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Research article

A web-based pesticide risk assessment tool for drinking water protection zones in Sweden

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A B S T R A C T

To protect human health, wildlife and the aquatic environment, "safe uses" of pesticides are determined at the EU level while product authorization and terms of use are established at the national level. In Sweden, extra precaution is taken to protect drinking water, and permits are therefore required for pesticide use within abstraction zones. This paper presents MACRO-DB, a tool for assessing pesticide contamination risks of groundwater and surface water, used by authorities to support their decision-making for issuing such permits. MACRO-DB is a meta-model based on 583,200 simulations of the physically-based MACRO model used for assessing pesticide leaching risks at EU and national level. MACRO-DB is simple to use and runs on widely available input data. In a qualitative comparative assessment for two counties in Sweden, MACRO-DB outputs were in general agreement with groundwater monitoring data and matched or were more protective than the national risk assessment procedure for groundwater.

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1. Introduction

Simulation models are used to assess the risks of leaching to groundwater and surface waters in the approvals procedure in the European Union (EU) for the active ingredients in plant protection products under regulation no. 1107/2009 (European Commission, 2009). The modelled scenarios used in these risk assessments at the EU level are designed to identify "safe uses" and are intended to represent "realistic worst-case" agro-environmental conditions. Similar model-based risk assessment procedures are also often employed for product authorizations at the member state level. For example, the leaching model MACRO (Larsbo et al., 2005) has been parameterized for three national groundwater scenarios to support risk assessments of plant protection products in Sweden. MACRO is also one of four leaching models recommended for use in pesticide leaching risk assessments at the harmonized EU-level, and the only leaching model used for drainage risk assessment at EU level. It is also the only model that considers preferential flow.

Despite the intended worst-case (i.e. protective) nature of these risk assessments at national and European scales, it can be argued that there is a need for additional precautionary measures at the local level, for example in drinking water abstraction zones. Thus, in Sweden, farmers and landowners are legally obliged to apply to local authorities for permits to use pesticides, if their land lies within a drinking water abstraction zone (Swedish EPA, 2015). Clearly, in such cases, reliable, transparent and easy-to-use methods are needed to support local

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authorities in their decision-making. In the past, the regulatory body responsible for national authorizations (the Swedish Chemicals Agency, KEMI), supported local authorities in this work by identifying a list of substances that were thought to represent a risk to groundwater on the basis of model simulations performed using the MACRO model during product authorization. In practice, local authorities did not issue permits for the use of these compounds within drinking water abstraction zones. This approach was necessarily conservative and prescriptive, as it could not account for local and regional variations in soil, land use and climatic conditions. Furthermore, KEMI did not have the resources to maintain an up-to-date list as new compounds came onto the market and it was subsequently withdrawn in 2011. Consequently, the SLU Centre for Pesticides in the Environment (CKB) at the Swedish University of Agricultural Sciences (SLU) received funding from the Swedish Government and public authorities to develop a decision-support tool for site-specific pesticide risk assessments for drinking water abstraction zones in Sweden based on the MACRO model used for EU and national authorization. This tool should give accurate predictions, as well as being fast to run, easy-to-maintain, simple to use and understand by stakeholders, and only requiring data inputs that are widely available nationally. These multiple aims are not easy to reconcile. Empirical leaching indices or analytical (steady-state) solutions of physically-based models of pesticide leaching are simple and require few inputs (e.g. Jury et al., 1987; Gustafson, 1989; Stenemo et al., 2007a; Pavlis et al., 2010), but they cannot adequately reflect pesticide leaching in strongly heterogeneous soil profiles where adsorption and degradation vary with depth, nor under the highly transient conditions prevailing in the field driven by weather conditions in relation to the timing of pesticide applications. These approaches may provide reliable rankings of relative risk for pesticides of contrasting properties, but this is of little use when predictions must be compared to acceptable concentrations in a legislative context (e.g. the drinking water standard of 0.1 μg L^{-1} in the EU). Numerical solutions of process-based models are better able to reflect the complexities of the processes determining pesticide leaching risks, but they require extensive parameter inputs, which poses serious difficulties for large-scale model applications.

Meta-models can enable and simplify the use of complex numerical simulation models, whilst retaining much of their realism. Meta-models are designed and constructed to approximate the (usually) non-linear input-output mappings produced by simulation models (Piñeros-Garcet et al., 2006). Various methods have been used to develop meta-models of numerical pesticide leaching models including simple "look-up" tables (e.g. Holman et al., 2004), analytical models assuming steady-state water flow (Tiktak et al., 2006) and various machine learning techniques (Stenemo et al., 2007b; Lindahl and Bockstaller, 2012; Trépos et al., 2012).

Here, we present a new web-based decision-support tool for local pesticide leaching risk assessments in Sweden called MACRO-DB (https://macrodb.slu.se/shinyMACRO_DB/). This tool has been constructed as a meta-model of MACRO based on the results of pre-calculated simulations stored in "look-up tables". The simulations are parameterized using a comprehensive suite of pedotransfer functions (i.e. a soil inference system, McBratney et al., 2002) that includes a novel approach to predict the strength of preferential flow (e.g. Jarvis et al., 2009; Moeys et al., 2012). We also linked the parameterization of the MACRO model to a novel hydrological classification scheme, such that the simulations are capable of reflecting contrasting water balances found at sites characterized by different geological and pedological conditions. In this paper, we describe the meta-model and decision-support tool MACRO-DB and perform a global sensitivity analysis to better understand the main factors controlling its predictions of leaching risk in different situations. We also show the results of a qualitative "reality check" comparing risks of leaching predicted for six widely used pesticides of contrasting properties with relevant groundwater monitoring data in south-west Sweden. These predictions also allowed us to judge the protectiveness of MACRO-DB in relation to the three national groundwater assessment scenarios used in Sweden for authorizing the use of plant protection products.

2. Materials and methods

2.1. General approach, overview and scope

MACRO-DB is a web-based risk assessment tool that predicts the 20-year average pesticide concentrations in either surface water or groundwater. In the context of surface water, it should be noted that MACRO-DB is only used to estimate the long-term average concentrations in larger surface water bodies that are relevant for drinking water supply and not the short-term peak concentrations in surface water that determine acute toxicity to aquatic life, especially in smaller streams. This latter aspect is handled at the national level during product authorization. Similarly, the tool only considers inputs of pesticides to surface waters via drainage and subsurface flow and not via surface runoff or spray drift. Losses of pesticides by spray drift and runoff/erosion are considered at product authorization and are also targeted by mandatory and voluntary risk management practices (e.g. no-spray zones and vegetated buffer strips) designed to minimize impacts on surface water (Reichenberger et al., 2007). Even without the adoption of these mitigation measures, surface runoff/erosion and spray drift are thought to be generally less important than drainage losses to surface waters under the agro-environmental conditions prevailing in Sweden (e.g. Boye et al., 2012; Larsbo et al., 2016; Sandin et al., 2018), although they clearly do occur on occasions and losses can become significant locally.

MACRO-DB comprises a web user interface connected to look-up tables containing the results of more than half a million simulations with the MACRO model, and algorithms for calculating and presenting the results (Fig. 1). These MACRO simulations were performed for 150 hypothetical substances and representative scenarios covering the whole of Sweden, accounting for the variability of climate, crop development and associated agricultural practices, soils and parent materials (Fig. 1). The development of meta-models necessarily involves many simplifications and limitations. For example, in the development of MACRO-DB we did not account for the impacts of contrasting soil and crop management systems (e.g. tillage and irrigation). This is partly due to a lack of knowledge of the impacts of soil management practices on important model parameters (Larsbo et al., 2009), but also because it would have multiplied the number of simulations, to the point where it would not be practicable to implement. Another limitation is that the tool cannot simulate the potential impacts of climate change on leaching risks (e.g. Steffens et al., 2015), since the climate driving variables are fixed in our approach based on "look-up" tables. However, although climate variables can be treated as predictors in other types of meta-models, the relationships between weather patterns and leaching risks are so complex that they cannot be easily captured or summarized by simple climate variables (e.g. annual precipitation and temperature), especially for a model like MACRO that accounts for preferential flow (e.g. Nolan et al., 2008).

The MACRO simulations were parameterized for the scenarios using the model inference system (McBratney et al., 2002) developed by Moeys et al. (2012) and Steffens et al. (2015). A tri-linear interpolation in the substance parameter space (i.e. for the sorption constant, the slope of the Freundlich sorption isotherm and the degradation half-life) of the results of the MACRO simulations for hypothetical compounds is performed in MACRO-DB in order to estimate 20-year average pesticide concentrations in leachate for the actual active ingredient of interest. Again, to limit the number of simulations to a manageable number, we used a fixed dose (1 kg ha^{-1}) in the leaching simulations for these hypothetical compounds. Such a large dose will generally result in precautionary assessments, as a linear scaling is applied to estimate leaching of the actual substance, which will overestimate risk for non-linearly adsorbing compounds used at lower doses.

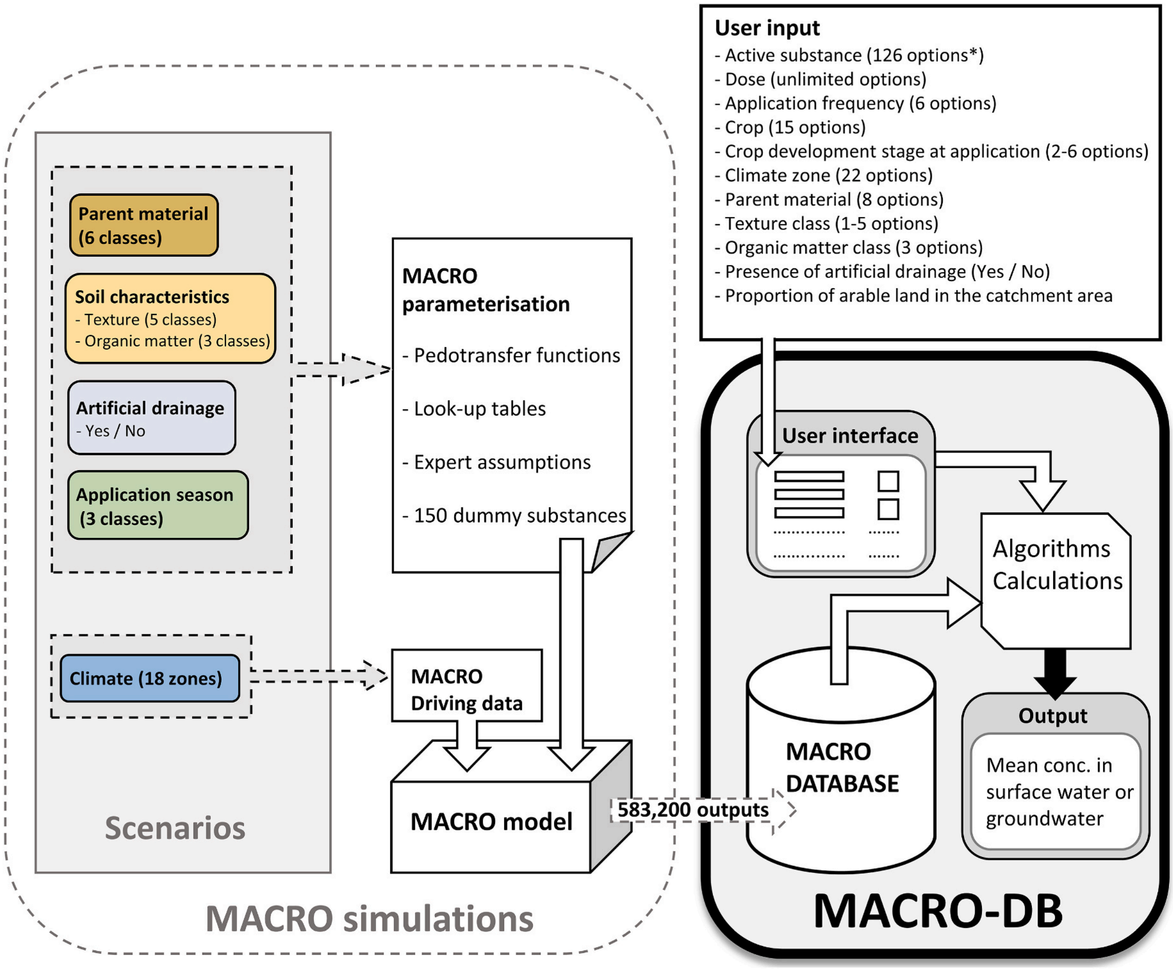

Fig. 1. Schematic view of MACRO-DB including the pre-preparations and simulations with MACRO v.5.2.

The end-users of MACRO-DB are farmers and their advisors who are applying for permits to use plant protection products in water protection areas. Local authorities base their decisions on exceedance of the acceptable concentration for a single pesticide in drinking water in the EU (i.e. 0.1 μg L^{-1}). In their decision-making, users at the local authorities can account in a simple way for dilution from water originating from non-agricultural land in the catchment, by making the simplifying assumption that groundwater recharge from the non-sprayed land is the same as that from the treated field. However, the groundwater and surface water risk assessments in MACRO-DB are also to some extent precautionary, as they do not account for dissipation processes that can reduce pesticide concentrations both in surface-water and groundwater bodies. In Sweden, surface water is pumped up from both rivers and larger lakes. MACRO-DB should give reasonable worst-case estimates for river water as residence times are usually short in relation to time-scales of dissipation. However, the approach will likely severely overestimate pesticide concentrations in the large lakes with long residence times that are commonly utilized for drinking water supplies in Sweden. It should be possible to include simple algorithms in future versions of MACRO-DB to estimate pesticide concentrations in large groundwater reservoirs and lakes based on estimated dissipation rates and information on hydrological residence times.

2.2. The MACRO model and its parameterization

MACRO (Larsbo et al., 2005; Jarvis and Larsbo, 2012) is a one-dimensional process-based model developed to simulate the field water balance and the fate and transport of pesticides at plot and field scales. A full water balance is considered including precipitation, evapotranspiration, percolation to groundwater and water flow to field drains. MACRO is a dual-permeability model, with water flow and solute transport simulated in two interacting pore regions (matrix and macropores) defined at a matric potential equivalent to the diameter of the smallest macropore (Šimůnek, et al., 2003). Soil water retention in the micropores is given by a modified version of the van Genuchten (1980) equation (Vogel et al., 2000). Water flow is calculated using Richards' equation in the micropores and by a kinematic wave equation (Germann and Beven, 1985) in the macropores. Water flow to field drains is calculated from saturated soil layers in the profile using seepage potential theory (Leeds-Harrison et al., 1986). Solute transport in the micropores is calculated using the advection-dispersion equation. Dispersion is neglected in the macropores, since transport is assumed to be dominated by convection. The solute concentration in water routed into macropores at the soil surface is calculated assuming immediate equilibrium and complete mixing of infiltrating water with the water stored in a shallow surface soil layer, or 'mixing depth' (Steenhuis and Walter, 1980). A proxy parameter ('effective diffusion pathlength') reflecting soil structure controls the exchange of both water and solute between the two pore regions. Pesticide degradation is assumed to follow first-order kinetics, with the rate coefficients given as a function of soil temperature (Boesten and van der Linden, 1991) and moisture content (Schroll et al., 2006). Pesticide sorption is calculated with a Freundlich isotherm and can either be simulated as an instantaneous or kinetic process using a two-site model (Altfelder et al., 2000).

The MACRO model has been extensively tested against numerous experiments carried out at column and plot scales in both the laboratory and in the field (see the review by Köhne et al., 2009a, 2009b). The model was generally shown to perform satisfactorily and was therefore considered "fit for purpose" for use in pesticide regulation in the EU (FOCUS, 2000; FOCUS, 2001). However, these research applications of the model invariably involved a considerable degree of model calibration against the measurements in order to obtain estimated values for various parameters that are either difficult or impossible to measure (Jarvis and Larsbo, 2012). For this reason, the modelling scenarios for MACRO that are used in the pesticide authorization procedures in the EU are mostly based on real field sites for which the MACRO model has been calibrated. The three national groundwater scenarios that are used for product authorization in Sweden were parameterized from a combination of direct measurements, model calibration and expert judgement based on previous model applications to similar sites in other locations. Clearly, the use of a model such as MACRO for site-specific simulations of leaching risk without the benefit of extensive site data to support model calibration is a challenge.

The parameterization of the MACRO simulations in MACRO-DB constitutes a complete parameter "inference system" based on a suite of class and continuous pedotransfer functions for the soil and crop parameters in the model presented by Moeys et al. (2012). This system to support model predictions with the MACRO model was successfully tested against comprehensive data on water outflows and the leaching of non-reactive tracers obtained from a series of long-term outdoor lysimeter experiments (Moeys et al., 2012). Steffens et al. (2015) further developed this parameter inference system to enable applications at the regional scale by accounting for site hydrological conditions. They compared MACRO simulations parameterized with this updated inference system with groundwater monitoring data for the county of Skåne in the far south of Sweden and found that the model correctly distinguished "leachable" from "non-leachable" compounds.

The parameter inference system, which is now embedded in MACRO-DB, utilizes information on scenario definitions as input. These scenarios are described in the following sections. The MACRO parameterization algorithms are described in section S1 in Supplementary Material.

2.3. Scenario definitions

In MACRO-DB, user-supplied information on parent material, soil texture, soil organic matter and drainage status completely and uniquely defines one of 72 representative soil scenarios. Likewise, 54 representative scenarios on application dates are defined through user choices concerning climate zone and season of application. These scenarios are described in detail below.

2.3.1. Parent material and soils

Each soil scenario is based on a soil profile divided into five horizons down to a depth of 200 cm, with horizon thicknesses and designations determined by the parent material (see Table S1, Supplementary Material). Eight types of parent materials are considered by MACRO-DB (Esker, Sedimentary rock, Moraine, Hard rock, Coarse silt/fine sand, sand or gravel, Clay/silt, Alluvium and Organic soil) based on a simplification of the classification system for quaternary geology developed by the Swedish Geological Survey. However, no soil scenarios were defined for organic soils, since this parent material is assumed to pose no risk of pesticide leaching.

Five different texture classes are included in the soil scenarios based on a modified version of the texture triangle of the Soil Map of Europe (Fig. 2 and Table S2 in the Supplementary Material). According to the inventory of arable land in Sweden (Eriksson et al., 2010), texture class 5 is very unusual (approximately 3% of the land area) and was considered to be sufficiently represented by texture class 4 without compromising the risk assessment (see Fig. 2). On the other hand, preliminary analyses showed a necessity to split texture class 2, which is by far the most common texture class for arable land in Sweden (see Fig. 2), into two classes. The class representing the coarser part of texture class 2 (where

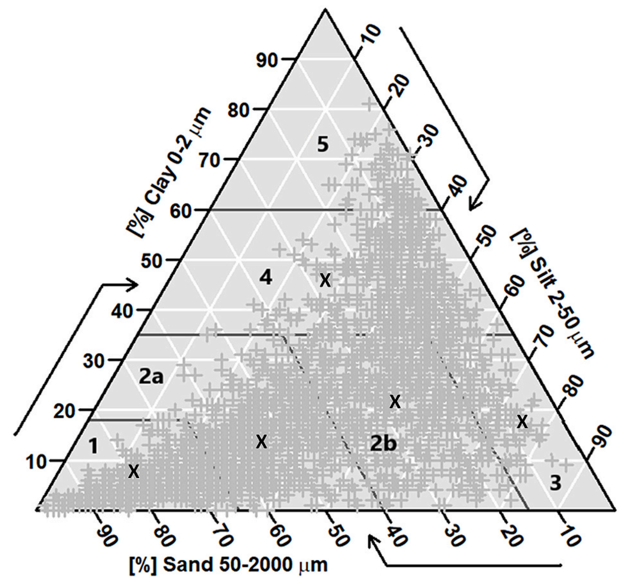

Fig. 2. Topsoil texture for 3,303 arable soils in Sweden (+ *in grey) and topsoil textures included in the soil scenarios (*x *in black) on the texture triangle of the Soil Map of Europe.*

the sand content exceeds 40%) is called 2a, and the other part representing the finer-grained part is called 2b. Representative values of clay, silt and sand content were selected for each texture class (Fig. 2 and Table S2 in the Supplementary Material). This particle size distribution is assumed constant throughout the whole soil profile in all of the scenarios since, in Swedish arable land, soil texture is usually very similar in the topsoil and subsoil (Eriksson et al., 2010). Unrealistic combinations of soil texture and parent material were omitted from the simulations i.e. all soil textures apart from class 1 for Esker, texture classes 1 and 2a for Clay/Silt and texture class 4 for Coarse silt/fine sand, sand or gravel.

The uppermost two horizons in each soil scenario are characterized by one of three different organic carbon contents (1.3%, 2.6% and 5.2% for organic matter class u, n and h, respectively as shown in Table S3, Supplementary Material). These represent a simplification of the six classes of soil organic matter content defined by the Swedish Board of Agriculture. Due to a lack of supporting data, the organic carbon contents in subsoil horizons were set to constant values (0.5% in the upper subsoil horizon 3, 0.3% in horizon 4 if it is not bedrock and 0.1% for horizon 5 and rock horizons) based on limited soil survey data for Swedish arable subsoils.

2.3.2. Site hydrology

Each soil profile belongs to one of four distinct hydrological classes.

- Class L represents highly permeable soils with drainage to deep-lying groundwater.
- Class W and Class Y represent soils with slowly-permeable parent materials that allow both percolation to groundwater and discharge into surface water either via field drainage systems or shallow lateral groundwater flow. The groundwater table is located within the soil profile. Class Y soils are artificially-drained soils with significantly lower permeability in the subsoil and/or in the parent material compared to class W, which means that the groundwater rises higher in the profile of class Y soils.
- Class U soils represent either impermeable parent materials (i.e. impermeable clay) or soils located in low-lying terrain within the catchment area (i.e. discharge areas).

The hydrological classes are determined from parent material, soil texture and drainage status according to the classification flow chart

Table 1
Hydrological classes within MACRO-DB. For class L soil water flow to groundwater which also reaches surface water via baseflow, for class W and the less permeable class Y soil water flow to both groundwater and surface water and for class U soil water flow to surface water only. Combinations of parent material, texture and presence or absence of artificial drainage that do not normally occur in practice are marked with a slash (/). Empty cells represents organic soils, which hydrologically behaves like U soils. However, MACRO-DB does not calculate pesticide concentrations for these soils since they are assumed to pose no risk of pesticide leaching.

Parent material	Texture class	Hydrologic class	
		Drained	Undrained
Esker	All relevant textures	/	L
Sedimentary rock	All relevant textures	/	L
Hard rock	All relevant textures	/	Y
Moraine	Coarse (=1), coarse medium (=2a)	/	W
	fine medium (=2b), medium-fine (=3)	Y	W
	Fine (=4)	Y	/
Alluvial sediment	All relevant textures	U	/
Coarse silt/fine sand, sand or gravel	All relevant textures	U	W
Clay/silt	All relevant textures	U	W
Organic soil			

shown in Table 1 and Fig. 3. The resulting hydrological classes of the 72 soil profiles are shown in Table S4 in the Supplementary Material. The bottom boundary condition of the 200 cm soil profile in the MACRO model depends on the soil hydrological class (L, W, Y or U). For class L, a hydraulic unit gradient is assumed, while the percolation rate is defined as a linear function of the height to the groundwater table for class W and Y. The chosen parameterization produces deeper water tables in class W soils. Zero flow at the base of the profile is assumed for class U soils. These four different boundary conditions translate into strong contrasts in simulations of site hydrology and the water balance.

2.3.3. Climate

Sweden is divided into 22 so-called crop production zones (see section S1.3, Supplementary Material) based on climate and other agro-environmental conditions. Twenty-six years of daily weather data (1970–1995) provided by the Swedish Meteorological and Hydrological Institute (SMHI) for representative climate stations located in each of these production zones was used to drive the MACRO simulations. The reason for using this period is that the MACRO-based tool (MACRO-in-FOCUS) used by the Swedish Chemicals Agency for assessing risks to Swedish groundwater during product authorization uses this same period and it was considered important to maintain compatibility between these two model tools.

Preliminary analyses of the simulated water balances showed that the weather data of zone 13 can be used for zone 14, and the data of zone 16 for the zones 15, 17 and 18, without compromising the risk assessment. The weather data comprised all input driving data required by MACRO, i.e. daily rainfall (mm), daily minimum and maximum temperatures (∘C), solar radiation (W m^{-2}), vapour pressure (kPa) and wind speed (m s^{-1}). The daily rainfall data from SMHI was disaggregated into hourly rainfall data using a cascade model developed by Olsson (1998), with the parameterization based on a time series of high time-resolution rainfall data from Lund in southern Sweden (Güntner et al., 2001).

2.3.4. Pesticide applications

Three pesticide application seasons (i.e. spring, summer and autumn) are considered. A set of 26 dates of application (one specific date for each simulation year) were defined for each of three aggregated climate zones (north, central, and southern Sweden) within pre-defined "application windows" (Table S8, Supplementary Material), resulting in a total of 9 possible scenarios of pesticide application dates. The actual dates of application were determined using the rule-based PAT ("Pesticide Application Timer") algorithm, which was developed for regulatory modelling within the EU (FOCUS, 2000). PAT determines "reasonable worst case" application dates depending on the rainfall pattern within the application window.

2.4. MACRO-DB

2.4.1. The simulation database

The MACRO-DB database contains the results of 583,200 MACRO simulations that were parameterized for every combination of 18 climate scenarios, 72 soil scenarios, three application seasons and 150 hypothetical compounds. A spring cereal crop was simulated in all cases (section S1.4 in Supplementary Material). This simplification was considered necessary in order to make significant savings in the computation time required by limiting the number of simulations. The impact of the different crops commonly grown in Sweden on the water balance is rather limited and preliminary analyses showed that the effects of these differences on pesticide leaching are small in comparison with the large sensitivity of leaching to pesticide properties.

The parameters describing adsorption and degradation of the 150 hypothetical substances were defined by combinations of eight normalized Freundlich coefficients, K_{foc}, ranging from 3 to 10,000 L kg^{-1} and seven reference degradation half-lives DT_{50}, ranging from 3 to 200 d (Table 2), combined with three different Freundlich exponents n_f (0.75, 0.85 and 1). Combinations of K_{foc} and DT_{50} that were considered unrealistic for authorized active ingredients or that would almost certainly not yield any leaching, were omitted to save computation time (Table 2). The substances were applied yearly at an effective dose (i.e. without crop interception) of 1 kg ha^{-1}.

Following the procedure used in risk assessment in the EU for groundwater (FOCUS, 2000), the MACRO simulations were run for 26 years, with the first six years discarded as a warm-up period. The average concentration in leachate percolating to groundwater under a treated field predicted by MACRO for the hypothetical compounds, $C_{gw(m)}$ (μg L^{-1}) is calculated as the total leached pesticide mass during the 20-year assessment period S_p (mg m^{-2}) divided by the total percolation W_p (m):

$$C_{gw(m)} = \frac{S_p}{W_p} \tag{1}$$

The average concentration of pesticide entering surface water from a treated field $C_{sw(m)}$ was calculated from the outputs of the MACRO simulations in a similar way, making the worst-case assumption that pesticide leached to groundwater is also routed to surface water through shallow groundwater flow without any degradation:

$$C_{sw(m)} = \frac{S_d + S_p}{W_d + W_p} \tag{2}$$

where S_d is the total pesticide mass loss in drainage in the 20 year assessment period (mg m^{-2}) and W_d is the total drainage (m). These post-processing calculations were performed in R using the R package macroutils (Moeys, 2017) and the results were stored in a MS Access database.

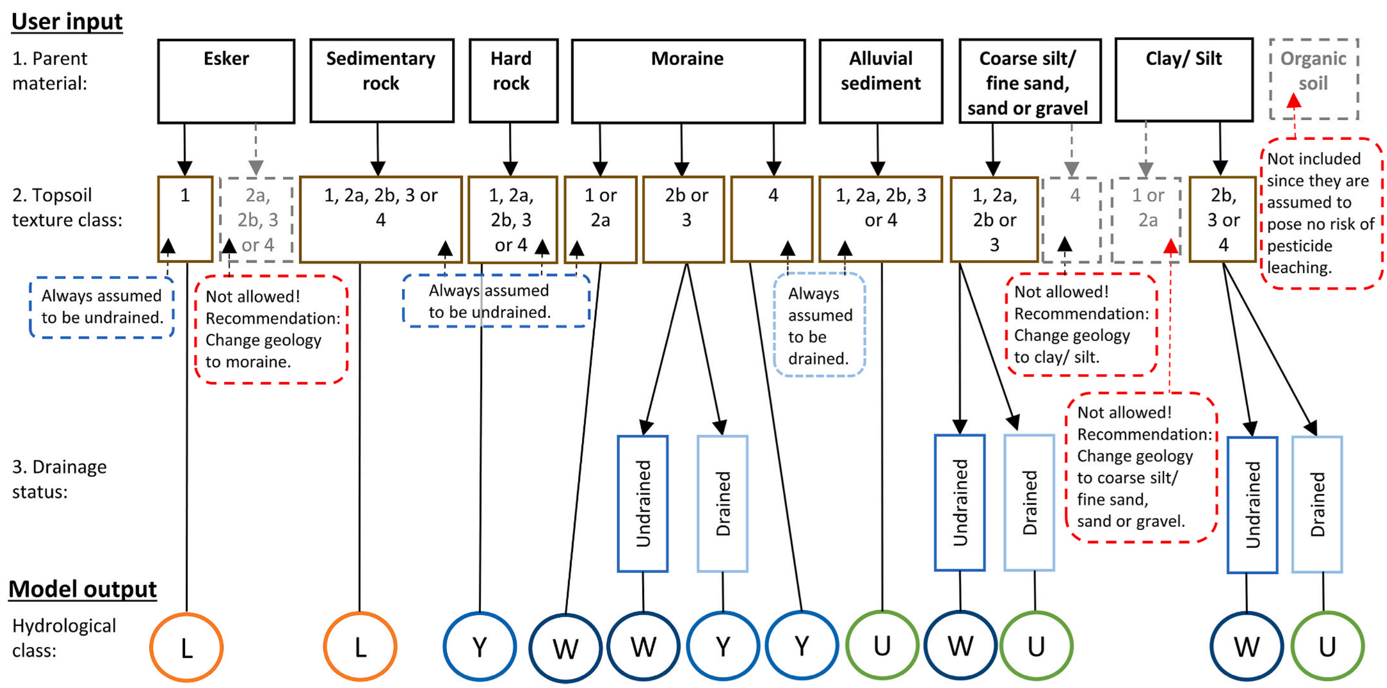

Fig. 3. Flow chart for determining hydrological class.

Table 2
Combinations of K_{foc} and DT_{50} simulated with MACRO (dotted cells). These 50 combinations are combined with 3 values of the Freundlich exponent (nf), resulting in a total of 150 hypothetical compounds. Combinations marked with crosses (X) were excluded.

		K_{foc} (L kg^{-1})							
		3	10	30	100	300	1000	3000	10,000
DT_{50} (d)	3	●	●	●	●	●	●	●	X
	6	●	●	●	●	●	●	●	X
	12	●	●	●	●	●	●	●	X
	25	●	●	●	●	●	●	●	●
	50	●	●	●	●	●	●	●	●
	100	X	●	●	●	●	●	●	●
	200	X	X	●	●	●	●	●	●

2.4.2. *Calculations for the selected active ingredient and scenario*

An estimate of the predicted leachate concentration under a treated field for the actual active ingredient selected by the user through the MACRO-DB interface is derived by performing a tri-linear interpolation (Akima, 1978) in the parameter space of K_{foc}, DT_{50} and nf for the logarithms of the two target variables (i.e. $\log_{10}(C_{gw(m)})$ and $\log_{10}(C_{sw(m)})$, making use of the stored results for the 150 hypothetical substances. The values of K_{foc}, DT_{50} and nf for the active ingredient of interest are taken from the PPDB database developed and maintained by the Agriculture & Environment Research Unit (AERU) at the University of Hertfordshire (Lewis et al., 2016), which summarizes the properties used in regulatory risk assessments at the harmonized EU level. The interpolation is performed using the nearest neighbours (up to 8) of the selected active ingredient in the 3D substance parameter grid. Since the target variables are logarithmic, censoring of very low simulated concentrations is necessary to avoid distortions of the estimate. Consequently, concentrations simulated with MACRO (equations (1) and (2)) were left-censored at 0.1 ng L^{-1}. A performance check of the trilinear interpolation method for 5,000 MACRO validation runs generated with Latin Hypercube Sampling and a training data set of 18,720 simulations showed some border effects due to the censoring, which however only produced a few false positives (erroneously predicted concentrations above 0.1 μg L^{-1}) for the application rate of 1 kg ha^{-1} (Fig. S6, Supplementary Material).

This interpolated concentration is then converted to an estimate for the defined scenario by accounting for the actual substance dose, crop interception and dilution. Thus, predicted concentrations in groundwater (C_{gw}, μg L^{-1}) and surface water (C_{sw}, μg L^{-1}) are calculated as:

$$C_{gw} = C_{gw(m)}\left(\frac{D}{1000}\right)(1 - f_{int})f_{app}f_{agr\_gw} \tag{3}$$

$$C_{sw} = C_{sw(m)}\left(\frac{D}{1000}\right)(1 - f_{int})f_{app}f_{agr\_sw} \tag{4}$$

where D is the dose of the compound being assessed (g ha^{-1}), f_{int} is the effective intercepted fraction, f_{app} is the application frequency (=1 for application every year, 0.5 for every other year, 0.3333 for every third year, etc.) and f_{agr_gw} is the proportion of agricultural land to the land area in the catchment while f_{agr_sw} is the proportion of agricultural land to the total area of the catchment since precipitation on water bodies also contributes to the dilution. In the case of metabolites, an effective dose is estimated from the maximum occurrence fraction (as a surrogate for the molar formation fraction) and the ratio of molar masses of the metabolite and parent compound. The intercepted fraction f_{int} is based on the crop type and its stage of development at the time of application specified by the user (see Supplementary Material, see section S2.6). Some plant protection products are applied multiple times in a single growing season to the same crop. Even though all the simulation results in the database are for single applications, a risk assessment can still be carried out in MACRO-DB for multiple applications by performing the calculations for all relevant crop development stages and then summing the resulting predicted concentrations to obtain a final estimate. Despite the rather gross approximation inherent in this approach, it does appear to produce reasonable results (Table S12 in supplementary information).

2.5. *Applications*

2.5.1. *Sensitivity analysis*

Global sensitivity analyses (GSAs) were conducted for MACRO-DB to illustrate the most important input factors influencing predicted pesticide concentrations in drinking water resources in Sweden. We used the

Sobol' method (Sobol', 1993; Gatel et al., 2020), since it does not rely on linearity, monotonicity or additivity of the model. The method ranks the input factors according to their importance and allows identification of both first-order (direct) and higher-order (interaction) effects for each input factor (Sobol', 1993; Saltelli et al., 2005; Lauvernet and Muñoz-Carpena, 2018). The first-order sensitivity index (S_i) for each input factor X_i is defined as the fraction of the output variance Y associated with the direct effect of that factor (Sobol', 1993). The total sensitivity index (S_{Ti}) is calculated as the fraction of output variance associated with factor X_i and its interactions with other input factors (Homma and Saltelli, 1996). In the case of a purely additive model (i.e. a model without interactions between inputs) both the sum of S_i and the sum of S_{Ti} are equal to 1. Otherwise, the sum of S_i is < 1 and the sum of S_{Ti} is > 1. Models with a sum of $S_i > 0.6$ can be considered as "mostly additive" (Saltelli et al., 2004).

The target variables for the GSAs reported here are C_{gw} and C_{sw} (equations (1) and (2)) in logarithmic form. Taking logarithms of the variables substantially reduces the impact of extremely high concentrations on their variances. Two GSAs were performed for the whole parameter space for substance properties (GSA_1) based on two variants for the input factors regarding soil type.

1) Variant GSA_1a: Soil type was sampled as a discrete variable (*Soil type*).
2) Variant GSA_1b: The four soil variables that together constitute the soil type were sampled individually: hydrological class (*HSG*), texture class (*TXT*), presence of hard rock in subsoil (*HR*), and organic matter class (*OMC*).

For both variants, the Freundlich exponent was sampled uniformly, whereas a uniform distribution of $\log(K_{foc})$ and $\log(DT_{50})$ was assumed. Application season (*Season*) and climate zone (*Climate*) were sampled as discrete variables (see Table S13, Supplementary Material). The remaining input factors, all of which have a linear effect on the (non-logarithmic) target variables, were kept constant, as follows.

- All land area within the catchment area is arable land, i.e. $f_{agr\_gw} = 1$.
- A dose (D) of 1 kg ha^{-1}.
- Yearly application, i.e. $f_{app} = 1$.
- No interception of the applied dose, i.e. $f_{int} = 0$.

The sample sizes for GSA_1a and GSA_1b were 32,000 and 66,000, respectively.

The contribution of a factor to the total output variance strongly depends on the input distribution of this factor. The chosen substance parameter distributions of GSA_1 reflect the whole substance parameter space included in MACRO-DB (Table S13, Supplementary Material). The obtained sensitivity measures will therefore correspond to the entire input factor space of the meta-model and not for an individual active substance. These sensitivity analyses are intended to give a broad perspective on the most important factors that will control overall pesticide contamination risks in drinking water protection areas at the national scale in Sweden.

The influence of substance parameters will be smaller for input distributions reflecting uncertainty for a single compound than for input distributions covering the whole simulated range. To quantify this difference in sensitivity, two additional GSAs (GSA_2) were carried out with a narrower range of substance properties (Table S14, Supplementary Material) for the same input factors and sample sizes as in GSA_1a and GSA_1b. These input ranges are intended to approximately reflect the natural variability of sorption and degradation parameters for a given substance across different soils and climates (e.g. Wauchope et al., 2002; Fenner et al., 2007; Ghafoor et al., 2011, 2013). The results of these second type sensitivity analyses provide information on the main causes of variation in the outcome of risk assessments for a given substance in water protection areas in Sweden with contrasting soil types and climates. The hypothetical compound studied in GSA_2 has a geometric mean K_{foc} value of 100 L kg^{-1} (range 50–200 L kg^{-1}) and a geometric mean DT_{50} value of 30 d (range 15–60 d) (also shown in Table S14, Supplementary Material). The mean value of the Freundlich exponent *nf* is 0.9 with a variation of $\pm$ 0.1.

All GSA calculations were done in R, making the use of the R script sobol_sensitivity from the European Commission Joint Research Centre (Zambrano-Bigiarini et al., 2013) for Sobol' quasi-random sampling and calculating Sobol' sensitivity indices.

2.5.2. Assessment of the protectiveness of MACRO-DB

MACRO-DB was run for the maximum recommended doses of some widely used active ingredients in the two southern-most climate zones (1a and 1b). Pesticide use is largest in the south of Sweden compared with the rest of the country, due to a favorable climate for cultivating a wider variety of crops as well as greater weed, pest and disease pressures. This analysis was carried out partly as a qualitative "reality-check" by comparing the results with available groundwater monitoring data and also to assess the protectiveness of MACRO-DB in comparison with the national groundwater risk assessment of pesticides for general approval in Sweden. Note that we do not compare MACRO-DB simulations with surface water monitoring data because these may be impacted by transport pathways not considered in MACRO-DB (i.e. point sources due to spills and accidents, surface runoff/erosion and spray drift).

The geographical distributions of the quaternary geology within climate zones 1a and 1b were retrieved from the Geological Soil Survey of Sweden at the scale of 1:25,000. Geographical distributions of classes of topsoil organic carbon content and texture were derived from digital soil maps available at CKB. The soil map is based on measurements of texture and organic carbon content made on 2200 samples in arable topsoil (0–30 cm) collected within the Swedish environmental monitoring program as well as aerial measurements of gamma emissions carried out by the Geological Soil Survey of Sweden (Tranter et al., 2011). Climate zone 1a includes 54 of the 72 soil scenarios of MACRO-DB (as well as the organic soil class). Fewer soil scenarios (39) are found in climate zone 1b (in addition to organic soils), which in contrast to climate zone 1a, completely lacks sedimentary rock. For soils that can either be artificially drained or not (see Fig. 3), both possibilities were assumed to be represented within the climate zones.

Commonly used pesticides relevant for the study areas were chosen based on sales for agricultural use according to the Swedish Chemicals Agency (KEMI, 2022) and reported use within two catchments, M42 in the county of Skåne and N34 in the county of Halland (see Fig. S8, Supplementary Material), that are part of the Swedish national environmental monitoring program for pesticides. These two catchments are included in the national monitoring program for pesticides because they are considered to be representative for Swedish agriculture.

Information on pesticide use and crop cultivation within these catchments are collected every year through interviews with the local farmers. Both catchments have a high proportion of agricultural land (89–95%) and 80–90% of the arable land is treated with pesticides.

The selection of pesticides to include in the assessment were based on three conditions.

1. The quantity of the pesticide sold in Sweden in 2022 should exceed 10 tonnes.
2. The pesticide must have been used every year during the ten-year period 2011–2020 in at least one of the two catchments M42 and N34. Such pesticides were assumed to be frequently used throughout both climate zones 1a and 1b.
3. The application frequency during the cropping season must be the same throughout the ten year period for a large proportion of the fields of catchments M42 or N34. Hence, pesticides with irregular application patterns in both catchments were not considered.

Six pesticides that met the requirements listed above were included

Table 3
Fate parameters according to PPDB (AERU, 2023) of the pesticides (parent or metabolite) included in the conservative assessment of MACRO-DB in climate zone 1a and 1b. Quantities of the pesticides sold in Sweden for agricultural use in 2022 and their frequencies of findings in groundwater in 1986–2014. N indicates the number of samples for which the substance has been analyzed.

Pesticide	K_{foc}[a] (mL g^{-1})	Soil DT_{50} Lab (days)	Freundlich exponent, nf	Quantity sold (tonnes)	Detection in groundwater samples 1986–2014[b]		
					Number of findings	Detection rate (%)	Mean of detected concentrations (μg L^{-1})
Bentazone	59.6	20	0.93	27.5	607 (N = 10,348)	5.9	1.2
Clopyralid	5	23.2	–	15.0	49 (N = 4,058)	1.2	1.2
Diflufenican	2,215	94.5	0.87	15.3	0 (N = 31)	0	–
MCPA	57.96	12.07	0.822	187.9	64 (N = 9,995)	0.6	39
Prosulfocarb	1,693	11.9	0.96	270.3	2 (N = 228)	0.9	0.02[c]
Prothioconazole-desthio[d]	575.4	215	0.91	38.5[e]	0 (N = 51)	0	–

[a] K_{oc} for Clopyralid since K_{foc} is not given by PPDB (AERU, 2023).
[b] According to a compilation by the Swedish Agency for Marine and Water Management (HaV, 2014).
[c] Both findings <0.1 μg L^{-1}.
[d] Since the DT_{50} of Prothioconazole is ≤ 2d, its metabolite Prothioconazole-desthio is assessed instead.
[e] The sold quantity applies for the parent compound, i.e. Prothioconazole.

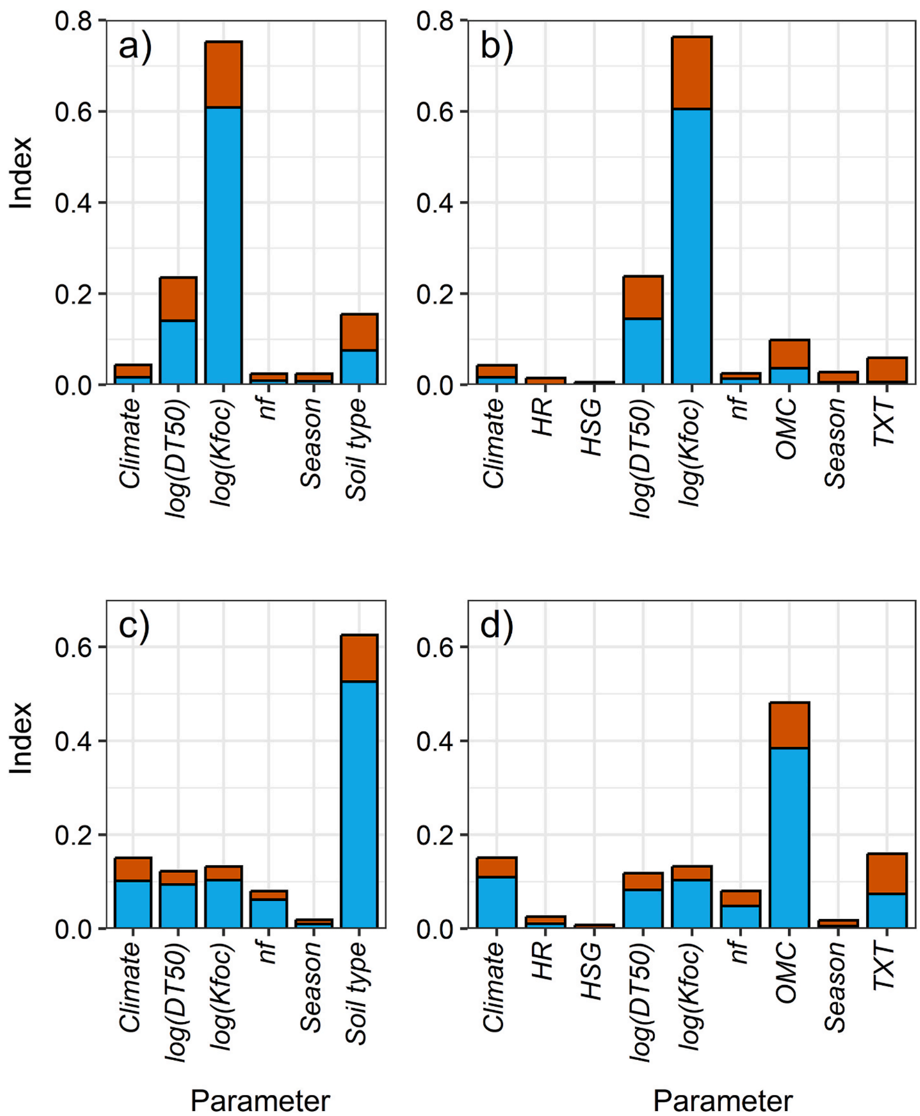

Fig. 4. Sobol' indices for logarithmised groundwater pesticide concentration for the entire parameter space using a) soil type (GSA_1a), and b) soil variables (GSA_1b) and with substance parameter input distributions reflecting variability for a single compound using c) soil type (GSA_2a), and d) soil variables (GSA_2b). Whole column: total sensitivity index S_{Ti}; blue: first-order sensitivity index S_i; red: interactions. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

in the analysis (see Table 3). These compounds had K_{foc} values ranging from 5 to 2,215 mL g^{-1}, with Freundlich exponents varying between 0.822 and linear adsorption (Clopyralid) and DT_{50} values between 11.9 and 215 days. For all the pesticides selected, the application frequency was once a year for more than 86% of pesticide application scenarios (PAS) were created by combining each of the selected substances with target crops, the timing of application in relation to their development stage and maximum permitted doses according to the terms of use for products containing the specific active ingredients as determined by the Swedish Chemicals Agency. The resulting 58 PAS are given in Table S18 in the Supplementary Material.

Combinations of the PAS and the soils for both climate zones (including the MACRO-DB soil scenarios and the relevant organic soil types) were then run in MACRO-DB to estimate pesticide concentrations in groundwater within hypothetical water protection areas, assuming 100% agricultural land (i.e. $f_{agr\_gw} = 1$). However, potatoes were assumed to be cultivated exclusively on coarse-textured soils (i.e. soils of texture class 1). All in all, the resulting numbers of runs were 3,495 and 2,444 for climate zones 1a and 1b, respectively.

3. Results and discussion

3.1. Sensitivity analysis

Both GSA_1 and GSA_2 showed only small differences in sensitivity indices between groundwater and surface water. The results for surface water are therefore presented in the Supplementary Material (Fig. S7). We focus here on the sensitivity analyses for groundwater.

The results of the groundwater GSA for the entire substance parameter space (GSA_1) are shown in Fig. 4a and b, while the results for the reduced substance parameter space reflecting uncertainty of sorption and degradation parameters for a given compound across different soils and climates (GSA_2) are shown in Fig. 4c and d. Sensitivity rankings of the input factors are given in Tables S15 and S16, while sums of first order and total sensitivity indices are shown in Table S17 in the Supplementary Material. The sums of the first-order indices S_i were 0.83–0.88 (GSA_1) and 0.79–0.90 (GSA_2). Hence the MACRO meta-model with logarithmic target variables can be considered as approximately additive.

For both variants 1a (soil type) and 1b (individual soil variables) of GSA_1 log(K_{foc}) was by far the most important factor followed by log (DT_{50}) (Fig. 4a, b and S7 and Tables S15 and S16). For variant 1b, the organic matter class (*OMC*), which determines sorption, was the most important of the four soil variables (Table S16, Supplementary Material). In contrast, the influence of the soil hydrological class (*HSG*) was comparatively small. At first sight, this is somewhat surprising, because for groundwater scenarios, if a larger proportion of excess percolating water is diverted to surface water via drainage systems (e.g. in class Y soils) then downwards transport velocities are smaller, which should reduce leaching to groundwater. One reason for the low sensitivity to hydrological class found here may be that, following FOCUS procedures, the MACRO-DB inference system assumes that there is no pesticide degradation below 1 m in the soil profile, equivalent to drain depth in class Y soils, so that pesticides will always leach to groundwater once they reach below this depth.

Given the narrower input distributions of substance parameters reflecting the natural variability of K_{foc}, DT_{50} and *nf* for a given substance across different soils and climates, GSA_2 must generally attribute less importance to substance properties than GSA_1, where the input distributions correspond to the entire substance parameter space in the MACRO meta-model. This is shown by the results of GSA_2, where *Soil type* was by far the most important factor for variant 2a, followed by *Climate,* log(K_{foc}) and log(DT_{50}), while for variant 2b the most important factor was *OMC*, followed by *TXT* and *Climate* (Fig. 4c, d and S7 and Tables S15 and S16). It should be recognized that a sensitivity analysis for another compound located somewhere else in the substance parameter space may have yielded qualitatively different results. A GSA reflecting a risk assessment with MACRO-DB for a single compound applied to a specific farmer's field would be run with a fixed climate and cover a narrower input distribution of soil parameters and would therefore almost certainly again give most weight to the sorption and degradation properties of the substance. Hence, the sensitivity and relative importance of the input factors depends very much on the scenario definition (i.e. the questions being asked) and the associated appropriate spatial scale.

3.2. Assessing the protectiveness of MACRO-DB

All in all, 22% of the 5,939 MACRO-DB runs using PAS approved by the Swedish Chemicals Agency gave predicted average groundwater concentration exceeding the EU limit for drinking water (0.1 μg L^{-1}; see Fig. 5 for soils of hydraulic classes L, W and Y). In accordance with the sensitivity analyses (section 3.1), the magnitude of the estimated concentrations in groundwater is largely controlled by the pesticide fate parameters. MACRO-DB suggests that the two least mobile pesticides (Diflufenican and Prosulfocarb) do not pose a risk of exceeding 0.1 μg L^{-1} within water protection areas for groundwater within the climate zones 1a and 1b, as all relevant soil types are predicted to give groundwater concentrations below the limit for drinking water (see Table 4 and Fig. 5). In contrast, more than half of the runs for the most mobile pesticide (Clopyralid) exceeded the limit for drinking water in both climate zone 1a and 1b (Table 4). Only soils belonging to hydraulic class U (U-soils) pose no risk of Clopyralid groundwater contamination due to the assumption of zero flow at the base of the profile for U-soils. Of the other two more moderately mobile pesticides, Bentazone gives rise to predicted average groundwater concentrations above the drinking water limit to a much higher degree than MCPA (Table 4), which is less persistent (see Table 3). A minority of the MACRO-DB runs for the slightly mobile and most persistent of the substances, Prothioconazole-desthio, exceeded the limit for drinking water.

A larger proportion of the results for climate zone 1a compared to climate zone 1b have concentrations above the drinking water limit (Table 4). This is largely due to differences in the soil scenarios occurring in the two climate zones, with a larger number of soils susceptible to leaching in climate zone 1a, rather than differences in climate and weather patterns. As also shown by the sensitivity analyses, Fig. 5 suggests the important role of organic carbon in reducing pesticide losses. With the exception of Clopyralid, none of the substances gave average groundwater concentrations exceeding 0.1 μg L^{-1} for soils with the highest organic matter class (h). For Clopyralid, which is very weakly adsorbed (Table 3), the highest leaching risk is predicted for coarse-textured soils (see Fig. 5), due to the potential for rapid transport through the soil matrix. The remaining five compounds are more strongly adsorbed, so that matrix leaching is negligible. For these substances, the largest average concentrations leaching to groundwater are predicted in fine-textured soils (i.e. texture class 4; Fig. 5), as the parameterization of the MACRO model reflects the fact that these soils are more prone to macropore flow (see Table S4 in the Supplementary Material). The overall effect of the other texture classes are weaker and overshadowed by interplay with other factors (i.e. effective dose, parent material and season of application), which is also the case for some fine-textured soils run for Prothioconazole-desthio. These differences in the effects of soil type on the leachate concentration demonstrate the complexity of the model in terms of the interplay of different input factors, such that the relative importance of input factors will vary depending on the investigated scenario.

The drained moraine of soil type Y2bu within climate zone 1a coincides with one of the national groundwater scenarios. Fig. 6 suggests that for Clopyralid and Bentazone in climate zone 1a, the MACRO-DB risk assessment is more protective for soil type Y2bu than the national approvals procedure based on MACRO simulations, as predicted concentrations are more than ten times larger than the allowable limit. Note

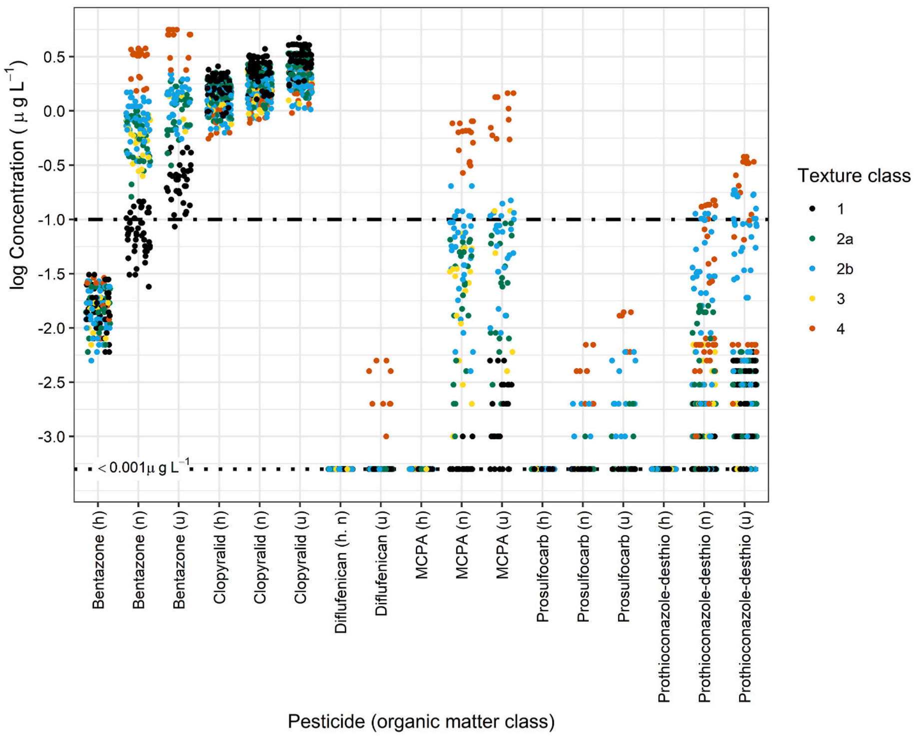

Fig. 5. MACRO-DB estimated 20-year average pesticide (or metabolite) concentrations leaching to groundwater for all soils belonging to hydrological classes L, W, or Y in climate zones 1a and 1b and all approved combinations of crops and doses for six common pesticides. For soils of hydrological class U, MACRO-DB does not generate any groundwater pesticide leaching for any pesticide application scenario.

Table 4
The proportions of MACRO-DB runs, and the proportions of arable land, exceeding the concentration limit for drinking water (0.1 μg L^{-1}) for approved pesticide application scenarios for six selected pesticides (parent or metabolite) on all arable soils occurring in climate zone 1a and 1b. N is the total number of MACRO-DB runs.

Pesticide	Proportion of MACRO-DB runs exceeding the limit for drinking water (%)		Proportion of arable land exceeding the drinking water limit (%)	
	Climate zone 1a	Climate zone 1b	Climate zone 1a	Climate zone 1b
Bentazone	41, N = 441	27, N = 308	60–85	4–41
Clopyralid	63, N = 945	55, N = 660	66–97	24–97
Diflufenican	0, N = 630	0, N = 440	0	0
MCPA	10, N = 315	9, N = 220	0.03–10	0–1
Prosulfocarb	0, N = 209	0, N = 148	0	0
Prothioconazole-desthio[a]	3, N = 955	2, N = 668	0–0.04	0–0.03

[a] Metabolite of Prothioconazole.

that both MACRO-DB and the national regulatory assessment should have used the same sorption and degradation properties (i.e. the substance properties used for active ingredients at the EU-level), although this cannot be guaranteed. For the other selected pesticides, MACRO-DB gives the same result as the risk assessment performed for the national groundwater scenario (i.e. predicted groundwater concentrations <0.1 μg L^{-1}).

The protectiveness of MACRO-DB in climate zones 1a and 1b can also be evaluated in relation to the national groundwater risk assessment by considering the proportion of different soil types on arable land with concentrations predicted to exceed the drinking water limit. While pesticide applications according to all the PAS studied are permitted based on the national groundwater risk assessment, the risk assessment of MACRO-DB (which forbids application if the concentrations exceed 0.1 μg L^{-1}) vary slightly between the different PAS and also depending on the proportions of the soils that are drained (see Table 4). For Clopyralid and Bentazone, MACRO-DB is more protective than the national scenario for a majority of the arable land of climate zone 1a. Compared with the national scenario, MACRO-DB gives additional protection for

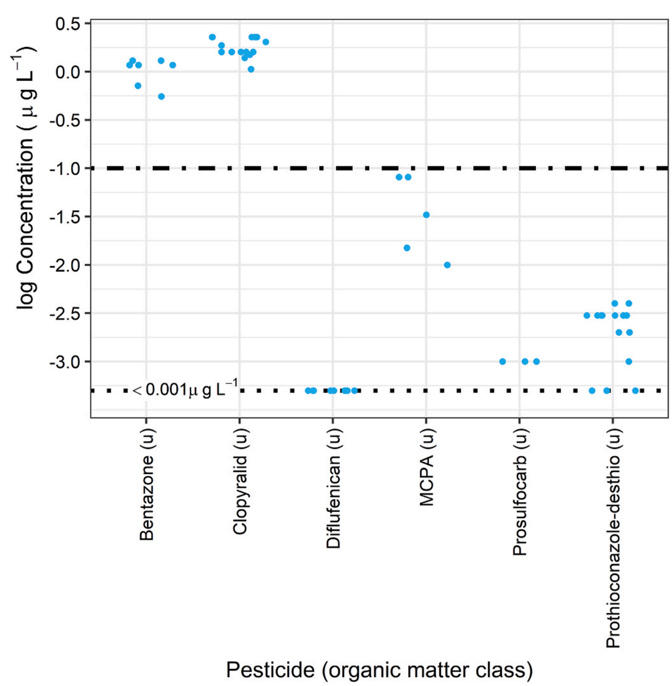

Fig. 6. MACRO-DB estimated 20-year average pesticide (or metabolite) concentrations leaching to groundwater for the soil (soil type Y2bu) of the national groundwater scenarios located in climate zones 1a and all approved combinations of crops and doses for six common pesticides.

up to 41% of the arable land of climate zone 1b for Bentazone and 97% for Clopyralid. However, the upper limits of these intervals are for the rather unrealistic condition that all soil types with drainage options within MACRO-DB were parameterized as undrained. For MCPA, MACRO-DB is more protective of up to 10% of the arable area within climate zone 1a but less than 1% for climate zone 1b, while MACRO-DB is more protective for less than 0.05% of the arable area of both climate zones for Prothioconazole-desthio.

The results of the MACRO-DB simulations can also be compared with groundwater monitoring data. Specifically for climate zones 1a and 1b, shallow groundwater is sampled at four locations, four times a year, in each of the two model catchments M42 and N34. Approximately 170 groundwater samples have been analyzed for pesticides during the period 2011 to February 2022 (SLU, 2023). In catchment M42, Bentazone and Clopyralid were detected in 28% and 0.6% (all findings at concentrations <0.1 μg L^{-1}) of the samples respectively, whereas the other four selected pesticides were never detected. None of the six selected pesticides were found in the groundwater samples taken in catchment N34. According to a compilation of several data sources from 1986 to 2014 at the national scale, Prothioconazole-desthio and Diflufenican have not been detected in Swedish groundwater, whereas the remaining four selected pesticides are occasionally found (HaV, 2014; see Table 3), although in the case of Prosulfocarb only at a maximum concentration of 0.02 μg L^{-1} (HaV, 2014) which is below the limit for drinking water. These results are in general qualitative agreement with MACRO-DB.

4. Conclusions

An online risk assessment tool (MACRO-DB) has been developed based on the simulation model MACRO which allows end-users (staff at local authorities, farmers/landowners and consultants) to perform fast and reliable risk assessments for drinking water protection areas in Sweden. Although MACRO-DB is specifically designed for use in Sweden, there is no reason why components of the tool and its supporting parameter inference system, for example the novel approaches used to link model parameters controlling site hydrology and the strength of preferential flow to soil type, could not be applicable to other parts of the world.

A Global Sensitivity Analysis of MACRO-DB suggested that the sorption and degradation properties of applied substances would be overall the most important factor influencing pesticide concentrations in Swedish drinking water resources. Soil type, climate zone and application season were much less important than compound parameters. However, the analysis also showed that variations in contamination risk among groundwater protection areas in Sweden for any given substance would be more likely dominated by variations in soil type and that in this context differences in soil organic matter content would be most critical.

In a qualitative "reality-check" using realistic application scenarios for six widely used pesticides in southern Sweden, the MACRO-DB tool clearly distinguished between substances that are detected in Swedish groundwater at concentrations above the limit for drinking water (e.g. Bentazone, Clopyralid and MCPA) and those that are not (e.g. Diflufenican, Prosulfocarb and Prothioconazole-desthio). Model outputs qualitatively coincided with, or were more restrictive than, the national groundwater risk assessment, which is a desirable outcome as a greater degree of precaution should apply for pesticide usage within drinking water abstraction zones. The outputs were also in general agreement with catchment and national-scale groundwater monitoring data.

CRediT authorship contribution statement

Anna Lindahl: Writing – original draft, Visualization, Validation, Investigation. **Stefan Reichenberger:** Software, Resources, Methodology, Formal analysis, Conceptualization. **Thorsten Pohlert:** Software, Resources, Methodology, Formal analysis. **Sebastian Multsch:** Software, Resources, Methodology, Formal analysis. **Gustaf Boström:** Project administration, Methodology. **Mikaela Gönczi:** Project administration, Methodology, Funding acquisition, Conceptualization. **Fredrik Stenemo:** Software. **Jenny Kreuger:** Project administration, Funding acquisition. **Hampus Markensten:** Software. **Nicholas Jarvis:** Writing – review & editing, Supervision, Project administration, Conceptualization.

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

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2024.120700.

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