Science of the Total Environment 918 (2024) 170589

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Stochastic modelling of pesticide transport to drinking water sources via runoff and resulting human health risk assessment

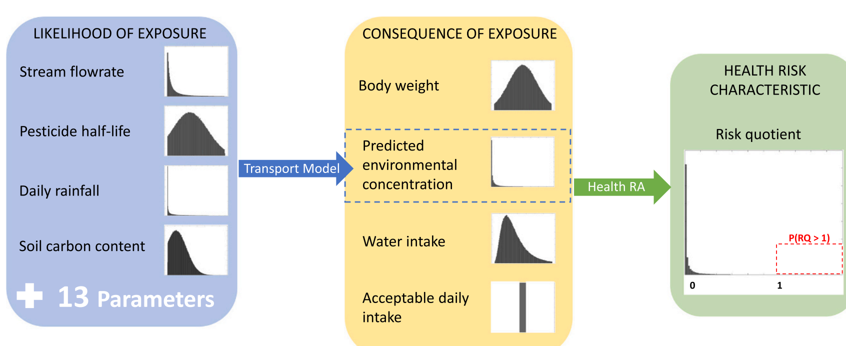
J. Harmon O'Driscoll [a], J. McGinley [b,c], M.G. Healy [b,c], A. Siggins [c,d], P.-E. Mellander [e], L. Morrison [c,f], E. Gunnigle [g], P.C. Ryan [a,h,*]

[a] Discipline of Civil, Structural and Environmental Engineering, School of Engineering, University College Cork, Ireland
[b] Civil Engineering, University of Galway, Galway, Ireland
[c] Ryan Institute, University of Galway, Galway, Ireland
[d] School of Biological and Chemical Sciences, University of Galway, Galway, Ireland
[e] Agricultural Catchments Programme, Teagasc Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland
[f] Earth and Ocean Sciences, Earth and Life Sciences, University of Galway, Galway, Ireland
[g] APC Microbiome Institute, University College Cork, Cork, Ireland
[h] Environmental Research Institute, University College Cork, Cork T23 XE10, Ireland

HIGHLIGHTS

- Probabilistic risk assessment framework used to assess pesticide health risks.
- Model implementation demonstrated using Irish case-study.
- Pesticides were found to pose little health risk at current exposure levels.
- Model sensitivity to various site conditions were assessed.
- Proposed framework may be used for environmental management and decision support.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Yolanda Picó

Keywords:
Pesticide transport
Probabilistic modelling
Drinking water contaminants
Health risk assessment
Monte-Carlo simulations

ABSTRACT

A modelling framework was developed to facilitate a probabilistic assessment of health risks posed by pesticide exposure via drinking water due to runoff, with the inclusion of influential site conditions and in-stream processes. A Monte-Carlo based approach was utilised to account for the inherent variability in pesticide and population properties, as well as site and climatic conditions. The framework presented in this study was developed with an ability to integrate different data sources and adapt the model for various scenarios and locations to meet the users' needs. The results from this model can be used by farm advisors and catchment managers to identify lower risk pesticides for use for given soil and site conditions and implement risk mitigation measures to protect water resources. Pesticide concentrations in surface water, and their risk of regulatory threshold exceedances, were simulated for fifteen pesticides in an Irish case study. The predicted concentrations in surface water were then used to quantify the level of health risk posed to Irish adults and children. The analysis

* Corresponding author at: Discipline of Civil, Structural and Environmental Engineering, School of Engineering, University College Cork, Ireland.
E-mail address: Paraic.ryan@ucc.ie (P.C. Ryan).

https://doi.org/10.1016/j.scitotenv.2024.170589
Received 21 September 2023; Received in revised form 5 December 2023; Accepted 29 January 2024
Available online 1 February 2024

indicated that herbicides triclopyr and MCPA occur in the greatest concentrations in surface water, while mecoprop was associated with the highest potential for health risks. The study found that the modelled pesticides posed little risk to human health under current application patterns and climatic conditions in Ireland using international acceptable intake values. A sensitivity study conducted examined the impact seasonal conditions, timing of application, and instream processes, have on the transport of pesticides to drinking water.

1. Introduction

The global population is predicted to increase by 25 % by 2050 (United Nations, 2019), and the resulting demand on food supplies is expected to more than double when compared to 2010 levels (Van Dijk et al., 2021). Pesticides are key in securing high crop yields, meaning agriculture has depended heavily on their use (Tudi et al., 2021). However, it has been suggested that as little as 1 % of applied pesticides reach target organisms, resulting in potential contamination of surrounding environments and non-target organisms exposure (Ali et al., 2019). Pesticides have been found to be harmful to non-target terrestrial and aquatic organisms (Malaj et al., 2014; Wang et al., 2022), and it has been suggested that repeated ingestion of low doses of pesticides may cause chronic health effects in humans (Aloizou et al., 2020; Giambò et al., 2021; Kalyabina et al., 2021). Therefore, both the likelihood of exposure to pesticides via water supplies, and the consequence of this exposure should be assessed to help understand potential risks posed by pesticide usage.

Pesticide risk models have been widely used as a cost-effective method to provide information on the level of exposure to pesticides and resulting health implications, helping to limit potential risks to human health (Abreu-Villaça and Levin, 2017; Li and Niu, 2021). However, there is extensive literature examining the large variability in factors that influence pesticide impacts and exposure to consumers, and how this affects model outputs (USEPA, 2004b; Lammoglia et al., 2018; EFSA and BfR, 2019; Troldborg et al., 2022). Therefore, probabilistic pesticide models are an important tool in higher-tier risk assessment, as they can quantify the uncertainty associated with model parameters and prediction, offer additional information to catchment and risk managers, and assist in making risk-informed management decisions (Asfaw, 2018). Probabilistic modelling is already widely used in assessing risks from pesticide exposure to humans via food to account for the variability in consumption patterns and the uncertainty associated with pesticide contamination and other contaminants (Bosgra et al., 2009; van der Voet et al., 2015; Stephenson and Harris, 2016; Liu et al., 2022).

Studies probabilistically modelling pesticide risks arising from drinking water are however relatively limited (Cantoni et al., 2021), when compared to the wide use of probabilistic approaches in health risk via food. This is likely due to the reliance on pesticide transport model outputs in analysing likelihood of exposure within such models, for example Teklu et al. (2015) and Brodeur et al. (2023), which tend to adopt the traditional deterministic approach. Therefore, they rely on average values as input parameters to develop point estimate outputs, as highlighted by Gagnon et al. (2014) and Piffady et al. (2021). The use of average values, or point estimates, as input parameters means that the high level of uncertainty associated with input data and the resulting risks of exposure to pesticides cannot be fully accounted for (Troldborg et al., 2022). A number of studies have examined the suitability of adopting a stochastic approach to several process-based transport models (i.e. SWAT, PRZM, etc.) in order to address these limitations (Young and Carleton, 2006; Tasdighi et al., 2018; Winchell et al., 2018; Mentzel et al., 2022). However, these process-based transport models are computationally complex, requiring significant processing power and data input for model parameterisation (Wang et al., 2019). Therefore, attempts to apply probabilistic approaches to these process-based models tend to be limited to a handful of parameters, such as probabilistically modelling pesticide application scenarios only (Winchell et al., 2018; Rathjens et al., 2022) or rainfall and runoff parameters only (Tasdighi et al., 2018), with all other parameters modelled deterministically. While very insightful, this approach cannot fully account for variability and uncertainty associated with the broad range of parameters within the base models i.e. SWAT alone can require up to 60 user-defined parameters (Arnold et al., 2012).

In order to apply a more fundamental probabilistic approach, with the majority of parameters considered modelled stochastically, a number recent of studies have combined Monte Carlo simulations or Bayesian belief networks with simpler computational models, which require less parameterisation and are thus more user-friendly. Monte Carlo risk assessment approaches have been applied by Clarke et al. (2016) to develop a health risk assessment posed by biosolids in surface water. Within the pesticide field, a similar approach was taken to assess pesticide risk from groundwater (Labite and Cummins, 2012), but this study did not consider more vulnerable surface water supplies. Both Cantoni et al. (2021) and Rezaei Kalantary et al. (2022) applied similar approaches to assess resulting health risks from treated water, however initial pesticide concentrations in raw water were obtained from monitoring data, which somewhat limits the application of these approaches to site with available monitoring data. Troldborg et al. (2022) developed a comprehensive model to assess concentrations in both groundwater and surface water using Bayesian network beliefs, but resulting health risks were not considered. Additionally, the simpler computational models used in these studies could not account for the effects of natural processes, such as soil retention, and instream degradation, have on pesticide fate. All studies have contributed to the literature by offering more accessible probabilistic modelling approaches for pesticide risk assessment. However, the work in this paper seeks further contribute to this limited body of work and build on these existing studies in a number of ways.

This paper builds on current research through the modification of an existing pesticide transport model to be integrated into a quantitative health risk assessment. The study seeks to address identified shortcomings in the literature by 1) developing a probabilistic pesticide risk model based on a simple computational model resulting in a more user-friendly option for assessing pesticide risk probabilistically, 2) including model modifications, such as in-stream reduction process, which increases the models ability to better represent real-world scenarios while maintaining broad appeal, and 3) the progression of the framework beyond pesticide transport modelling, to include health risk by incorporating a widely used approach to quantify health risks, which may increase the user base for such a framework to include not just pesticide researchers and water quality managers, but also those interested in public health. The next section of this paper describes the development of a probabilistic modelling framework to assess pesticide health risks via drinking water. This framework is then applied to an Irish case-study in Section 3 to quantitatively assess the health risk, a comprehensive sensitivity study is presented in Section 4 which assesses overall model sensitivity, and the impact that seasonal conditions, timing of application, instream processes, and site location, have on the model output.

2. Methodology

2.1. Summary of transport model selection

This sub-section provides a brief summary of the selection process used to identify the appropriate pesticide runoff model for probabilistically modelling a consumer's likelihood of exposure to pesticides via surface waterbodies. In this process several deterministic pesticide fate and transport models were examined for suitability for probabilistic modelling. As the aim of this study was develop a fully quantitative risk assessment approach that is accessible to a range of users from different backgrounds, and can be easily adapted and to suit the user's needs, the models were assessed based on the balance between accuracy, complexity, required parametrisation and the practicality of adapting the model to facilitate representation of the majority of the model parameters probabilistically. Factors such as 1) balance between model complexity and proven realistic representation of pesticide transport process, 2) the level of expertise required for users of the framework to apply the model i.e. the mathematical complexity of the model, including number of equations and theoretical complexity of the equations, and 3) the availability of probabilistic data for the majority of the model parameters. A more detailed discussion of the model selection process is provided in Section S1 of the Supporting Information document.

In summary, a variety of models ranging from simple transport indicators and conceptual mathematical models to detailed, process-based models such as FOCUS modelling software and SWAT were considered. Indicator-based models are some of the most widely used methods to assess the likelihood of exposure to pesticides due to their easy application and low data requirement. They allow pesticide mobility to be scored using physio-chemical properties (e.g. California's SWPP approach (Luo et al., 2014)) or a site's vulnerability to pesticide pollution can be estimated based on geological features like DRASTIC (Aller et al., 1985). However, such methods cannot be used to assess health risks arising from pesticide exposure as they cannot provide probabilistic data on exposure concentrations. Conversely, a range of computational software has been developed to assess pesticide transport to surface waterbodies such as watershed models SWAT (Arnold et al., 2012), AGNPS (Bingner and Theurer, 2001) or, SWASH, an edge-of-field assessment framework developed for use within the EU by FOCUS (Te Roller et al., 2015). Within the EU SWASH, which combines models PRZM, MACRO and TOXSWA, is widely used in pesticide regulation, while both SWAT and AGNPS are used internationally for pesticide research.

However, the application of models such as those in the SWASH framework and SWAT to individual sites or regions, outside of FOCUS surface water scenarios for example, requires a knowledge of hydrological processes, a high-level of programming competence and large resource and time demands (Wang et al., 2019). For example, using $PRZM_{SW}$ within the SWASH framework, may require up to 40 user-defined input parameters (FOCUS, 2010), while users may need to input up to 60 parameters to run SWAT depending on their site scenario (Arnold et al., 2012). This makes model parameterisation for specific study sites time consuming and data intensive (Adu and Kumarasamy, 2018), and the limited availability of localised datasets can affect the model accuracy (Troldborg et al., 2022). Both the large data demands and the complex computational nature of the models also result in significant resource challenges when attempting to apply probabilistic approaches to the majority of the parameters for such models. The processing power required to run process-based models is significant, and can take a very long time to produce results if run for multiple scenario combinations, as may be required for probabilistic analysis (Bach et al., 2017). As a result, a relatively simple model, that could be more easily parameterised for a probabilistic approach, was selected herein to provide a practical compromise between comprehensive modelling and computational costs, and ease of use for users. The Simplified Formula for Indirect Loading caused by runoff (SFIL) (OECD, 2000) was chosen as a suitable runoff model for the application of probabilistic methods. This model allows for the incorporation of a range of factors that influence pesticide transport and facilitates estimation of actual exposure concentrations, unlike simple environmental indicators. Despite this, it requires less data input (with only 22 input parameters in total), and expert knowledge than the more complex modelling (Troldborg et al., 2022). Its relatively simple theoretical basis also allows for modifications to be made to the model to improve its representation of study scenarios (Berenzen et al., 2005) and it has also been shown to compare well to observed data when used deterministically (Utami et al., 2020). The model used herein is not without its own limitations, however. In order to address some of these limitations, this study utilised a probabilistic approach to account for data uncertainty and variability. Additional pesticide processes were also integrated into the modelling framework to improve the representation of in-stream processes. The output of this model was then used to assess level of resulting health risk as described in Section 2.3.

2.2. Predicted concentrations in surface water

A probabilistic model, in accordance with the framework outlined in Fig. 1, was applied to predict the concentration of a single pesticide in a surface waterbody due to runoff. The theoretical model that forms the basis of this framework was adapted from Berenzen et al.'s (2005) modified SFIL (Eqs. 1–5 & 8) (OECD, 2000). This model allows factors that influence pesticide environmental fate and transport, such as pesticide physiochemical properties, rainfall and runoff volumes, site topography and agricultural processes, to be considered in estimations of concentration. It was further modified here by 1) the use of the US Soil Conservation Service (SCS) curve number method (Eq. 6 and 7) to assess runoff volume, and 2) the reduction of in-stream concentrations due to adsorption and degradation (Eqs. 9–11). A probabilistic approach, detailed in Section 2.4, was then applied to this model utilising the statistical parameters described in Section 3. This methodology was adapted for an Irish case study, described in Section 3, to demonstrate how regional and national datasets may be applied to assess pesticide transport and resulting health risks in local areas. It is important to note in this context that water treatment processes that may reduce pesticide concentrations in drinking water were therefore not considered in this study, as effective pesticide removal processes are not currently available in water treatment plants within the Republic of Ireland (Uisce Eireann, 2021).

The original SFIL estimates the percentage of the applied pesticide dose that will be lost to runoff. This was determined using the pesticide's physiochemical properties and several site conditions:

$$L_{\%} = \frac{Q}{P}\, x\, \frac{e^{\frac{-t ln2}{DT_{50,s}}}\, x\, 100}{1 + K_d}\, x\, f_1\, x\, f_2\, x\, f_3 \tag{1}$$

where Q is the runoff volume (mm), P is the daily average rainfall (mm), t is the number of days between application and rainfall event. The SFIL model runs on the assumption that there will be three days between pesticide application and a rainfall event (OECD, 2000). In Ireland it is advised to ensure there is no rainfall forecast for 48 h after pesticide application (Teagasc, 2020). $DT_{50,s}$ is the pesticide half-life in soil (days). K_d is the ratio of dissolved to adsorbed pesticide and is calculated as:

$$K_d = \frac{K_{oc}\, x\, OC}{100} \tag{2}$$

where K_{oc} is the pesticide adsorption coefficient (l/kg), and OC is the soil's organic carbon content (%).

The correction factors f_1, f_2, f_3 account for the effects of site conditions and agricultural practices on pesticide loss. Correction factor f_1 considers how site slope affects potential runoff based on the relationship developed by Beinat and Van den Berg (1996), whereby:

$$\begin{gathered} f_1 = 0.02153 slope + 0.001423 slope^2; \text{for slope} < 20\% \\ f_1 = 1; \text{for slope} \geq 20\% \end{gathered} \tag{3}$$

The effect that the distance between application site and closest waterbody has on pesticide loss is considered using the correction factor f_2 developed for the RETOX model (OECD, 2000):

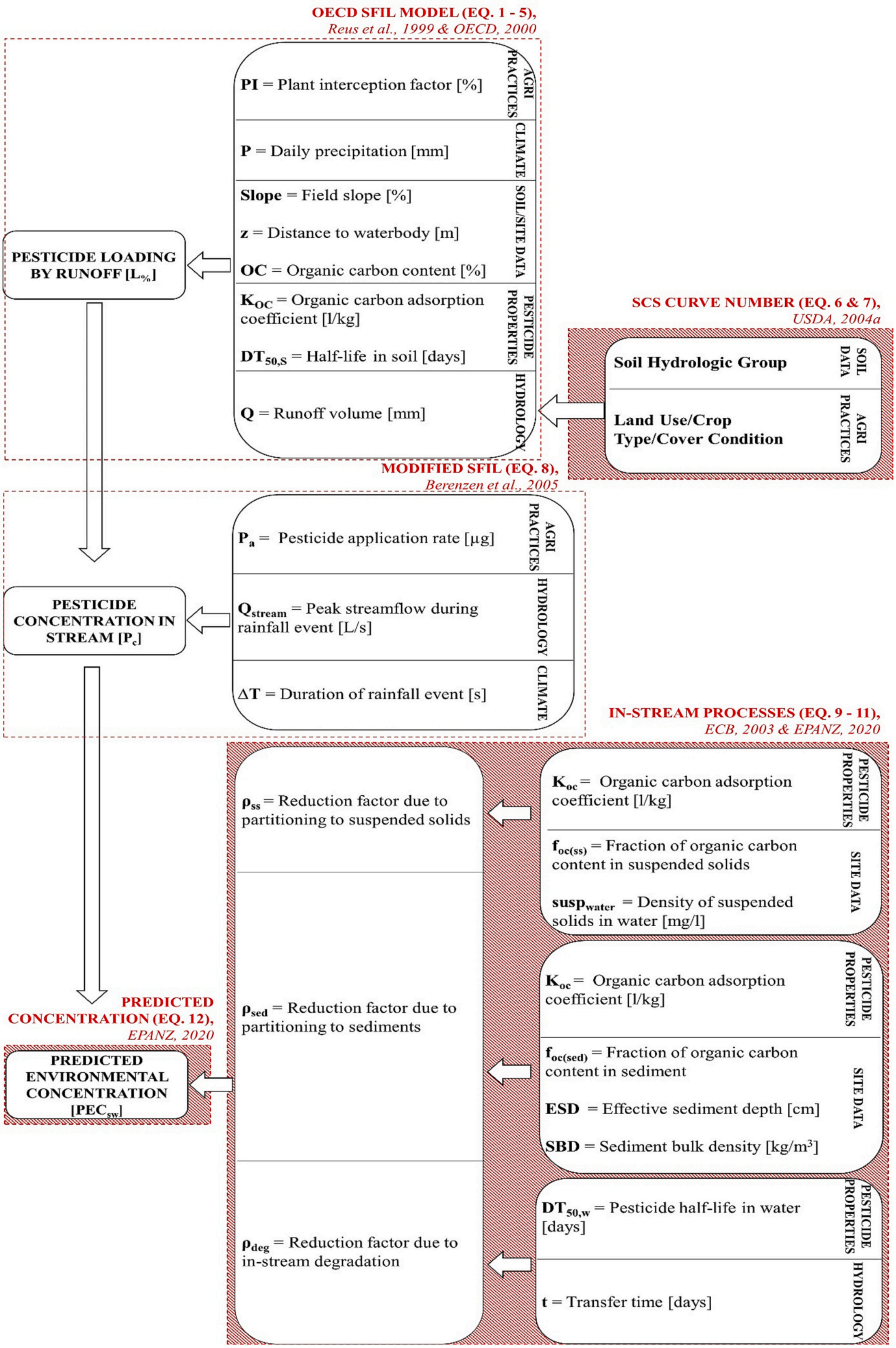


Fig. 1. Modified surface runoff model framework; Modifications to existing model shown in hatched areas.

$$f_2 = 0.83^z \tag{4}$$

where z is the distance to the waterbody (m). In this study, a buffer zone of zero metres was assumed in line with findings in literature that this factor overrepresents the effects of buffer zones on pesticide mobility (Schriever and Liess, 2007).

The amount of applied pesticide intercepted by crop cover was included using factor f_3, whereby:

$$f_3 = 1 - \frac{PI}{100} \tag{5}$$

where PI is the plant interception factor (%), based on the crop type and its growth stage, as adapted for FOCUS (2002).

To date, runoff volume (Q) was obtained from methods described by Lutz (1984) and Maniak (1992), which were only available for two soil types: sandy and loamy, and only applied to three site scenarios: Scenario 1, bare soil (i.e. pre-emergence) with high moisture content; Scenario 2, bare soil with low moisture; and Scenario 3, covered soil (i.e. crops in growth stages) with low moisture. This limits the ability of the SFIL model to represent a variety of sites as there are various combinations of soil types, moisture content and crop cover not considered. Consequently, the current study applied an approach of obtaining runoff volume through the use of the SCS Curve Number method. The SCS Curve Number method is used by the USDA to estimate runoff volumes from small agricultural catchments (USDA, 2004) in order to provide more site-specific estimations of runoff volumes. A curve number was obtained based on a specific combination of a site's hydrologic soil group, land use and crop type (USDA, 2009) (Table S1 & S2). The curve number (CN) was then used herein to assess the maximum potential soil retention (S) of a site before runoff occurs:

$$S = \frac{25400}{CN} - 254 \tag{6}$$

Runoff is expected to occur when precipitation exceeds 20 % of the soil's maximum potential retention, and the resulting runoff volume was calculated as follows (USDA, 2004):

$$\begin{aligned} Q &= \frac{(P - 0.2S)^2}{(P + 0.8S)}; \text{for } P \geq 0.2\text{S} \\ Q &= 0; \text{for } P < 0.2\text{S} \end{aligned} \tag{7}$$

Many of the more complex edge-of-field runoff models such as PRZM (Suárez, 2005), as well as catchment-scale models such as AGNPS and SWAT (Bingner and Theurer, 2001; Arnold et al., 2012), use the SCS Curve Number method for their runoff estimations. This method was utilised herein for a more detailed representation of site conditions by considering soil texture, land use, and growth stage.

As shown in Fig. 1, the pesticide loading by runoff ($L_{\%}$) obtained in Eq. 1 was then used to calculate P_c, the edge-of-field concentration (μg/l) as per Berenzen et al. (2005):

$$P_c = L_{\%}\ x\ P_a\ x \frac{1}{Q_{stream}\ x \Delta t} \tag{8}$$

where P_a is the pesticide application rate to the site (μg), Q_{stream} is the flowrate of the stream during the rainfall event (l/s), Δt is the duration of the rainfall event (s).

The SFIL is an edge-of-field model and cannot account for the fate or behaviour of a pesticide once it enters a waterbody. However, this study expands upon previous studies by considering the potential reduction in pesticide concentration resulting from instream processes. Adsorption of pesticides to suspended solids and sediment (Eqs. 9 and 10), and in-stream degradation (Eq. 11) were considered as suggested by the European Chemical Bureau (ECB, 2003), and modified by the EPA NZ (2020). The reduction due to adsorption to suspended solids in the waterbody was calculated as follows:

$$\rho_{ss} = \frac{1}{1 + \left(f_{oc(ss)}\ x\ K_{oc}\ x\ susp_{water}\right)\ x\ 10^{-6}} \tag{9}$$

where $f_{oc(ss)}$ is the fraction of organic carbon content in suspended solids, and $susp_{water}$ is the density of suspended solids in water (mg/l) (ECB, 2003).

The reduction of pesticide concentration due to adsorption to sediment was accounted for as follows:

$$\rho_{sed} = \frac{z}{z + ESD\ x\ SBD\ x\ f_{oc(sed)}\ x\ K_{oc}} \tag{10}$$

where z is the depth of the waterbody (cm), ESD is the effective sediment depth (cm), SBD is the sediment bulk density (kg/m^3) and $f_{oc(sed)}$ is the fraction of organic carbon in sediment in accordance with ECB (2003) and FOCUS (2015) guidelines.

Pesticide concentrations are also reduced through in-stream chemical and biotic degradation processes. These were considered in the following first-order degradation factor:

$$\rho_{deg} = e^{\frac{-ln2t_r}{DT_{50,w}}} \tag{11}$$

where $DT_{50,w}$ is the pesticide half-life in water (days) and t_r is the residence time (days). A residence time of five days was assumed based on FOCUS (2015).

These factors are combined with the edge-of-field pesticide concentration, P_c, so that the final predicted environmental concentration (PEC_{sw}) may be calculated:

$$PEC_{SW} = \rho_{ss}\ x\ \rho_{sed}\ x\ \rho_{deg} x\ P_c \tag{12}$$

where the reduction factors ρ_{ss}, ρ_{sed} and ρ_{deg} represent the reduction in pesticide concentration due to adsorption to suspended solids and sediment, and in-stream degradation, respectively (Eqs. 9, 10 & 11), and P_c is the edge-of-field surface water concentration (Eq. 8).

2.3. Human health risk assessment

Firstly, the estimated daily intake of a pesticide was obtained for adult and child population using FAO and WHO guidelines (FAO and WHO, 1997):

$$EDI = \frac{PEC\ x\ WC}{BW\ x\ 1000} \tag{13}$$

where EDI is the estimated daily intake (mg/kg/day), PEC is the predicted environmental concentration (μg/l) obtained from Eq. 12, WC is daily water consumption (l/day), BW is body weight (kg) and 1000 is a conversion factor to convert micrograms to milligrams. A probabilistic approach, as described in Section 2.4, was applied to this model using statistical parameters presented in Section 3.

The calculated EDI was then compared to the acceptable daily intake to assess the risk quotient (RQ), or the likelihood of chronic human health risk associated with exposure to an individual pesticide, as recommended by both the EU and WHO (EFSA, 2019):

$$RQ = \frac{EDI}{ADI} \tag{14}$$

where EDI is obtained from Eq. 13 and ADI is the acceptable daily intake (mg/kg/day), the level of daily pesticide exposure at which no adverse effects are expected which was obtained from EFSA reports for each pesticide (EFSA, 2021).

In order to quantify the risk resulting from pesticide mixtures, the concentration addition approach was applied as recommended by the EFSA (EFSA, 2019). In this study, it was conservatively assumed that all study pesticides were presented in the mixture. The resulting total health risk posed by the mixture is calculated as the sum of risk quotients for individual pesticides (i):

$$RQ_{sum} = \sum_{i=1}^{n} RQ_i = \sum_{i=1}^{n} \frac{EDI_i}{ADI_i} \tag{15}$$

In either case, if the risk quotient is greater than one, the risk associated with the level of pesticide exposure was deemed unacceptable and adverse health effects may occur. If the risk quotient is less than one, there is no likelihood of health risk and therefore the level of exposure is deemed acceptable.

2.4. Probabilistic model methodology

A probabilistic approach was adopted using the Monte-Carlo technique, as it is recognised as a useful and reliable method for probabilistic assessments and uncertainty analysis. Monte-Carlo simulations involve random sampling of input parameters and successive model runs to produce statistical distributions of outputs. For each model iteration one value is randomly selected from the probability distribution of each input parameter and the model output results in a probability distribution, in this case a distribution of pesticide concentrations, and subsequently risk quotients. To ensure the statistical stability of the model's outputs, the Monte Carlo simulation was run for 1,000,000 iterations. Both the model developed in this study and the Monte Carlo simulation were programmed using MATLAB®. Distributions were selected for several of the model inputs, e.g. Irish rainfall data from Met Éireann (2022), based on best-fit analysis of recorded data on MATLAB®, and a review of distributions used in literature to date for parameters. The distributions and statistical parameters used in the models are presented in Tables 1 and 2.

2.5. Sensitivity analysis methodology

Analysis was conducted to test the sensitivity of the model to variation in input parameters, thus identifying critical input parameters. In this study overall model sensitivity, as well as the influence of five important factors: rainfall pattern, timing between application, curve number, instream processes and seasonal conditions, were examined. Triclopyr was selected in this case as it had the highest modelled concentrations as discussed in Section 4.1 and the results were discussed in terms of the effects on its 95th percentile concentration. However, where the model results are particularly affected by pesticide properties, additional analysis was included to highlight these affects. Model sensitivity was assessed using the simple approach of one-at-a-time sensitivity analysis (Dabrowski and Balderacchi, 2013). This involves varying each input parameter independently within a realistic range, and then observing the resulting impact on the model predictions. In this study a ± 10 % range was used, as has been used in literature (Probst et al., 2005; Faúndez Urbina et al., 2020) and its impact was observed. To investigate how the model may respond to different rainfall levels, the model was run using rainfall data from the west coast of Ireland, the wettest part of the country (μ = 4.1 mm/day, σ = 5.89; 1187 mm/year), in place of original rainfall data (μ = 2.7 mm/day, σ = 5.28; 847 mm/year). The impact of application timing has on pesticide runoff was examined by running the model for one, two and five days between application and rainfall. To assess the impact that different site conditions, and resulting curve numbers, have on the results, the model was run for a grassland site with alternative soil conditions. The effects of the additional instream processes were assessed by running the model with and without these instream processes. The model was also run for two climatic scenarios using annual rainfall (μ = 2.7 mm/day, σ = 5.28) and the rainfall levels prevalent during the growing season, assumed to be March – October (μ = 2.4 mm/day, σ = 5.19), to assess the impact on the modelled results.

Table 1
Statistical parameters for probabilistic runoff model.

Parameter	Unit	Distribution/ model	Parameters utilised	Source
$DT_{50,s}$	days	Normal*	Pesticide Specific (see Table S4)	
t	days	Fixed	3	(OECD, 2000)
K_{OC}	l/kg	Normal*	Pesticide Specific (see Table S4)	
OC	%	Normal*	μ = 2.36; σ = 2.79	(Fay et al., 2007; EPA, 2021b)
PI	%	Uniform	min = 0; max = 70	(Labite and Cummins, 2012; FOCUS, 2015)
P	mm	Gamma*	a = 0.255; b = 10.457	(Mockler et al., 2016; Met Éireann, 2022)
S	mm	Based on Curve Number	–	(USDA, 2004)
slope	%	Fixed	3	(Clarke et al., 2016)
z	m	Fixed	0	(Berenzen et al., 2005)
P_a	μg	Fixed	Pesticide Specific (see Table S4)	
Q_{stream}	l/s	Lognormal*	μ = 6.602; σ = 1.562	(WMO, 1989; EPA, 2021a)
Δt	s	Fixed	3600	(APVMA, 2020)
$f_{oc(ss)}$	kg	Fixed	0.1	(ECB, 2003)
$susp_{water}$	mg/l	Fixed	15	(ECB, 2003)
$f_{oc(sed)}$	–	Fixed	0.05	(ECB, 2003)
ESD	cm	Fixed	0.8	(FOCUS, 2015)
$DT_{50,w}$	days	Normal*	Pesticide Specific (see Table S4)	
t_r	days	Fixed	5	(FOCUS, 2015)

* Distribution type has been selected based on recommendations from literature, distribution parameters developed from best-fit analysis to data.

Table 2
Population data and statistical parameters.

Parameter	Unit	Distribution	Statistical parameters	Source
Adult Body Weight	kg	Normal	μ = 78.0, σ = 16.5	(IUNA, 2011)
Child Body Weight	kg	Normal	μ = 32.5, σ = 11.4	(IUNA, 2021)
Adult Water Intake*	l/day	Lognormal	μ = 1.2, σ = 0.68	(USEPA, 2004a; IUNA, 2011)
Child Water Intake*	l/day	Lognormal	μ =0.5, σ = 0.32	(USEPA, 2004a; IUNA, 2021)

* Includes water-based drinks such as tea and coffee.

3. Case study

An Irish case study was used herein to illustrate how the proposed framework can be applied to estimate pesticide concentrations in waterbodies and assess resulting health risks due to pesticide use on an agricultural site. Site specific data was obtained from national pesticide, soil, and weather databases, while pesticide properties were obtained from European databases. A hypothetical site of a field with a stream running alongside was developed to represent an Irish agricultural scenario using dominant and/or average conditions for land use, soil properties, climate conditions and agricultural practices. Model simulations were carried out for a grassland site (pasture, rough grazing, silage, hay or any combination), as it makes up approximately 90 % of Irish agricultural land (Cawkwell et al., 2017). Irish soil maps, reports and databases were used to identify the dominant soil hydrologic groups in Ireland (EPA, 2021b). Based on USDA classifications (USDA, 2009), approximately 48 % of soils were found to be Group C soils, and 39 % of soils were Group B soils (Table S1 description of soil groups). Group C was selected for modelling as it was the more prevalent soil type in Ireland, and associated properties were identified based on analysis of the EPA Soils database (EPA, 2021b). However, as Group B is the second most prevalent soil group, (39 % compared to 48 %), and therefore is also widely representative of Irish soils additional analysis was carried out for this soil type in Section 4.3. Precipitation and hydrologic data were obtained from Met Éireann (Met Éireann, 2022), and EPA (EPA, 2021a) or GSI (GSI, 2021) databases, respectively and analysis of the rainfall data was carried out to assess the likelihood of runoff events for the selected site scenario.

Pesticide usage surveys carried out by the Department of Agriculture, Food and the Marine (DAFM) have identified 82 pesticides used on grassland and fodder crops in Ireland for the years 2016 and 2017 (DAFM, 2020, 2021). The DAFM publishes national data over a five-year reporting period, therefore 2016/2017 data was used in this study as it was the most recent data available. Results of risk screening study of pesticides used in Irish agriculture were used to select 15 pesticides due to their mobility, potential impact on human health, quantity of use, or a combination of the three (Harmon O'Driscoll et al., 2022). Relevant pesticide specific data used in the modelling process are presented in Table S4. Pesticide risk was assessed for both Irish adults and children. Statistical parameters and distributions for population data were obtained from the Irish Universities Nutritional Alliance and the USEPA to allow for this probabilistic approach to be applied (Table 2) (IUNA, 2011, IUNA, 2021, USEPA, 2004a).

4. Results and discussion

4.1.1. Predicted concentrations in surface water

As stated in Section 2.1, the incorporation of the SCS curve number method allows site properties to be accounted for in the rainfall-runoff relationship, i.e., the amount of rainfall required to result in a runoff event is dictated by a site's soil type and land use. The daily likelihood of rainfall exceeding required levels for runoff occurring for a number of site combination in the east of Ireland is presented in Fig. 2.

The grassland site with group C soils selected for this study requires a minimum of 8.3 mm of rainfall for runoff to occur (Fig. 2). Based on 35 years of rainfall data in the east of Ireland, such a rainfall event is expected to occur approximately 10 % of the time, an average of 36 days each year. Consequently, the vast majority of modelled days will result in no runoff and, as a result, the model will predict a zero result for in-stream pesticide concentrations. However, there is a variation of pesticide concentrations predicted on the days where runoff will occur; this bimodal nature of modelled results is demonstrated for triclopyr in Fig. S1 in the Supplementary Information. The likelihood of no runoff, and as a result no pesticide detection, is very high in Fig. S1. This is consistent with monitoring programmes of Irish rivers carried out by the EPA over a five-year period, which detected pesticides in 4.1 % of 16,069 measurements (EPA, 2019).

The pesticides have been ranked based on their predicted 95th and 99th percentile concentrations in Table 3 for 1 million model runs, as is the likelihood of exceeding the 0.1 μg/l legal limit. Only the 95th and 99th percentile values are presented as there are no predicted concentrations below the 90th percentile due to rainfall not exceeding 8.3 mm for 90 % of model runs (see Fig. 2). Triclopyr was found to have the highest concentration of 8.7 μg/l, followed by 2-methyl-4-chlorophenoxyacetic acid (MCPA) (7.56 μg/l), and mecoprop (5.13 μg/l). All three pesticides have very low K_{oc} values – in fact they have the second, third and sixth lowest, respectively, of the 15 pesticides. Therefore, they are unlikely to adsorb to soil, making them more available to surface runoff. Mecoprop is not very persistent in soil but is very persistent once in water, with an average half-life of approximately 155 days, and has a relatively high legal application dose. Hence it ranks higher than more mobile pesticides like 2,4-Dichlorophenoxyacetic acid (2,4-D), which rapidly breaks down in water with a half-life of 9.4 days, or clopyralid

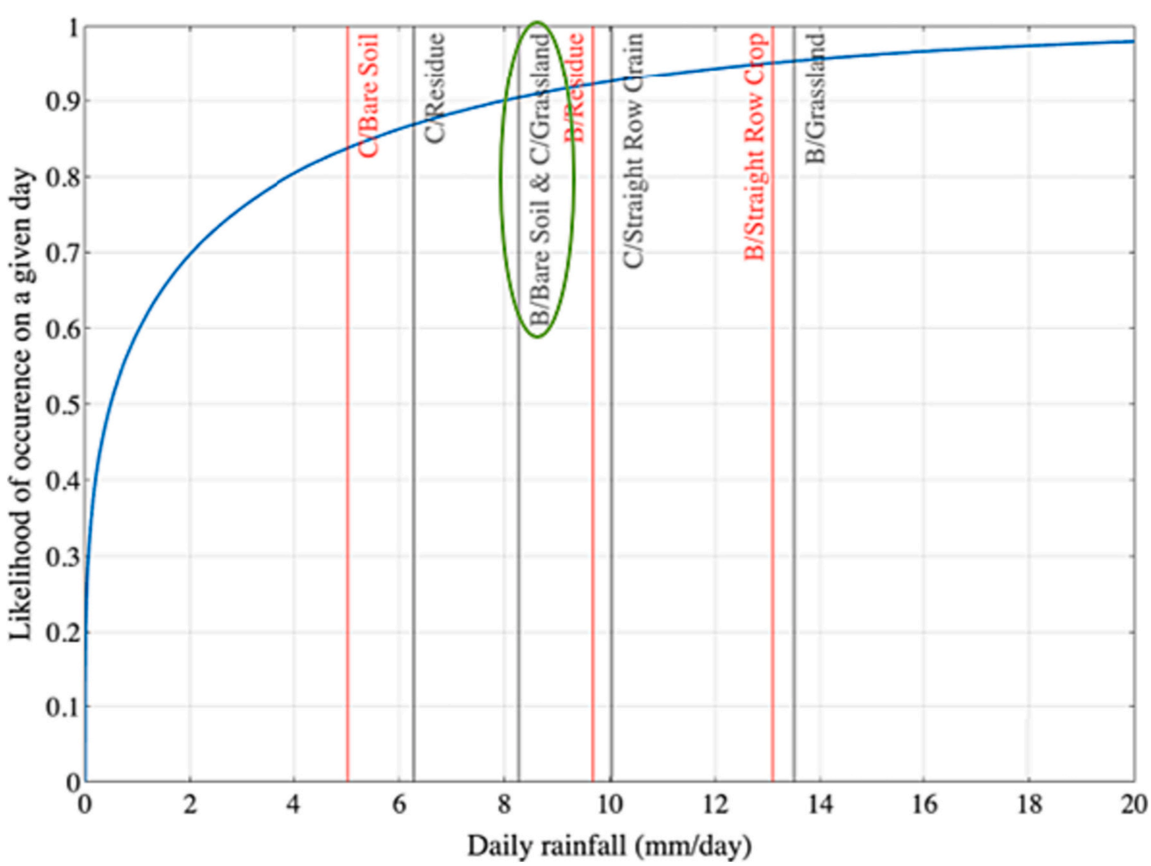


Fig. 2. Likelihood required rainfall in East Ireland for different combinations of land use and soil groups common in Ireland. Site scenario used in case study highlighted.

Table 3
Ranking of selected pesticides based on predicted concentration in surface water (including zero-runoff days).

Pesticide	95th Percentile (μg/l)	99th Percentile (μg/l)	Likelihood of exceedance (%)	Rank
Triclopyr	0.49	8.7	7.2	1
MCPA	0.38	7.56	6.8	2
Mecoprop	0.27	5.13	6.4	3
2,4-D	0.27	4.85	6.4	4
Clopyralid	0.21	3.48	6.1	5
Fluroxypyr	0.1	1.76	5.0	6
2,4-DB	0.04	1.13	3.6	7
Terbuthylazine	0.036	0.72	3.4	8
Penthiopyrad	4.3e-3*	0.095	0.95	9
Propyzamide	2.2e-3*	0.06	0.63	10
Prochloraz	1.2e-4*	4.0e-3*	0.05	11
Glyphosate	5.5e-5*	2.6e-3*	0.07	12
Pendimethalin	3.1e-5*	7.7e-4*	0.005	13
Prothioconazole	1.8e-5*	5.7e-4*	0.003	14
Phenmedipham	1.3e-12*	2.1e-8*	0	15

* Predicted concentration less than the limit of detection (LOD) (Table S5).

which is applied at a much lower dose than mecoprop. Conversely, the two lowest ranked pesticides, prothioconazole and phenmedipham, have 99th percentile concentrations of 7.7e-4 μg/l and 2.1e-8 μg/l, respectively. Both are relatively immobile as they readily adsorb to soil with high K_{OC} values. Prothioconazole is the least persistent pesticide in soil and is also non-persistent in water, while phenmedipham rapidly degrades in water with an average $DT_{50,W}$ of <5 h. It is to be expected that concentrations of such immobile and non-persistent pesticides would be nearly undetectable in surface water, as has been found in monitoring studies (Aamlid et al., 2021). The modelled ranking of the pesticides is in broad agreement with the ranking of pesticides detected in Irish EPA monitoring. Of 14 pesticides monitored in 144 rivers in Ireland over a five-year period found that MCPA was the most widely detected pesticide in Irish rivers, followed by mecoprop and 2,4-D (EPA, 2019). The ranking of the modelled pesticides agrees with most commonly detected pesticides in this nationwide monitoring programme, whereby MCPA, mecoprop and 2,4-D were also predicted to have three of the four highest concentrations in this study.

Pesticide detections in Irish surface water are relatively infrequent and the majority of model runs in this study result in no pesticide runoff. However, it is important to recognise that pesticide runoff can still occur with concentrations exceeding legal limits for drinking water. The legal limits set within the EU were not based on toxicological studies, and are therefore not significantly relevant in terms of health risk assessments (Dekant et al., 2010). However, these threshold values are important in assessing water quality due to their practical application within the EU in a legislative context. To better investigate potential pesticide transport, and allow for comparisons between pesticides, the model results were truncated to only include runoff events i.e. the distribution shown in the inset of Fig. S1. Henceforth only the pesticide concentrations from rainfall events exceeding the required level to result in runoff are assessed, and the resulting concentration distributions of the 15 pesticides modelled in this study are presented in Fig. 3. It is important to keep in mind the context of likelihood of exposure when examining the predicted concentrations of the selected pesticide. The 90th percentile concentrations of several pesticides presented in Fig. 3 are relatively high when compared to the EU's legal limit of 0.1 μg/l for individual pesticides in drinking water (European Commission, 1998), and even the limit of 0.5 μg/l for total pesticide concentration set out by the original drinking water quality directive 75/440/EEC (European Commission, 1975) which is still in place today. However, these limits were derived using the lowest limit of detection at the time, rather than actual pesticide toxicology, and are perceived by some to represent the EU's desire to have no level of pesticides in drinking water (Dolan et al., 2013). Additionally, Fig. 3 relates only to simulations when runoff occurs i.e. approximately 10 % of days annually, as stated above. In that context, a 9.37 μg/l concentration of triclopyr is predicted to occur less than four times a year. These concentrations will be further investigated in terms of their toxicity in Section 4.2.

Only one of the fungicides selected for this study, penthiopyrad, is predicted to reach the legal limit of 0.1 μg/l at the 90th percentile concentration, the resulting health implication of these exceedances will be discussed in Section 4.2. In general, fungicides are relatively immobile with moderate to high adsorption coefficients (Zubrod et al., 2019), while the herbicides selected in this study tend to be very mobile. Penthiopyrad has a comparatively low adsorption coefficient of 796.8 l/kg for a fungicide and is also significantly persistent in both soil ($DT_{50,s}$ of 122 days) and water ($DT_{50,W}$ of 279 days). The other fungicides selected for this study either rapidly breakdown in soil and water, such as prothioconazole (14th of 15) (Fig. 3), or are very immobile, such as prochloraz. This is also reflected in data from monitoring programmes of European surface waters from 2007 to 2017, which found that herbicides were the cause of the majority of pesticide exceedances, with 5–15 % of herbicide detections resulting in an exceedance, while fungicides exceeded limits in <1 % of cases (Mohaupt et al., 2020). This suggests that fungicides tend to be of lesser concern in surface water despite being used in similar quantities as herbicides within the EU (McGinley et al., 2023a).

4.1.2. Comparison of predicted concentrations with measured data

In order to assess whether the model produced realistic results, the predicted environmental concentrations were compared to monitoring data from a two-year long field study (McGinley et al., 2023b). These field studies were carried out at two locations in the north and east of the country, monitoring surface waterbodies for some of the most widely used pesticides in Ireland: MCPA, fluroxypyr, triclopyr, 2,4-D, mecoprop and clopyralid. The monitoring sites were predominately grassland, with moderate-to-poor draining soils, similar to the hypothetical site developed for the case study. Passive water samplers were in-situ for two weeks every month during the monitoring periods of April to November, inclusive, for the years 2021 and 2022. For each month a 14-day time-weighted average concentration was obtained for the monitored pesticides. In order to compare the predicted surface water concentrations in this study to the measured data, an average daily concentration was calculated every 14 model runs (representing 14 days in the model) to develop comparable concentrations. The 14-day average concentrations obtained from the field studies and the modelled results were compared in Fig. 4 to assess whether the model produced realistic results for Irish agricultural sites. It is noted that this comparison is intended as a form of 'reality check' on the model output, rather than a direct comparison. The hypothetical modelled site used was developed based on the most common features of Irish agriculture land (soil conditions, crop type, etc), so that it could be widely representative of many agriculture sites in Ireland, rather than a single localised monitored location. Direct comparison between the model results and the measured concentrations thus cannot made as the modelled site conditions are not an exact replica of the conditions present at the monitored sites. Comparison with real monitoring data within Ireland is still however useful. Overall the modelled concentrations showed broad agreement with the monitored concentrations, with both the monitoring programme and the model detecting relatively high 95th percentile concentrations of MCPA, 2,4-D and triclopyr compared to the legal limit in drinking water. Agreement between the monitored and modelled concentrations of the other three pesticides was not as good, this may reflect the extent of usage of these pesticides in the field studies, and modelling assumptions. All pesticides were modelled for their full recommended doses, which may not be the case in reality. Mecoprop and clopyralid made up only 8 % and 10 % of detections, compared to MCPA and fluroxypyr 25 % and 22 %, suggesting that the pesticides with poorer agreement are not widely used in the areas where the monitoring was carried. Additionally, some disparity between the model results and measured concentrations are to

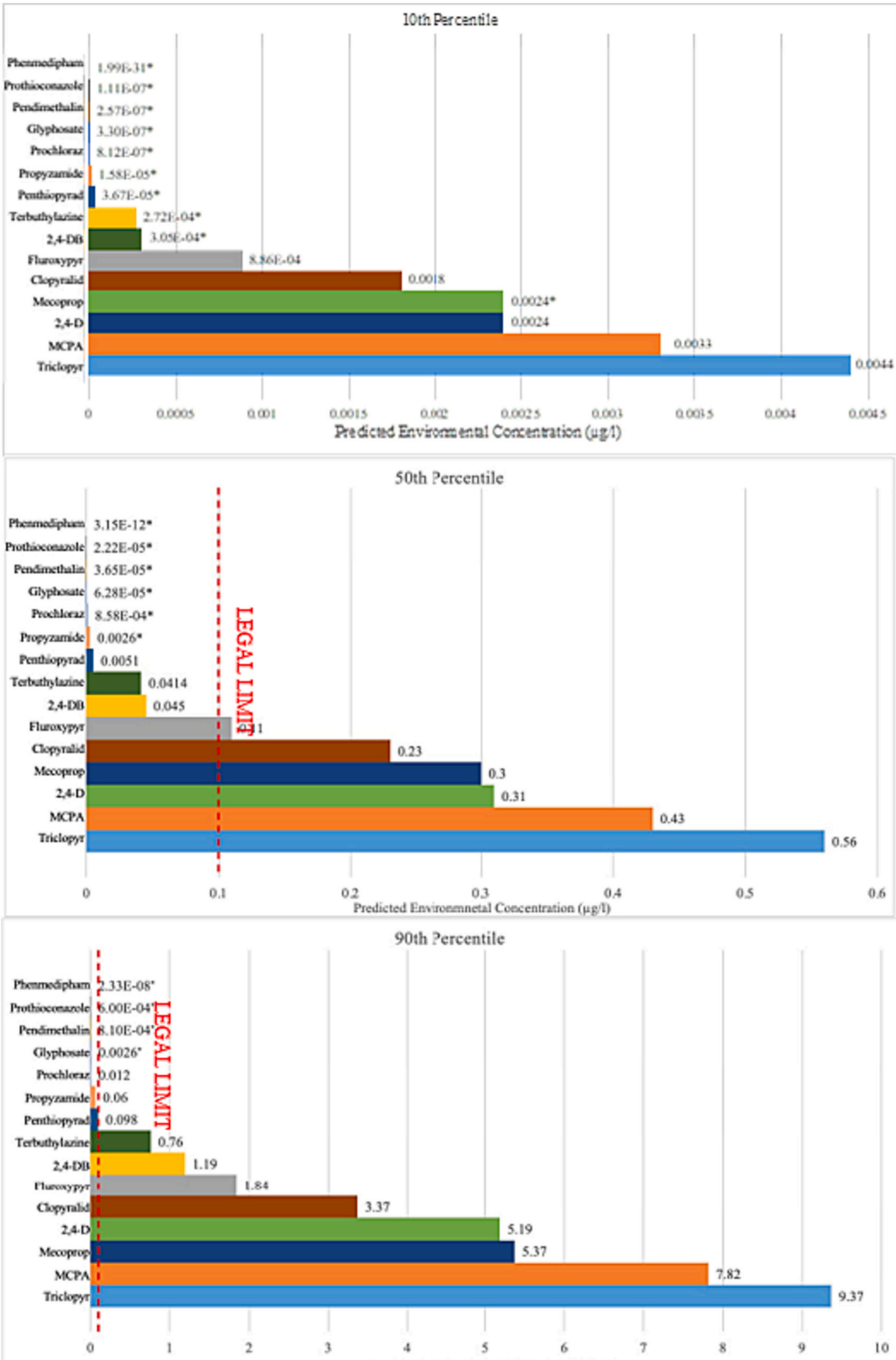


Fig. 3. a) 10th, b) 50th, and c) 90th percentile concentrations on days when rainfall exceeds 8.3 mm (* denotes less than LOD (Table S5)).

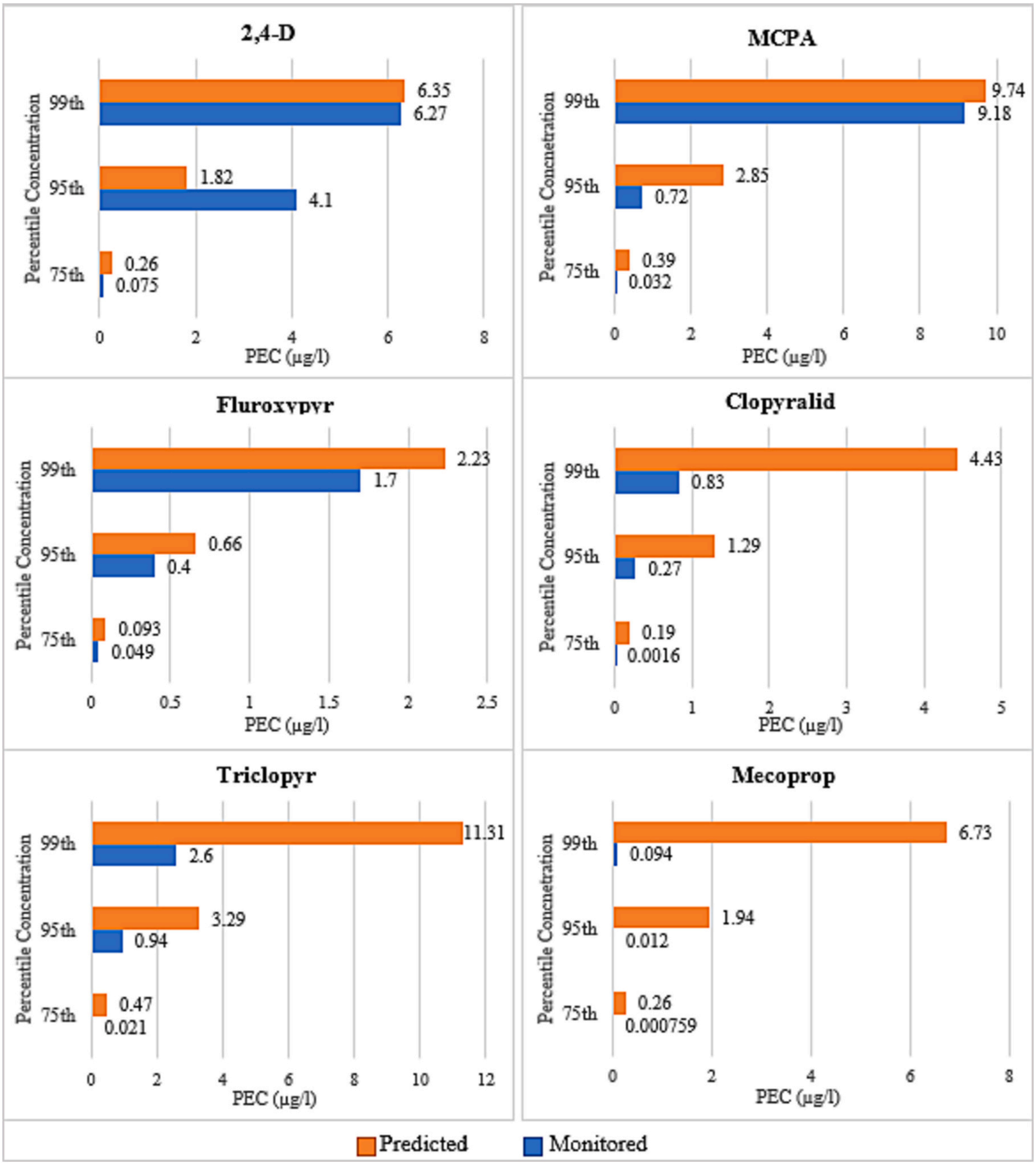


Fig. 4. Predicted vs monitored concentrations of pesticides in runoff.

be expected due to the differences in site conditions and model limitations. These limitations include the lack of consideration of some factors that may further influence pesticide transport, including alternative degradation pathways and volatilisation, have not been included. However, the comparison presented here suggests that the model can produce relatively realistic results for the modelled conditions, while remaining simple enough to encourage adoption across a broad user base.

4.2. Human health risk assessment

For the sake of brevity only the 99th percentile EDIs, the fixed ADI values obtained from the EFSA and risk quotient values are presented in Table 4. Triclopyr has the highest EDI for adults and children. Overall children have a higher rate of exposure to pesticides in drinking water due to their higher water consumption rate in terms of body weight (Rezaei Kalantary et al., 2022). However, the daily levels of exposure for both adults and children are predicted to be well below the acceptable daily intake for all pesticides, even at the most extreme concentrations.

As was the case for the modelled EDIs, the risk quotient for children's health is higher than adults for example, exposure to mecoprop results in a 99th percentile risk quotient of 0.015 for adults but 0.019 for children. From Table 4, the pesticides with the highest potential to harm human health due to exposure via surface water were mecoprop, triclopyr and 2,4-D (risk quotients of 0.023, 0.013 and 0.011, respectively). It is interesting to note that despite terbuthylazine's relatively low concentrations in drinking water (8th out of 15, Table 3), it has the 4th highest risk quotient. This may be explained by its very low ADI of 0.004 mg/kg/day, compared to pesticides such as mecoprop (ADI = 0.01 mg/kg/day), and triclopyr (ADI = 0.03 mg/kg/day). However, terbuthylazine is

Table 4
99th percentile estimated daily intake (mg/kg/day) for adults and children, pesticides' acceptable daily intake (mg/kg/day), and resulting 99th percentile risk quotient.

Pesticide	Rank	EDI Ranking			Health Risk Ranking		
		EDI_{adult}	EDI_{child}	ADI	Rank	RQ_{adult}	RQ_{child}
Mecoprop	3	1.50e-4	1.92e-4	0.01	1	0.008	0.023
Triclopyr	1	1.17e-4	3.24e-4	0.05	2	0.005	0.013
2,4-D	4	1.34e-4	1.70e-4	0.02	3	0.004	0.011
Terbuthylazine	8	1.93e-5	2.42e-5	0.004	4	0.003	0.008
MCPA	2	2.02e-4	2.54e-4	0.05	5	0.002	0.007
2,4-DB	7	3.10e-5	3.94e-5	0.02	6	9.1e-4	0.003
Clopyralid	5	9.57e-5	1.20e-4	0.15	7	3.7e-4	0.001
Fluroxypyr	6	4.91e-5	6.27e-5	0.8	8	3.5e-5	9.6e-5
Propyzamide	10	1.59e-6	2.04e-6	0.05	9	1.9e-5	5.2e-5
Penthiopyrad	9	2.50e-6	3.14e-6	0.1	10	1.5e-5	4.2e-5
Prochloraz	11	9.98e-8	1.27e-7	0.01	11	6.0e-6	1.7e-5
Prothioconazole	14	1.91e-8	2.43e-8	0.05	12	1.8e-7	4.9e-7
Pendimethalin	13	2.06e-8	2.60e-8	0.125	13	9.7e-8	2.7e-7
Glyphosate	12	6.78e-8	8.52e-8	0.5	12	7.9e-8	2.2e-7
Phenmedipham	15	5.1e-13	6.5e-13	0.03	15	1.1e-5	3.0e-11
TOTAL						**0.023**	**0.066**

not widely used in Ireland, with its annual quantity of use 3 % that of the quantity of applied MCPA, therefore it is unlikely to be a major risk to the health of the general public in Ireland. Of the most widely used pesticides in Ireland, both fluroxypyr and glyphosate are ranked very low (8th and 14th lowest). MCPA, however, has a much higher risk quotient score due to its mobility to water supplies, and as a result ranks in the top five pesticides in terms of risk quotient. However, no EDIs exceed their respective ADIs, even the 99th percentile risk quotients are well below an unacceptable level of risk of one. The total level of risk posed by exposure to all pesticides is also well below one for both adults and children at the 99th percentile, with total risk quotients of 0.023 and 0.066 respectively. This suggests that despite concentrations occurring at levels higher than the EU legal limit of 0.1 μg/l, the results indicate that there is currently a very low level of risk to human health via drinking water under normal pesticide application patterns. In fact, if a child with average weight (32.5 kg) and water consumption (0.5 l/day) (IUNA, 2021) was exposed to legal concentrations (0.1 μg/l) of terbuthylazine, the most toxic pesticide in the study, and fluroxypyr, the least toxic, the resulting risk quotients would be 3.85e-4 and 1.92e-6, respectively. Conversely, in order to be exposed to an unacceptable level of risk, a child would have to be exposed to a concentration of terbuthylazine of 260 μg/l, which is over 350 times the 99th percentile of modelled concentration (Table 2). These findings broadly agree with Dekant et al.'s (2010) suggestion that the EU limits were set with little consideration of a pesticide's evaluated toxicological significance and therefore can be overly restrictive for pesticides that have been found to have low human toxicity.

On the basis of the study site conditions and the fifteen pesticides assessed, it suggests that there is little risk associated with the level of pesticide contamination of Irish drinking water sources. However, different agricultural management practices and site conditions will result in varying levels of exposure and health risks, therefore it cannot be assumed that the contamination of Irish water supplies pose no risk to human health. Additionally, a fundamental issue with pesticide health risk assessment lies with classification of pesticide toxicity. It has been suggested that some pesticides have been incorrectly classified as low-risk due to misreporting of some pesticides' neurotoxicity by the pesticide industry (Mie and Rudén, 2023), and contradicting reports on the toxicity of pesticides (Kalofiri et al., 2021). Conversely, restrictions on the use of other may be overprotective, as they have been found to have overly conservative exposure limits (Moxon et al., 2020). It is therefore important to interpret the results of this study in the context of the recently revealed limitations that exist around international pesticide toxicity classification, in addition to the issues associated with assessments on a site-specific level, and modelling limitations.

4.3. Sensitivity analysis

The impact of variation in input parameter on the final output, risk quotient, was assessed in accordance with the + − 10 % of mean approach outlined in Section 2.5 above. The health risk model was most sensitive to variation to the pesticide's ADI (+15 %,-11 %). The in-stream concentration was found to be almost as influential (+15 %,-10 %), and was followed by body weight (+9 %, − 5 %) and finally water consumption (+3 %, − 1 %). As the in-stream concentration was found to be a highly influential parameter, and involves a number of parameters and computational processes, further analysis of the influence of parameter variability and model sensitivity was carried out as presented in the following sections.

4.3.1. Model sensitivity

The runoff model was most sensitive to a variation in rainfall (+22 %, −25 %), distance to waterbody (−16 %), field slope (+14 %, −10 %), pesticide application rate, (+10 %, −9 %), and stream flowrate (+3 %, −7 %). Both distance to waterbody and slope were identified as critical parameters by Probst et al. (2005), while Schriever and Liess (2007) and Utami et al. (2020) found that daily average rainfall was one of the most influential parameters. Most of the influential parameters in this study are modelled as fixed variables due to their localised nature. This highlights the importance for obtaining site-specific data where possible for best representation of the modelled site.

4.3.2. Impact of rainfall data on model output

Rainfall was identified as the most important parameter for runoff. The change in rainfall data, using precipitation data from the west of the country, represented a 51 % increase in daily average rainfall and, resulted in a 210 % increase in 95th percentile concentration of triclopyr in surface water. This most likely due to an increase in days where rainfall exceeds the level required for runoff to take place in accordance with the SCS curve number approach (USDA, 2004).

4.3.3. Impact of timing of application on model output

The resulting impact of varying application timing for one, two and five days on triclopyr's 95th percentile concentration was +6.1 %, +4.1 % and − 4.1 % respectively. Triclopyr is moderately persistent with a mean $DT_{50,s}$ of 35 days, therefore changing the number days between application and rainfall by a few days does not have as large an impact as it would for a pesticide that rapidly degrades such as prothioconazole with a half-life of 2.8 days (+11 %, +50 % and − 40 % impact on 95th percentile concentrations).

4.3.4. Impact of curve number on model output

The change in site scenario was found to have a significant impact on the modelled results, as much more rain is required for runoff to occur. Rainfall of 13.5 mm is required for group B soils, with only 4.5 % of model runs exceeding this, compared to 8.3 mm or 10 % of model runs for group C soils. As a result, triclopyr's 95th percentile concentration for the new scenario was zero, and there was a 78 % decrease in the 99th percentile concentration. This highlights the importance of site-specific conditions in pesticide transport and illustrates the impact improvements made to the model developed with the addition of the curve number to the SFIL approach, may have to model results.

4.3.5. Impact of in-stream process on model output

Overall, the inclusion of instream processes results in a 51 % decrease in the 95th percentile concentration of triclopyr, with adsorption to sediment contributing most to the reduction in concentration (26 % reduction) and adsorption to suspended solids contributing the least (0.4 % reduction). However, instream processes would have a much greater impact on pesticides with very high adsorption coefficients such as prochloraz, or very short $DT_{50,W}$ such as prothioconazole. If they are removed, the 95th percentile concentrations for these pesticides increase by +3233 % and 11,011 % respectively.

4.3.6. Seasonal analysis

The variation of site conditions and agricultural practices due to seasonal effects can also impact pesticide transport. In Ireland, pesticides tend to be used in the greatest quantities shortly before and during the growing season, which begins in spring and extends until the end of autumn. However, Ireland can experience some of its most extreme periods of rainfall during the winter months, when pesticides are not in use. Therefore, it is important to consider the climatic conditions prevalent during the growing season and avoid including extremely heavy rainfall events that are less likely to occur during this period. As expected, the simulated concentrations of triclopyr were lower for the growing season than the annual conditions, with a 25 % decrease in the 95th percentile concentration over the growing season. This is most likely due to the reduced number of rainfall events that will result in runoff during the growing season, with <8.5 % of rainfall events during the growing season expected to result in runoff, compared to 10 % annually.

5. Conclusions and recommendations

A probabilistic modelling framework was developed, by adapting existing pesticide transport models and combining them with a quantitative health risk assessment approach, to improve the representation of real-world scenarios and quantitatively assess potential human health risks. This framework offers a useful step towards the use of probabilistic analysis in pesticide risk assessment. Although this modelling approach does not incorporate detailed considerations of some of the pesticide transport models, its comparative simplicity facilitates the integration of important uncertainty. Thus, the model provides valuable insights into the relative risks of various pesticides, while using an accessible approach for a wide user base.

An Irish case study was developed to illustrate how the model may be applied and facilitate study of the potential health risks arising from contamination of drinking water by several pesticides used in Ireland. The modelled concentrations were shown to be in broad agreement with the measured concentrations of an Irish field study, and the modelled ranking of pesticides most likely to be detected in surface waters compares well with the findings of Irish and European monitoring studies. Triclopyr, MCPA and clopyralid were found to be the most mobile pesticides and predicted to occur in the highest concentrations. The three highest risk pesticides in terms of human health were found to be mecoprop, triclopyr and 2,4-D, however all pesticides were found to be well below an unacceptable level of risk currently and may only need increased monitoring in areas of high usage in Ireland to ensure levels of risk do not exceed acceptable level. The modelling framework in this study was developed in such a way to allow catchment managers and water quality monitors to adapt the model for their own use. The model was found to be sensitive to variation in localised parameters, suggesting a need for site-specific parameters when using the model. Additional factors such as site location, timing of pesticide application, and the addition of instream processes were all found to affect the modelled results.

The model may be improved through the incorporation of more health data from literature and lab studies, in addition to the use of regulatory thresholds, to allow for greater consideration of uncertainty associated with pesticide toxicity. Future works may include combining this model with environmental risk models to quantitatively assess pesticide risk to aquatic or terrestrial organisms, or the incorporation of geospatial datasets to develop a GIS-based tool. Additionally, input parameters may also be adapted to account for potential effects resulting from climate change.

CRediT authorship contribution statement

J. Harmon O'Driscoll: Formal analysis, Methodology, Software, Writing – original draft, Writing – review & editing, Data curation, Investigation. **J. McGinley:** Data curation, Writing – review & editing. **M.G. Healy:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **A. Siggins:** Funding acquisition, Project administration, Writing – review & editing. **P.-E. Mellander:** Writing – review & editing. **L. Morrison:** Writing – review & editing. **E. Gunnigle:** Writing – review & editing. **P.C. Ryan:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This project is funded under the Irish EPA Research Programme 2014-2020 (Project reference number 2019-HW-LS-3). The EPA Research Programme is a Government of Ireland initiative funded by the Department of Communications, Climate Action and Environment. It is administered by the Environmental Protection Agency, which has the statutory function of co-ordinating and promoting environmental research.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.170589.

References

Aamlid, T.S., Almvik, M., Pettersen, T., Bolli, R., 2021. Leaching and surface runoff after fall application of fungicides on putting greens. Agron. J. 113, 3743–3763.

Abreu-Villaça, Y., Levin, E.D., 2017. Developmental neurotoxicity of succeeding generations of insecticides. Environ. Int. 99, 55–77. https://doi.org/10.1016/j.envint.2016.1011.1019.

Adu, J.T., Kumarasamy, M.V., 2018. Assessing non-point source pollution models: a review. Pol. J. Environ. Stud. 27, 1913–1922.

Ali, I., Alharbi, O.M.L., Alothman, Z.A., Al-Mohaimeed, A.M., Alwarthan, A., 2019. Modeling of fenuron pesticide adsorption on CNTs for mechanistic insight and removal in water. Environ. Res. 170, 389–397.

Aller, L., Bennett, T., Lehr, J., Petty, R., 1985. DRASTIC: A Standardised System for Evaluating Groundwater Pollution Potential Using Hydrogeologic Settings.

Aloizou, A.-M., Siokas, V., Vogiatzi, C., Peristeri, E., Docea, A.O., Petrakis, D., Provatas, A., Folia, V., Chalkia, C., Vinceti, M., Wilks, M., Izotov, B.N., Tsatsakis, A., Bogdanos, D.P., Dardiotis, E., 2020. Pesticides, cognitive functions and dementia: a review. Toxicol. Lett. 326, 31–51.

APVMA, 2020. (Australian Pesticide and Veterinary Medicines Authority) aquatic exposure estimates in Australian pesticide environmental assessments, runoff risk assessment methodology, April 2020.

Arnold, J.G., Kinky, J.R., Srinivasan, R., Williams, J.R., Haney, E.B., Neitsch, S.L., 2012. Soil and Water Assessment Tool (SWAT) input/output documentation. In: Version 2012. Chapter 1: SWAT Input Data - Overview. Texas Water Resources Institute.

Asfaw, A.S., 2018. Development of Real-Time Surface Water Abstraction Management Tools.

Bach, M., Diesner, M., Großmann, D., Guerniche, D., Hommen, U., Klein, M., Kubiak, R., Müller, A., Preuss, T.G., Priegnitz, J., 2017. Pesticide exposure assessment for surface waters in the EU. Part 2: determination of statistically based run-off and drainage scenarios for Germany. Pest Manag. Sci. 73, 852–861.

Beinat, E., Van den Berg, R., 1996. EUPHIDS, a Decision-support System for the Admission of Pesticides.

Berenzen, N., Lentzen-Godding, A., Probst, M., Schulz, H., Schulz, R., Liess, M., 2005. A comparison of predicted and measured levels of runoff-related pesticide concentrations in small lowland streams on a landscape level. Chemosphere 58, 683–691.

Bingner, R.L., Theurer, F.D., 2001. AGNPS 98: a suite of water quality models for watershed use. pp. 1-8.

Bosgra, S., Voet, H.V.D., Boon, P.E., Slob, W., 2009. An integrated probabilistic framework for cumulative risk assessment of common mechanism chemicals in food: an example with organophosphorus pesticides. Regul. Toxicol. Pharmacol. 54, 124–133.

Brodeur, J.C., D'Andrea, M.F., Dip, C., 2023. Statistically based soil–climate exposure scenarios for aquatic pesticide fate modeling and exposure assessment in the Pampa Region of Argentina. Integr. Environ. Assess. Manag. 19, 626–637.

Cantoni, B., Penserini, L., Vries, D., Dingemans, M.M.L., Bokkers, B.G.H., Turolla, A., Smeets, P.W.M.H., Antonelli, M., 2021. Development of a quantitative chemical risk assessment (QCRA) procedure for contaminants of emerging concern in drinking water supply. Water Res. 194, 116911.

Cawkwell, F., Barrett, B., Nitze, I., Green, S., Black, K., Hallahan, P., 2017. Report 198: the Irish Land Mapping Observatory: mapping and monitoring land cover, use and change. EPA Research Report (2011-CCRP-MS1.4).

Clarke, R., Healy, M.G., Fenton, O., Cummins, E., 2016. A quantitative risk ranking model to evaluate emerging organic contaminants in biosolid amended land and potential transport to drinking water. Hum. Ecol. Risk. Assess. 22, 958–990.

Dabrowski, J.M., Balderacchi, M., 2013. Development and field validation of an indicator to assess the relative mobility and risk of pesticides in the Lourens River catchment, South Africa. Chemosphere 93, 2433–2443.

DAFM, 2020. (Department of Agriculture, Food and the Marine) pesticide usage in Ireland - arable crop survey report 2016.

DAFM, 2021. (Department of Agriculture, Food and the Marine) Pesticide usage in Ireland - 2017 Grassland and fodder crop survey report. Available at: https://www.pcs.agriculture.gov.ie/media/pesticides/content/sud/pesticidestatistics/2GrasslandReport2017FinalVersion290520.pdf (accessed on: 11 November 2022).

Dekant, W., Melching-Kollmuß, S., Kalberlah, F., 2010. Toxicity assessment strategies, data requirements, and risk assessment approaches to derive health based guidance values for non-relevant metabolites of plant protection products. Regul. Toxicol. Pharmacol. 56, 135–142.

Dolan, T., Howsam, P., Parsons, D.J., Whelan, M.J., 2013. Is the EU drinking water directive standard for pesticides in drinking water consistent with the precautionary principle? Environ. Sci. Technol. 47, 4999–5006.

ECB, 2003. (European Chemicals Bureau) Technical Guidance Document on Risk Assessment Part II in support of Commission Directive 93/67/EEC on Risk Assessments for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market.

EFSA, 2019. (European Food Safety Authority) Scientific Committee: Guidance on Harmonised Methodologies for Human Health, Animal Health and Ecological Risk Assessment of Combined Exposure to Multiple Chemicals.

EFSA, 2021. (European Food Safety Authority) Pesticide peer review reports database. Available at: https://www.efsa.europa.eu/en/publications (accessed on 17 September 2021).

EFSA, BfR, 2019. European food safety authority and German federal institute for risk assessment. In: International Conference on Uncertainty in Risk Analysis, Berlin.

EPA, 2019. (Environmental Protection Agency for Ireland) Water quality in Ireland 2013–2018.

EPA, 2021a. (Environmental Protection Agency for Ireland) HydroNet: hydrometric database for Ireland. Available at: https://epawebapp.epa.ie/hydronet/#Water%20Levels (accessed on: 22/11/2022).

EPA, 2021b. (Environmental Protection Agency) Irish Soil Information System, Available at: http://gis.teagasc.ie/isis/map.php (Accessed on 8/09/21).

EPA NZ, 2020. (Environmental Protection Agency New Zealand) Risk Assessment Methodology for Hazardous Substances, How to assess the risk, cost and benefit of new hazardous substances for use in New Zealand, January 2020.

European Commission, 1975. Council Directive 75/440/EEC Concerning the Quality Required of Surface Water Intended for the Abstraction of Drinking Water in Member States.

European Commission, 1998. Council Directive 98/83/EC on the 3 November 1998 on the Quality of Water Intended for Human Consumption.

FAO and WHO, 1997. (Food and Agricultural Orginisation for the United Nations, World Health Organisation) Guidelines for predicting dietry intake of pesticide residues. Joint FAO/WHO Food Contamination Montioring Programme.

Faúndez Urbina, C.A., van den Berg, F., van Dam, J.C., Tang, D.W.S., Ritsema, C.J., 2020. Parameter sensitivity of SWAP–PEARL models for pesticide leaching in macroporous soils. Vadose Zone J. 19, e20075.

Fay, D., McGrath, D., Zhang, C., Carrigg, C., O'Flaherty, V., Carton, O.T., Grennan, E., 2007. Towards a national soil database. Associated datasets and digitial information objects connected to this resource are available at: Secure Archive For Environmental Research Data (SAFER) managed by Environmental Protection Agency Ireland. http://erc.epa.ie/safer/resource.

FOCUS, 2002. (Forum for Co-ordiantion of pesticide fate models and their Use) Generic guidance for FOCUS groundwater scenarios. Version 1, 1.

FOCUS, 2010. (Forum for Co-ordination of pesticide fate models and their Use) PRZM - parameterisation for the FOCUS groundwater scenarios. Version 2.0. December 2010.

FOCUS, 2015. (Forum for Co-ordination of pesticide fate models and their Uses) generic guidance for FOCUS surface water scenarios. Version 1, 4.

Gagnon, P., Sheedy, C., Farenhorst, A., McQueen, D.A.R., Cessna, A.J., Newlands, N.K., 2014. A coupled stochastic/deterministic model to estimate the evolution of the risk of water contamination by pesticides across Canada. Integr. Environ. Assess. Manag. 10, 429–436.

Giambò, F., Teodoro, M., Costa, C., Fenga, C., 2021. Toxicology and microbiota: how do pesticides influence gut microbiota? A review. Int. J. Environ. Res. Public Health 18.

GSI, 2021. Groundwater Data Viewer. Geological Survey Ireland, Department of Environment, Climate and Communications. Available at: https://dcenr.maps.arcgis.com/apps/webappviewer/index.html?id=7e8a202301594687ab14629a10b748ef (accessed on 28/11/2022).

Harmon O'Driscoll, J., Siggins, A., Healy, M.G., McGinley, J., Mellander, P.E., Morrison, L., Ryan, P.C., 2022. A risk ranking of pesticides in Irish drinking water considering chronic health effects. Sci. Total Environ. 829, 154532.

IUNA, 2011. Irish Universities Nutrition Alliance. National Adult Food Survey.

IUNA, 2021. (Irish Universities Nutrition Alliance) National Children's Food Survey II.

Kalofiri, P., Balias, G., Tekos, F., 2021. The EU endocrine disruptors' regulation and the glyphosate controversy. Toxicol. Rep. 8, 1193–1199.

Kalyabina, V.P., Esimbekova, E.N., Kopylova, K.V., Kratasyuk, V.A., 2021. Pesticides: formulants, distribution pathways and effects on human health – a review. Toxicol. Rep. 8, 1179–1192.

Labite, H., Cummins, E., 2012. A quantitative approach for ranking human health risks from pesticides in Irish groundwater. Hum. Ecol. Risk. Assess. 18, 1156–1185.

Lammoglia, S.-K., Brun, F., Quemar, T., Moeys, J., Barriuso, E., Gabrielle, B., Mamy, L., 2018. Modelling pesticides leaching in cropping systems: effect of uncertainties in climate, agricultural practices, soil and pesticide properties. Environ. Model. Softw. 109, 342–352.

Li, Z., Niu, S., 2021. Modeling pesticides in global surface soils: evaluating spatiotemporal patterns for USEtox-based steady-state concentrations. Sci. Total Environ. 791, 148412.

Liu, X., Han, H., Xu, H., Zhang, H., Fang, M., Wang, Q., Li, J., Wu, Y., Gong, Z., 2022. Integration of probabilistic exposure assessment and risk characterization for perchlorate in infant formula and supplementary food. Food Chem. Toxicol. 168, 113347.

Luo, Y., Ensminger, M., Budd, R., Deng, X., DaSilva, A., 2014. Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agriculture and Urban Areas II: Refined Priority List. Department of Pesticide Regulation Environmental Monitoring Branch, Sacramento, California.

Lutz, W., 1984. Berechnung von Hochwasserabflüssen unter Anwendung von Gebietskenngrößen. Hydrologie Wasserwirtschaft, Karlsruhe University, Mittlg. Inst.

Malaj, E., Peter, C., Grote, M., Kühne, R., Mondy, C.P., Usseglio-Polatera, P., Brack, W., Schäfer, R.B., 2014. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc. Natl. Acad. Sci. 111, 9549–9554.

Maniak, U., 1992. Regionalisierung von Parametern für Hochwasserabflußganglinien. In: Regionalisierung der Hydrologie (H.B. Kleeberg), DFG, Mittlg. Senatskomm. für Wasserf. 11, S. 325–332.

McGinley, J., Healy, M.G., Ryan, P.C., O'Driscoll, H., Mellander, P.E., Morrison, L., Siggins, A., 2023a. Impact of historical legacy pesticides on achieving legislative goals in Europe. Sci. Total Environ. 873, 162312.

McGinley, J., Healy, M.G., Scannell, S., Ryan, P.C., O'Driscoll, J.H., Mellander, P.-E., Morrison, L., Siggins, A., 2023b. Field assessment of coconut-based activated carbon systems for the treatment of herbicide contamination. Chemosphere 140823.

Mentzel, S., Grung, M., Tollefsen, K.E., Stenrød, M., Petersen, K., Moe, S.J., 2022. Development of a Bayesian network for probabilistic risk assessment of pesticides. Integr. Environ. Assess. Manag. 18, 1072–1087.

Met Éireann, 2022. Historical Weather Database for Ireland. Available at: https://www.met.ie/climate/available-data/historical-data (accessed on 22/11/2022).

Mie, A., Rudén, C., 2023. Non-disclosure of developmental neurotoxicity studies obstructs the safety assessment of pesticides in the European Union. Environ. Health 22, 44.

Mockler, E.M., Chun, K.P., Sapriza-Azuri, G., Bruen, M., Wheater, H.S., 2016. Assessing the relative importance of parameter and forcing uncertainty and their interactions in conceptual hydrological model simulations. Adv. Water Resour. 97, 299–313.

Mohaupt, V., Völker, J., Altenburger, R., Birk, S., Kirst, I., Kühnel, D., Küster, E., Semerádová, S., Šubelj, G., Whalley, C., 2020. Pesticides in European rivers, lakes and groundwaters–data assessment. In: ETC/ICM Technical Report 1/2020: European Topic Centre on Inland, Coastal and Marine Waters.
Moxon, M., Strupp, C., Aggarwal, M., Odum, J., Lewis, R., Zedet, S., Mehta, J., 2020. An analysis of the setting of the acute reference dose (ARfD) for pesticides in Europe. Regul. Toxicol. Pharmacol. 113, 104638.
OECD, 2000. (Organisation for Economic Co-operation and Development) annex 2. Report of phase 1 of the aquatic risk indicators project.
Piffady, J., Carluer, N., Gouy, V., le Henaff, G., Tormos, T., Bougon, N., Adoir, E., Mellac, K., 2021. ARPEGES: a Bayesian belief network to assess the risk of pesticide contamination for the river network of France. Integr. Environ. Assess. Manag. 17, 188–201.
Probst, M., Berenzen, N., Lentzen-Godding, A., Schulz, R., 2005. Scenario-based simulation of runoff-related pesticide entries into small streams on a landscape level. Ecotoxicol. Environ. Saf. 62, 145–159.
Rathjens, H., Kiesel, J., Miguez, M.B., Winchell, M., Arnold, J.G., Sur, R., 2022. Simulation of pesticide and metabolite concentrations using SWAT+ landscape routing and conditional management applications. Water 14.
Rezaei Kalantary, R., Barzegar, G., Jorfi, S., 2022. Monitoring of pesticides in surface water, pesticides removal efficiency in drinking water treatment plant and potential health risk to consumers using Monte Carlo simulation in Behbahan City. Iran. Chemosphere 286, 131667.
Schriever, C.A., Liess, M., 2007. Mapping ecological risk of agricultural pesticide runoff. Sci. Total Environ. 384, 264–279.
Stephenson, C.L., Harris, C.A., 2016. An assessment of dietary exposure to glyphosate using refined deterministic and probabilistic methods. Food Chem. Toxicol. 95, 28–41.
Suárez, L.A., 2005. PRZM-3, a model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones: users manual for release 3.12. In: 2. US Environmental Protection Agency (EPA), Washington, DC.
Tasdighi, A., Arabi, M., Harmel, D., 2018. A probabilistic appraisal of rainfall-runoff modeling approaches within SWAT in mixed land use watersheds. J. Hydrol. 564, 476–489.
Te Roller, J.A., Van den Berg, F., Adriaanse, P.I., De Jong, A., Beltman, W.H.J., 2015. Surface WAter Scenario Help (SWASH) version 5.3: technical description. Statutory Research Tasks Unit for Nature & the Environment (WOT Natuur & Milieu).
Teagasc, 2020. Sustainable Use of Pesticides Directive, Media Article, Available at: https://www.teagasc.ie/publications/2020/sustainable-use-of-pesticides-directive.php.
Teklu, B.M., Adriaanse, P.I., Ter Horst, M.M.S., Deneer, J.W., Van den Brink, P.J., 2015. Surface water risk assessment of pesticides in Ethiopia. Sci. Total Environ. 508, 566–574.
Troldborg, M., Gagkas, Z., Vinten, A., Lilly, A., Glendell, M., 2022. Probabilistic modelling of the inherent field-level pesticide pollution risk in a small drinking water catchment using spatial Bayesian belief networks. Hydrol. Earth Syst. Sci. 26, 1261–1293.
Tudi, M., Daniel Ruan, H., Wang, L., Lyu, J., Sadler, R., Connell, D., Chu, C., Phung, D.T., 2021. Agriculture development, pesticide application and its impact on the environment. Int. J. Environ. Res. Public Health 18, 1112.
Uisce Eireann, 2021. Irish Water, Interim Pesticide Strategy: a collaborative approach with catchment stakeholders, Document No. IW-AMT-STR-010, 2021.
United Nations, 2019. Department of Economic and Social Affairs, Population Division, World Population Prospects: Highlights.
USDA, 2004. (United States Department of Agriculture) chapter 10: estimation of direct runoff from storm events. Part 630 National Engineering Handbook. Natural Resources Conservation Centre.
USDA, 2009. (United States Department of Agriculture) chapter 7:hydrologic soil groups. In Part 630 Hydrology, National Engineering Handbook. Available online. https://directives.sc.egov.usda.gov/OpenNonWebContent.aspx?content=22526.wba.
USEPA, 2004a. (Environmental Protection Agency of the United States) risk assessment guidance for superfund. Volume I: human health evaluation manual (part A). Washington D.C.: Office of Emergency and Remedial Response.
USEPA, 2004b. (Environmental Protection Agency United States of America) an examination of EPA risk assessment principles and practices, Office of the Science Advisor, US Environmental Protection Agency, Washington D.C.
Utami, R.R., Geerling, G.W., Salami, I.R.S., Notodarmojo, S., Ragas, A.M.J., 2020. Environmental prioritization of pesticide in the Upper Citarum River Basin, Indonesia, using predicted and measured concentrations. Sci. Total Environ. 738.
van der Voet, H., de Boer, W.J., Kruisselbrink, J.W., Goedhart, P.W., van der Heijden, G. W.A.M., Kennedy, M.C., Boon, P.E., van Klaveren, J.D., 2015. The MCRA model for probabilistic single-compound and cumulative risk assessment of pesticides. Food Chem. Toxicol. 79, 5–12.
Van Dijk, M., Morley, T., Rau, M.L., Saghai, Y., 2021. A meta-analysis of projected global food demand and population at risk of hunger for the period 2010–2050. Nature Food 2, 494–501.
Wang, R., Yuan, Y., Yen, H., Grieneisen, M., Arnold, J., Wang, D., Wang, C., Zhang, M., 2019. A review of pesticide fate and transport simulation at watershed level using SWAT: current status and research concerns. Sci. Total Environ. 669, 512–526.
Wang, Y.Y.L., Xiong, J., Ohore, O.E., Cai, Y.-E., Fan, H., Sanganyado, E., Li, P., You, J., Liu, W., Wang, Z., 2022. Deriving freshwater guideline values for neonicotinoid insecticides: implications for water quality guidelines and ecological risk assessment. Sci. Total Environ. 828, 154569.
Winchell, M.F., Pai, N., Brayden, B.H., Stone, C., Whatling, P., Hanzas, J.P., Stryker, J.J., 2018. Evaluation of watershed-scale simulations of in-stream pesticide concentrations from off-target spray drift. J. Environ. Qual. 47, 79–87.
WMO, 1989. (World Meteorological Organisation) statistical distributions for flood frequency analysis. Oper. Hydrol. Rep. No. 33.
Young, D.F., Carleton, J.N., 2006. Implementation of a probabilistic curve number method in the PRZM runoff model. Environ. Model Softw. 21, 1172–1179.
Zubrod, J.P., Bundschuh, M., Arts, G., Brühl, C.A., Imfeld, G., Knäbel, A., Payraudeau, S., Rasmussen, J.J., Rohr, J., Scharmüller, A., 2019. Fungicides: an overlooked pesticide class? Environ. Sci. Technol. 53, 3347–3365.