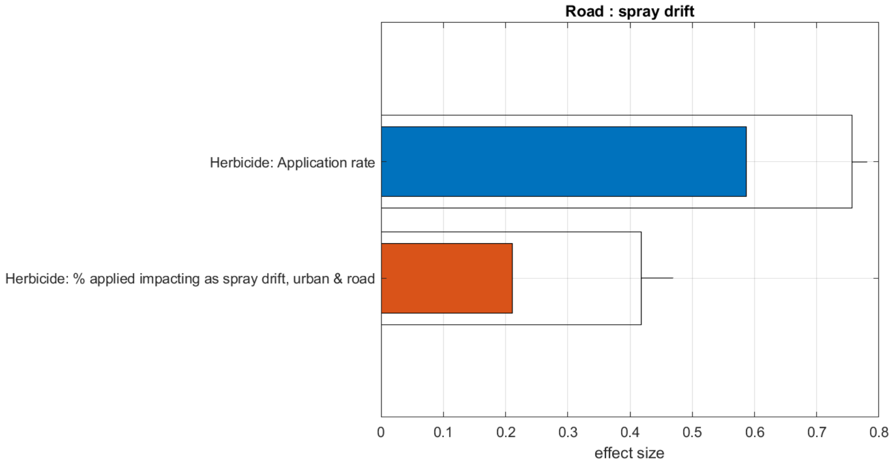


Figure C3: Global sensitivity analysis output for the major road scenario.

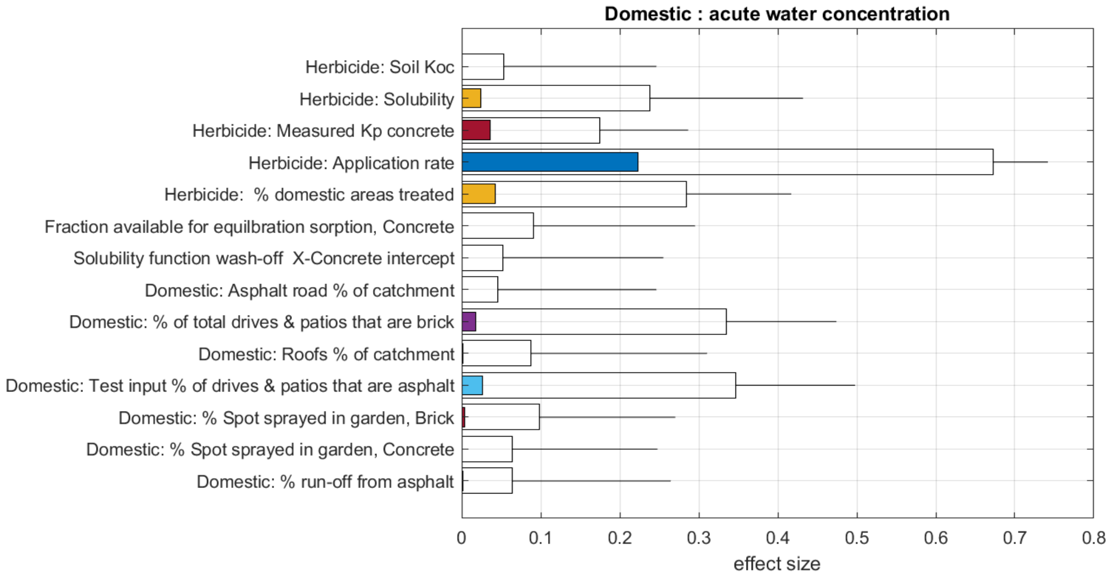
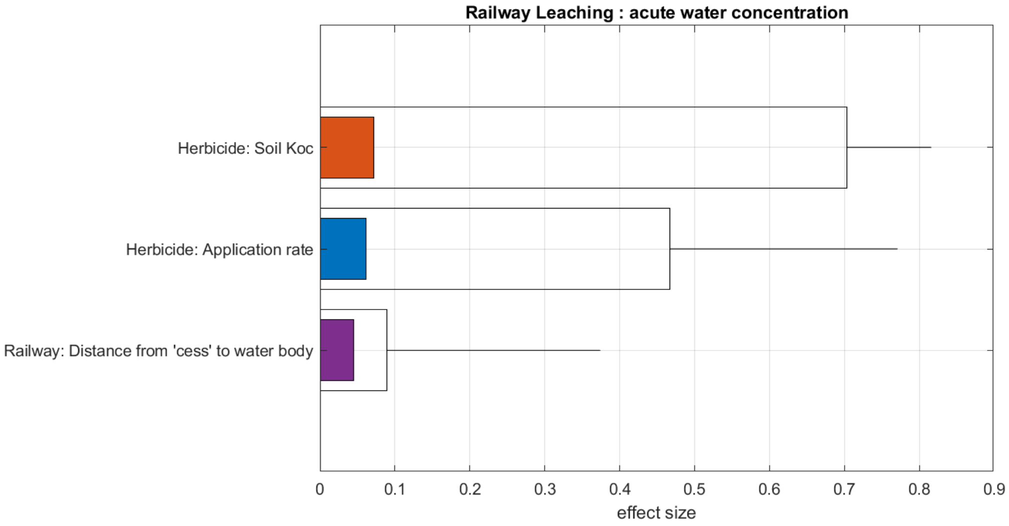


Figure C4: Global sensitivity analysis output for the domestic use scenario (there is no spray drift contribution to surface water for this scenario).



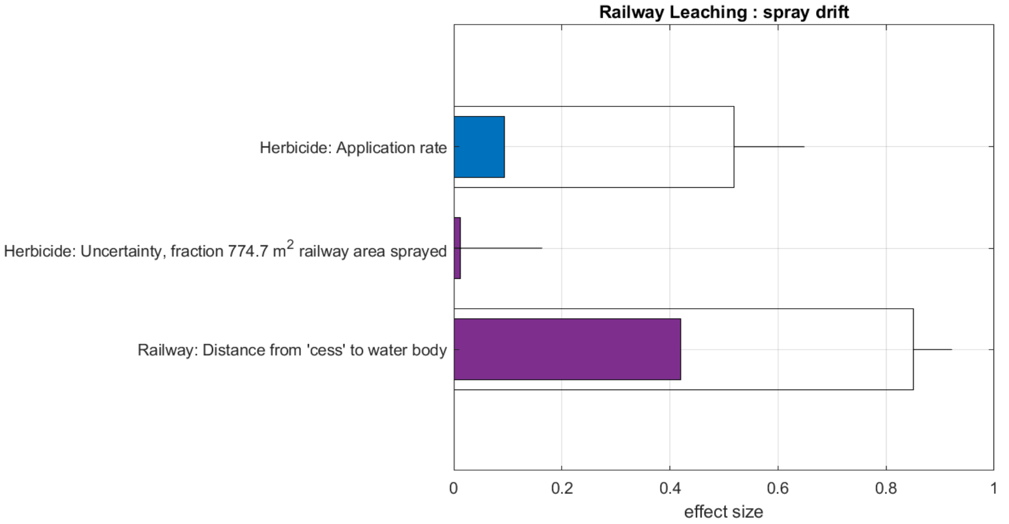


Figure C5: Global sensitivity analysis output for the railway leaching scenario. Note that for spray drift (bottom plot), the central estimate of the total effect size for ‘Fraction 774.7 m^2 railway area sprayed’ is zero, hence the clear bar has a length of zero, although the upper bound indicated by the error bar is non-zero.

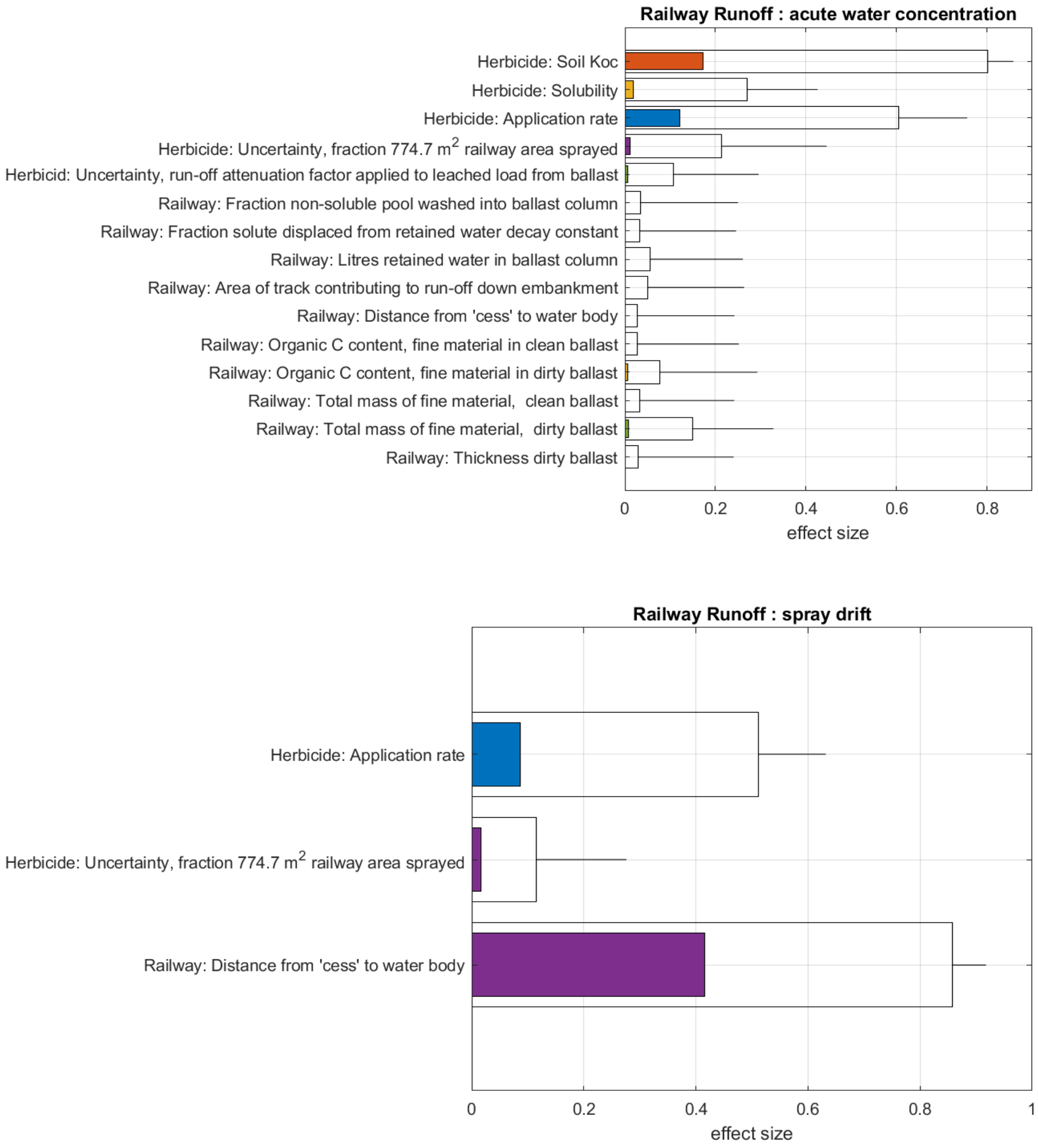
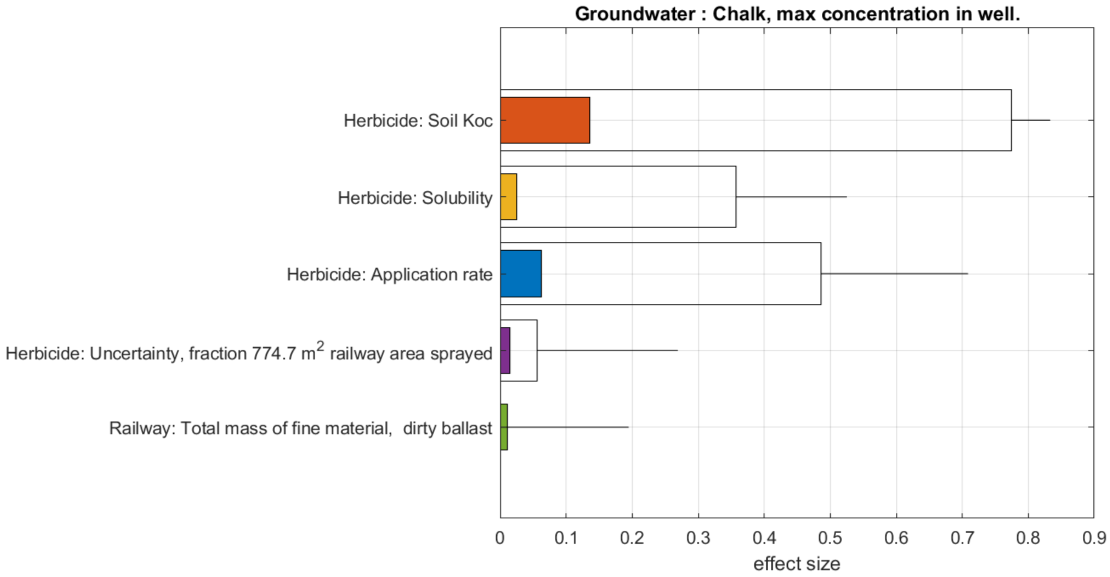


Figure C6: Global sensitivity analysis output for the railway runoff scenario



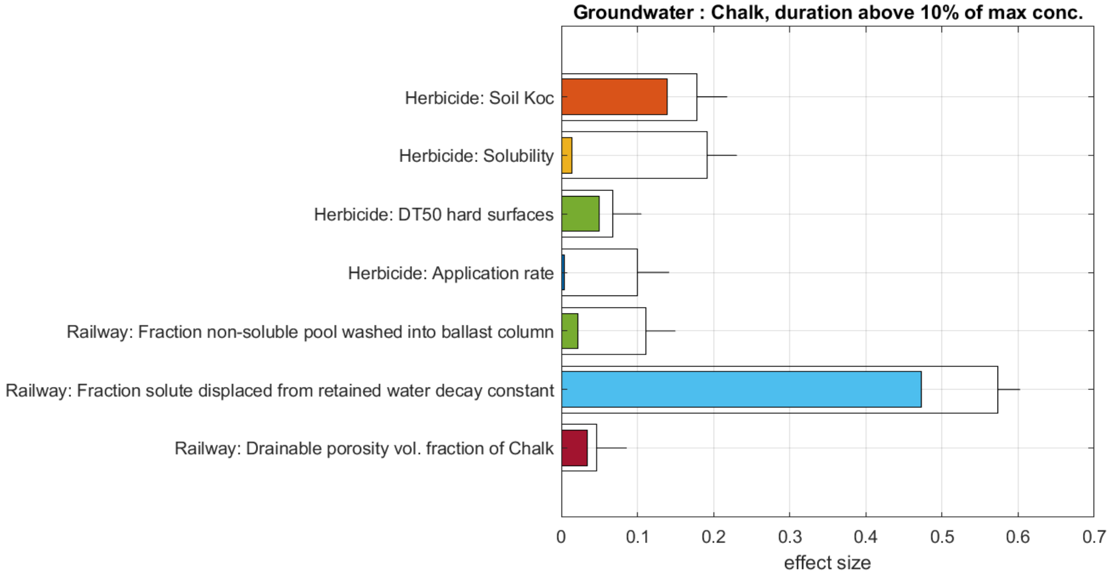


Figure C7: Global sensitivity analysis output for the groundwater scenario with chalk aquifer. Note that for maximum concentration in the well (top plot), the central estimate of the total effect size for ‘Total mass of fine material, dirty ballast’ is zero, hence the clear bar has a length of zero, although the upper bound indicated by the error bar is non-zero.

Sensitivity and uncertainty analysis of the HardSPEC model

HardSPEC is a model used by HSE in regulatory risk assessment of pesticides. It predicts concentrations of pesticides in surface and groundwater following pesticide use for weed control on areas like pavements and roads. The concentrations predicted by the model are used to help determine whether the risk posed by the pesticide use is acceptable.

The model is important in decisions on the authorisation of some pesticide uses. Applicants for pesticide uses sometimes ask HSE to consider a change to the properties of the substance or a change in the model. This is because the applicant wishes to make the assessment more realistic. HSE wanted to explore how sensitive the model is to changes in the assumptions used in the model. HSE also wanted to understand the uncertainties associated with such changes. In addition, HSE wanted to write the model into a different computer language to enable future development of a more easily maintained model.

The project found that HardSPEC output was most sensitive to substance properties and usage details. Output was also sensitive to a number of parameters built into the standard exposure scenarios within the model. This will help HSE understand the significance of changes requested by applicants.

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