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Review

A review of modeling pesticides in freshwaters: Current status, progress achieved and desirable improvements.☆

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ABSTRACT

This study comprises a critical review of modeling of pesticides in surface waters. The aim was to update the status of the use of models to simulate the fate of pesticides from diffuse sources. ISI papers were selected on Scopus and the information concerning the study areas, type of pesticides (herbicides, fungicides and insecticides), the model, and the methodology adopted (i.e., calibration and/or validation, spatial and temporal scales) were analyzed. The studies were carried out in Europe (55.5%), North America (22.3%), Asia (13.9%) and South America (8.3%). The Soil and Water Assessment Tool proved to be the most used model (45.95%). Herbicides were the most modeled pesticides (71.4%), followed by insecticides (18.2%) and fungicides (10.4%). The main herbicides modeled were atrazine, metolachlor, isoproturon, glyphosate, and acetochlor. Insecticides such as chlorpyrifos and metaldehyde. Chlorothalonil, and fungicides (i.e., tebuconazole) were the most widely investigated. Based on published studies, it was found that modeling approaches for assessing the fate of pesticides are constantly evolving and the model algorithms work well with diverse watershed conditions, management strategies, and pesticide properties. Several papers reported concentrations of pesticides exceeding ecotoxicological thresholds revealing that water contamination with pesticides used in agriculture and urban areas is a priority issue of current global concern.

1. Introduction

Pesticides are largely used in agriculture for plant protection; they are useful in meeting global supply needs anticipated by the UN Sustainable Development Goal 2 (United Nations, 2015; McDougall, 2018). However, the use of pesticides in agriculture has been constantly debated (Lykogianni et al., 2021). On the one hand, chemicals such as pesticides can contribute to increasing food production with the same cultivated surface areas (McDougall, 2018); on the other hand, their excessive use represents a threat for soil and water quality (Holvoet et al., 2007; Alletto et al., 2010; Zikankuba et al., 2019; Barreto et al., 2020), non-targeted organisms (i.e. pollinators; Olaya-Arenas et al., 2020) and human health (Lykogianni et al., 2021). Indeed, intensive agriculture, which is the main source of pesticides, is also considered one of the main drivers of land degradation, habitat loss and climate change (European Environment Agency (EEA), 2020; EU, 2020; Montanarella and Panagos, 2021; Ricci et al., 2022a).

In recent years, the use of pesticides has also risen a lot in the urban environment due to weed control in parks, insect regulation and urban agriculture (Meftaul et al., 2020). Monitoring activities confirmed that pesticide concentrations are often higher than acceptable water quality limits (Proia et al., 2013; Stone et al., 2014; Wang et al., 2019) and that more of the 80% of European soil is characterized by the presence of one or more residue substance (Silva et al., 2019). To counteract this issue, in 2015 the European Union (EU), with the aim of reaching the water standard quality expected by the Water Framework Directive (European Commission (EC), 2000), introduced a Watch List (WL) consisting of 10 priority groups of substances that are potentially risky for the aquatic environment, an indication of the monitoring matrices and the possible methods of analysis (JRC Publications Repository, 2020. Moreover, the main environmental strategies on a global and European scale, such as the 2030 Agenda for Sustainable Development and the "Farm to Fork Strategy", target improving water quality and minimizing the release of chemicals, such as pesticides, by 50% (United Nations, 2015; EC, 2020).

In this context, it is necessary to monitor these substances to update the WL and to better define the water policy for implementing programs

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of measures for reducing their use (Pietrzak et al., 2019). Sampling campaigns are an important aspect to be considered while carrying out studies on pollutants such as pesticides, which are considered of particular environmental interest due to their potential toxicity, high persistence and mobility (D'Ambrosio et al., 2019; Manjarres-López et al., 2021). The more accurate the monitoring program is, the more accurate the estimation of the potential ecological risks will be, thus making it possible to properly define the mitigation strategy to be adopted (Wang et al., 2019). Field activities are expensive and time consuming and may represent limited spatial areas (D'Ambrosio et al., 2019; Ricci et al., 2022a). Hence, alongside sampling campaigns, eco-hydrological models are increasingly being used to assess pesticide concentration, fate and transport processes (Fohrer et al., 2014).

The selection of the most appropriate model is subjective and depends on the purpose of the work, on the input data availability and on the ability to represent the physical and chemical processes by means of parameterization (Abdelwahab et al., 2018; Wang et al., 2019). Different authors tried to address these aspects in their review articles. Quilbé et al. (2006), in its multi-criterial analysis based on model ease of use, model applicability, model characteristics and the possibility of simulating Best Management Practices (BMPs), identified thirty-six models. Payraudeau and Gregoire (2011) compared 10 models to assess their ability to simulate some principal hydrological processes and pesticide dynamics occurring in water, plants and the atmosphere and their ability to represent some mitigation measures. The authors showed that physically based models better represent the interaction between hydrological and chemical processes. Wang et al. (2019) focused their review on the different Soil and Water Assessment Tools (SWAT), (Arnold et al., 1998), applications considering aspects such as pesticide type, the link with other models to better represent some processes and possible algorithm improvements. In their review, Mottes et al. (2013) analyzed 16 models applied at the field scale to evaluate the effects of agricultural practices on the predicted distribution and transfer of pesticides. Starting from the results of the previous reviews, this work presents a review aimed at (i) updating the status of the development, use and diffusion, globally, of models to simulate pesticides coming from diffuse pollution (ii) analyzing the models (e.g. spatial and temporal scales, input requirements and model outputs), and (iii) investigating possible relationships between the single compound and the models used for predicting its transport and fate. By providing an overview of the studies on modeling pesticides, the final aim of this work was to facilitate water resource managers in selecting a model to assess the transport and fate of pesticides.

2. Material and methods

To better organize the papers to be included in the review, the flow diagram illustrated in "The PRISMA 2020 statement" (Page et al., 2021) was taken as a model and adapted to the aims of this research. The bibliographic research was carried out on Scopus using the following keywords: "pesticides, model, watershed, hydrology, water quality, diffuse pollutant"

The database, which was queried in May 2021, returned 596 records. Considering the aim of updating the status of the use of hydrological models, globally, to simulate pesticides, the years prior to 2013 were excluded because already analyzed by other review articles. Moreover, since 2021 was not yet concluded, and some other papers might still have been published, 2020 was adopted as the final year of investigation. This resulted in 254 records (Fig. 1), 79 records were removed since belonging to books, book chapters, editorial, notes and other reviews. Subsequently, articles not in English, not available and papers focused on subjects not related to this paper (i.e., monitoring or

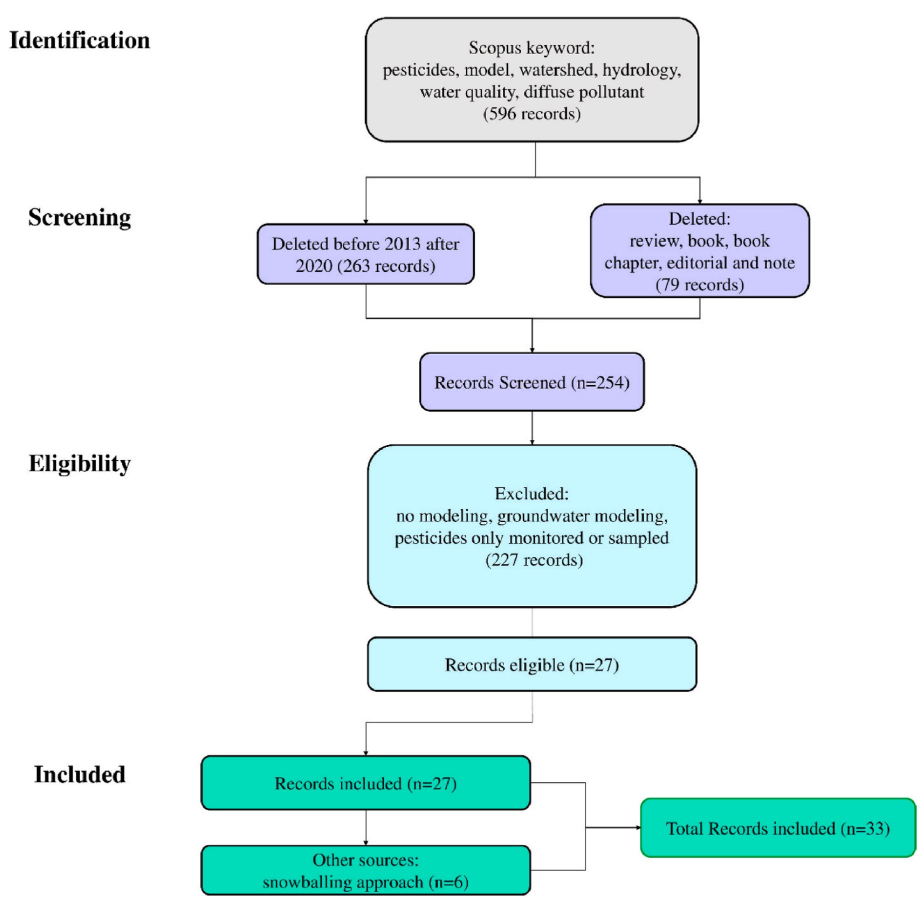

Fig. 1. Diagram of the methodological approach adopted for the review.

sampling, modeling pesticides only in groundwater or aquifers, studying the effect of pesticides on human health, the use of pesticides to increase crop production) were also excluded. The resulting eligible articles were used as a start-set of papers for the snowballing procedure. The guidelines of the "Snowballing Approach" (Wohlin, 2014) were followed to select papers. Specifically, a new list of articles was defined by going through the reference list of the start-set of papers and looking at titles. The papers were examined, and those that do not fulfill the basic criteria defined above were excluded. The remaining papers were selected. This process was reiterated until no new papers were found. Six papers were added to the database since they were deemed fundamental to the topic. A total of 33 articles were therefore obtained (Fig. 1).

Each article was analyzed and a database containing relevant information with respect to the aims of the study was built (Annex A1). The dataset was composed of seven main sections collecting general information (i.e. title, doi, year of publication, authors), the study area (i.e. geographical position, size), the model (i.e. model used, calibration or validation, temporal scale considered, modeled scenarios), the pesticide (i.e. herbicides, fungicides, insecticides), field activities (i.e. frequency, measurement period) and modeling results (i.e. spatial and temporal scale, average concentration). Whenever data were available in the paper analyzed, the table was completed appropriately. Multiple records for a single article were accepted when the study area belonged to more than one nation. In this case, one article was represented by two or more rows in the table (Annex AI).

3. Results

3.1. General data

A database was compiled with the information derived from the 33 articles, which were analyzed consistently with the aims of the study (Supplementary Material S1). During the study period, the number of papers per year ranged from 2 (2015 and 2019) to 11 (2017).

There were 17 ISI journals; the most important information (authors, journal and keywords) was summarized in Table 1. *Science of the Total Environment* (5 papers) was the journal with the highest number of published papers, followed by *Hydrology and Earth System Sciences* (4 papers) and *Environmental Pollution*, *Water Research* (3 papers) and the *Journal of Environmental Management* (3 papers). The most commonly used keyword was "pesticide", followed by SWAT, pollution, model, water, quality, agriculture, diffuse pollution and water quality (Table 1).

Regarding the global distribution of the study areas (Fig. 2), Europe was the continent with the highest incidence of records (70.7%), followed by North America (14.6%), Asia (9.8%) and South America (4.9%). Considering the individual European countries, the highest number of studies was carried out in France (14.6%), followed by England and Switzerland (both 12.2%) and Belgium, Germany and Wales (4.8% each).

3.2. Models

The analysis of the models revealed that 17 different tools were cited and implemented to simulate the fate and transport of pesticides (Table 2). Among the models, SWAT was the one most used on a global scale (35.71%). In particular, the SWAT model was the only model utilized in the United States of America (USA), China and Thailand (Fig. 3, Table 2). The UK and France presented the greatest heterogeneity of methodological approaches adopted (Fig. 3). Indeed, SWAT, PSYCHIC (Phosphorus and Sediment Yield CHaracterisation In Catchments), INCA (INtegrated CAtchment contaminants model), IMPT (Integrated Model for Pesticide Transport) and PRZM (Pesticide Root Zone Model) were used in the UK, while SWAT, VFSMOD (Vegetative Filter Strip Modeling System), iWaQa (Integrated Water Quality Model) and a conceptual model were implemented in France. In all the other countries, except Switzerland in which 4 different models were applied (i.e.

Table 1
General data describing the analyzed papers.

Author	Year	Journal	Keywords
Ammann et al.	2020	Journal of Hydrology	Pesticide transport, Experimentalist knowledge, Controlled application, Conceptual model, High-frequency, Concentration data, Bayesian inference
Cambien et al.	2020	Water	Pesticide dynamics, Guayas, River basin agricultural intensification, Soil and Water Assessment Tool, Data scarcity, Freshwater, Ecosystem management
D'Andrea et al.	2020	Science of the total Environment	Risk assessment, Agriculture, Contamination, Agrochemicals, PWC, Water quality
Purnell et al.	2020	Water Research	SWAT, Metaldehyde, Pesticide, Management, Water framework directive
Comber et al.	2019	Frontiers in Sustainable Food Systems	big data & analytics spatial data integration, Pesticides, Metaldehyde, Web-based model RAPI (application program interface) United Kingdom
Quaglia et al.	2019	Journal of Environmental Management	Surface water, Diffuse pesticide pollution, GIS modeling, Catchment scale, Pesticide risk areas, Field observations
Asfaw et al.	2018	Journal of Hydrology	Metaldehyde, Diffuse pollution modeling, Rainfall runoff, Surface water quality, Water resources
Lauvernet and Muñoz-Carpena	2018	Hydrology and Earth System Sciences	
Morselli et al.	2018	Science of the total Environment	Slope, Runoff, Curve number, DOC, Dynamic scenario, Orchard
Moser et al.	2018	Hydrology and Earth System Sciences	
Carluer et al.	2017	Science of the total Environment	Vegetative filter strip, Buffer zone modeling, Process-based model, VFS sizing, Shallow water table, Watershed
Chen et al.	2017	Water Research	Pesticide, SWAT, Calibration, Model evaluation, Uncertainty analysis, Delta
Jones et al.	2017	Journal of Applied Ecology	Axis II, Common Agricultural Policy, Diffuse agricultural pollution, LEAFPACS, Output measures, Policy evaluation, River Invertebrate Classification Tool, Tir Cynnal, Tir Gofal
Lu et al.	2017	Environmental Science: Processes & Impacts	
Lutz et al.	2017	Hydrology and Earth System Sciences	
Ouyang et al.	2017	Water Research	Pesticide, Diffuse pollution, Water quality, Agricultural exploitation, Watershed modeling
Serpa et al.	2017	Environmental Pollution	Agricultural pollution, Copper, Nitrogen, Phosphorus, Surface waters
Vernier et al.	2017	Environmental Science and Pollution Research	Agriculture, Data warehousing, Indicators, Integrated modeling,

(continued on next page)

Table 1 (*continued*)

Author	Year	Journal	Keywords
			Pesticides, Scenarios, Water management
Villamizar and Brown	2017	Catena	Pesticide, Preferential flow, MACRO, SPIDER, In-stream, Catchment
Winchell et al.	2017	Integrated Environmental Assessment and Management	SWAT model, Pesticide exposure, Ecological risk assessment, Model parameterization, Modeling monitoring comparison
Bannwarth et al.	2016	Journal of Environmental Management	SWAT, MPMAS, Thailand, Environment, Eco-toxicological threshold, Impact assessment, Multi-agent system
Ouyang et al.	2016	Science of the total Environment	Pesticide, Temporal–spatial pattern, Agricultural development, Diffuse pollution, Water risk, Uncertainty
Pullan et al.	2016	Science of the total Environment	Catchment scale model, Parameter-efficient, Diffuse pesticide transfer, Drainflow, Drinking water resources
Baffaut et al.	2015	Journal of Environmental Quality	
Gassmann et al.	2015	Journal of Environmental Management	SWAT, MPMAS, Thailand, Environment, Eco-toxicological threshold, Impact assessment, Multi-agent system
Ahmadi et al.	2014	Environmental Pollution	Climate change, Hydrology, Water quality, Modeling, Nutrients, SWAT
Bannwarth et al.	2014	Environmental Pollution	Pesticide simulation, SWAT, Tropical catchment, Atrazine, Chlorothalonil, Endosulfan, ANSELM
Boithias et al.	2014	Catena	Application timing, Sorption properties, Metolachlor, Aclonifen, SWAT model, Save river
Gagnon et al.	2014	Integrated Environmental Assessment and Management	Stochastic modeling, Pesticide fate modeling, Water quality, Pesticide risk assessment, Canada
Fohrer et al.	2014	Journal of Environmental Quality	
Ahmadi et al.	2013	Water Resources Research	Nonpoint source pollution, Soil and water conservation, Mixed-variable multiobjective optimization, Atrazine, Nitrate, SWAT
Bertuzzo et al.	2013	Advances in Water Resources	Herbicide transport, Travel time, Residence time, Atrazine
Gassmann et al.	2013	Hydrology and Earth System Sciences	

iWaQa, a perceptual model, a mathematical model and ZIN-AgriTra), the number of models implemented was limited to one or two (Fig. 3).

The spatial scales of the case studies included experimental plots (Lu et al., 2017), river basins (drainage areas from less than 5 km^2 to 160, 000 km^2) (Gassmann et al., 2015; Pullan et al., 2016; Moser et al., 2018; Ammann et al., 2020; Cambien et al., 2020) and regional areas (Gagnon et al., 2014; D'Andrea et al., 2020). More than half of the studies (66.66%) applied only one model (Table 2), while the rest (33.33%) used a principal model to determine pesticides coupled with a second model (e.g., hydrological or hydrogeological model) for simulating river or groundwater flow, plant stress or to carry out the economic analysis. Among the studies adopting a cascade model strategy, SWAT was the model most used, since it makes it possible to simulate hydrology and water quality. Finally, among the studies aiming at a scenario analysis, BMP evaluation was the most frequently developed topic (Table 2), followed by land use change and climate change.

Among the studies analyzed, 24 papers reported the model calibration, including 17 studies that also reported the validation. The calibration was mostly performed on a daily basis for a multiple year period, ranging from about one to 20 years. Simulations on a monthly or yearly time scale were carried out to a lesser extent. Field data (measured streamflow and pesticides) were used in 24 studies to calibrate the model, whereas nine studies did not report any information about field activities.

3.2.1. *Models: description and data requirement*

The SWAT model (Soil and Water Assessment Tool) is a semi-distributed and physically based hydrological and water quality model developed by USDA (Arnold et al., 1998). For the model set-up, spatial information such as land use, soil properties, DEM, agricultural management practices (i.e., fertilizers, pesticides applications, tillage operation, irrigation) and punctual data (weather) are needed. It works at the basin scale, which is divided into subbasins and into hydrologic response units (unique land use, slope and soil units). It develops the water balance, sediment transport and nutrient cycles. The movement of soluble and sorbed forms of pesticides from land areas to the stream network is described by algorithms taken from EPIC (Williams, 1975). SWAT integrates the mass balance developed by Chapra (1997) with the transformation and transport of pesticides in streams. Results are provided at the different temporal scales (daily, monthly, yearly) and spatial scales (basin, subbasin and reach scale).

SPIDER is a distributed model whereby the landscape is divided into fields and ditches/streams. It works on an hourly basis, but there are no restrictions on the simulation's duration. The model was developed for wet environments (Northern Europe) and for catchments of up to 10 km^2. Agricultural fields are hydrologically connected (via runoff, lateral flow, drain flow) to ditches and streams that receive pesticides that are dissolved in water and, directly, via spray drift. Water and pesticides are routed through the stream reach to the outlet of the catchment. SPIDER code was object-oriented (C++ language). The model allows several applications of pesticides throughout the simulation period. The main limitations are the input data requirements (e.g., hourly rainfall data and parameters for each field and river reach). SPIDER has been coupled with the MACRO model (Villamizar et al., 2017).

The Model-based (Mb) risk map is a theoretical, spatialized approach that makes it possible to determine the non-point source export of pesticides to surface waters (Quaglia et al., 2019). The model needs several input data (i.e., land cover, DEM, runoff map, soil properties, a potential erosion map and a mitigation measures map). The Mb model is composed of three different steps. The first, which determines the transported fraction of the applied compounds, is based on the Water Emission Inventory Support System (WEISS) approach. The second evaluates the reduction of the runoff transport capacity due to the presence of buffer strips. The third, based on topography and stream network, determines the connectivity between the different parcels of the basin. Lastly, for each parcel, the gross emission is calculated and the Mb risk map is generated (Quaglia et al., 2019). Results are provided annually and at the basin or parcel spatial scale.

The DynAPlus model (a spatially explicit, dynamic model for predicting pesticide exposure in the surface waters of cultivated mountain basins) (Morselli et al., 2018) is a conceptual model composed of two sub-models: the water-sediment model for river networks (DynANet; Di Guardo et al., 2006) and the spatially resolved air-soil model (SoilPlus; Ghirardello et al., 2010). The first (DynANet) assesses the fate of chemicals in the water-sediment systems and the second (SoilPlus) assesses the fate of chemicals in the air, litter and soil system. In both the sub-models, the chemical mass balance is described by a time-dependent

Country	Records
Argentina	1
Austria	1
Belgium	2
Canada	1
China	2
Ecuador	1
England	5
France	6
Germany	2
Italy	1
Liechtestein	1
Luxembourg	1
Netherlands	1
Norway	1
Portugal	1
Swiss	5
Thailand	2
United States	5
Wales	2

Fig. 2. Global distribution of the study areas.

equation solved using the Runge-Kutta numerical integration procedure (Di Guardo et al., 2006; Ghirardello et al., 2010). Data on land use, soil characteristics (i.e., texture, organic carbon fraction) and topography (DEM) are necessary to build up the model. In addition, meteorological data and chemical application rates are needed. The model divides the basin into sub-basins (each corresponding to a stream reach). Results are provided on a sub-basin or basin scale on an hourly, daily, monthly and annual basis.

The IMPT (Integrated Model for Pesticide Transport) model is a semi-distributed conceptual model used to predict the fate and transport of pesticides at the basin outlet (Pullan et al., 2016). The model set-up requires several input data such as a soil map, land cover data and meteorological data (i.e., rainfall and temperature). Pesticide properties, such as "disappearance time" of 50% (DT_{50}) and the organic carbon-water partition coefficient (K_{OC}) are also needed. The transport of pesticides from soil is described with different equations assuming that the compounds' mass bypasses the soil matrix and is transported into the surface water (Pullan et al., 2016). Results are provided at the basin outlet on a daily basis.

iWaQa (Integrated Water Quality Model) is a semi-distributed and conceptual pesticide management model. It was originally developed by the Swiss Federal Institute of Aquatic Science and Technology for the management of small streams (Honti et al., 2017). iWaQa was further modified to be applied in large basins by including an explicit routing component (Moser et al., 2018). The model is characterized by two modules including different equations: the substance transfer module (transfer of pesticide from the field to the outlet of one sub-basin) and the routing module (transfer of pesticide in the stream to the outlet). Rainfall, temperature, discharge, land use and chemical compounds are the main inputs of the iWaQa model. Results are provided at different temporal scales (daily, hourly) and spatial scales (basin, subbasin).

MACRO is a hydrological and water quality, physically based, one-dimensional numerical model developed by the Swedish University of Agricultural Sciences (Jarvis, 1995). To set up the model, weather data, soil characteristics, crop data and pesticide properties (i.e., half-lives, sorption constant) are needed. The model works at the field level and simulates both macropore and micropore flow with a two-flow system domain. The soil water flow and the transport of solutes in micropores were calculated with the Richards' equation, while the flow in macropores is computed with a similar approach to the kinematic wave (Jarvis, 1994). The model can be applied at the basin scale and it provides outputs on a daily basis and at the field level.

The United State (US) Environmental Protection Agency (EPA) Pesticide Water Calculator (PWC) is a software, applicable to different water bodies (i.e., reservoir, ponds, custom water bodies), which includes the PRZM and Variable Volume Water Body Model (VVWM, Young, 2016). The first (PRZM) is used to compute the runoff, water erosion and pesticide transport (Suarez et al., 2006). The second (VVWM) is a model composed of specific mathematical modules to simulate the transport processes of chemical substances in water bodies (Burns, 2004). PWC input data include pesticide application (time, rate, physiochemical properties), climate variables, soil characteristics, water body characteristics, erosion and runoff processes. The software, which can be also applied at a regional scale (D'Andrea et al., 2020), provides compound concentrations at events or on a daily basis.

The Vegetative Filter Strip Modeling System (VFSMOD) (Muñoz-Carpena et al., 1993) is a storm-based mathematical model for simulating runoff, infiltration sediment and pollutants filtered by vegetated strips. It works at the field or basin scale. It needs several input data such as, rainfall, soil properties, pesticide properties (i.e., transport, decay), DEM and filter strip properties (i.e., length, width). The pesticide transport and reduction due to the filtering capacity of the vegetation is computed using a generalized regression-based approach (Sabbagh et al., 2009). Results are provided in terms of efficiency reduction of the vegetated filter strip considered in the model simulation.

Zin-AgriTra is a distributed conceptual hydrological and water quality model (Gassmann et al., 2013). The model works at the basin scale, which is divided into raster cells based on soil and land use characteristics (Gassmann, 2013). Rainfall data, pesticide properties, land use and soil properties are the main input data required for the model set up. Pesticide mass transport processes (sorption, transformation) are calculated using first-order sorption kinetics and a first-order decay function, respectively (Gassmann et al., 2013). The model can be run at hourly or smaller intervals. Results are provided at the basin or sub-basin scale.

Bertuzzo et al. (2013) defined a mathematical model to assess hydrology and herbicide transports. Weather, pesticide application rates and properties (half-life) are needed to build up the model. The model works at the basin scale and its theoretical framework is based on three sections. The first is named travel time formulation of transport, which is composed of different equations formalizing the hydrological cycle, water storage, water and solute fluxes. The second, named mixing assumption, is specific for the determination of the travel time distribution of the water particles. The third, named solute transport, computes the mass flux of solute associated with the flow considering the quantity of solute lost via evapotranspiration (Bertuzzo et al., 2013). Results are provided at the outlet on an annual, monthly or daily scale.

Lutz et al. (2017) implemented a conceptual model aimed at

Table 2
Principal data of the papers: Authors and year, study area, model, substance, scenario.

Author, year	Study area	Km^2	Model	Coupled models	Pesticides			Model scenarios		
					H	F	I	BMP	CC	LUC
Ammann et al., 2020	Swiss, Eschibach basin	1.2	Perceptual model		x					
Cambien et al., 2020	Ecuador, Guayas basin	34,000	SWAT		x	x				
D'Andrea et al., 2020	Argentina, Pampa region[D]	500,000	PWC		x					
Purnell et al., 2020	England, Medway basin	2409	SWAT				x			
Comber et al., 2019	England, Wissey basin; Wales, Teifi basin		Landscape model	WaSim PSYCHIC	x		x			
Quaglia et al., 2019	Belgium, Cicindria basin	10.7	Model-based (Mb) risk	WEISS	x			x		
Asfaw et al., 2018	England Leam basin[B]	300	Physical model				x			
Lauvernet and Munõz-Carpena 2018	Francia[A]		VFSMOD	SWINGO	x	x		x	x	
Morselli et al., 2018	Italy, Novella basin	133	SoilPlus	DynANet (DynAPlus)			x			
Moser et al., 2018	Rhine basin	160,000	iWaQa	AQUASIM	x					
Carluer et al., 2017	France, Fontaine du Theil basin	1.28	VFSMOD							
Chen et al., 2017	USA, San Joaquin basin	15,000	SWAT		x			x		
Jones et al., 2017	Wales		MACRO					x		x
Lu et al., 2017	England, Thames basin		INCA							
Lutz et al., 2017	France, Bas Rhin[A]	0.47	Conceptual model		x					
Ouyang et al., 2017	China, Abujiao basin	141.5	SWAT		x			x		
Serpa et al., 2017	Portugal, São Lourenço basin	6.2	SWAT						x	x
Vernier et al., 2017	France, Charente basin	10,000	SWAT	GenLU2	x	x	x	x		
Villamizar and Brown 2017	Norwich, Wensum basin	650	MACRO&SPIDER		x					
Winchell et al., 2017	USA, Twenty-seven basin		SWAT		x					
Bannwarth et al., 2016	Thailand, Mae Sa basin	77	SWAT	MPMAS		x	x	x		x
Ouyang et al., 2016	China		SWAT		x	x	x	x		
Pullan et al., 2016	England, Cherwell basin[B]		IMPT		x			x		
Baffaut et al., 2015	USA, Mississippi basin	73.4	SWAT		x			x		
Gassmann et al., 2015	Swiss, Ror basin[B]	1.95	ZIN-AgriTra		x					
Ahmadi et al., 2014	USA, Eagle Creek basin	248	SWAT		x				x	
Bannwarth et al., 2014	Thailand, Mae Sa basin	77	SWAT	ANSELM	x	x	x			
Boithias et al., 2014	France, Save basin	1110	SWAT		x					
Gagnon et al., 2014	Canada, 2290 SLC polygons[C]		PRZM	Stochastic model						x
Fohrer et al., 2014	Germany, Kielstau basin	50	SWAT		x					
Ahmadi et al., 2013	USA, Eagle Creek basin	248	SWAT	NSGA-II	x			x		
Bertuzzo et al., 2013	Swiss, Aabach-Mönchaltorf basin	46	Mathematical model		x					
Gassmann et al., 2013	Swiss, Ror basin	1.95	ZIN-AgriTra		x					

A = Plot, part or strips.
B= Subbasin.
C= Polygon.
D = Region.
H= Herbicides.
F= Fungicides.
I= Insecticides.
BMP= Best Management Practices.
CC= Climate Change.
LUC = Land Use Change.

upscaling, at the basin scale, the sample-based Compound Specific Isotope Analysis (CSIA) information on pesticide degradation. The model is composed of two storage reservoirs: the first (source) represents the upper soil layer upon which the pesticide is applied, while the second (transport zone) represents the unsaturated soil and the groundwater layers (Benettin et al., 2013; Bertuzzo et al., 2013). Daily data of rainfall and potential evapotranspiration (ET_0) are necessary to set-up the model, as well as punctual pesticide application rates and dates. The results (i.e., quantification of pesticide transport and degradation) are provided on a daily basis.

Ammann et al. (2020) translated a perceptual model into a spatialized conceptual model, working into the "SUPERFLEX" hydrological modeling framework (Fenicia et al., 2011; Kavetski and Fenicia, 2011). It defines the water balance as well as the processes of transport degradation and sorption of pollutants. The model works at the basin scale, which is subdivided into homogenous HRUs based on the different paths existing in the study area (i.e., impervious, connected, drained, groundwater). Several equations describing the water balance and the main elements of the pollutant mass balance formalize the processes in the SUPERFLEX model (Ammann et al., 2020). The conceptual model makes it possible to record results sub daily and at the basin level.

Asfaw et al. (2018) proposed a physical distributed model, based on the travel time of surface runoff, to assess metaldehyde concentrations. The model can be applied at the basin scale and it requires rainfall data, land use, soil type and DEM. Surface runoff generation is computed with the Soil Conservation Service – Curve Number method (SCS–CN, Hjelmfelt, 1991). The runoff routing, within the flow pathways, is determined using a time variant travel time computation technique, which is composed of the kinematic wave approach proposed by Wong (1995). The metaldehyde wash-off is defined by the simplified formula for indirect loadings caused by runoff (Berenzen et al., 2005). Results are provided at the event scale.

Gagnon et al. (2014) constructed a stochastic model and coupled it with the Pesticide Root Zone Model (PRZM) to evaluate the change in the risk of water contamination by pesticides across Canada between 1981 and 2006. The pesticide fate model PRZM version 3.12.3 (Suarez, 2006) was developed by the United States Environmental Protection Agency (freely available at http://www2.epa.gov/exposure-assessment-models/przm3-version-3123).

Comber et al. (2019) developed a complex landscape scale

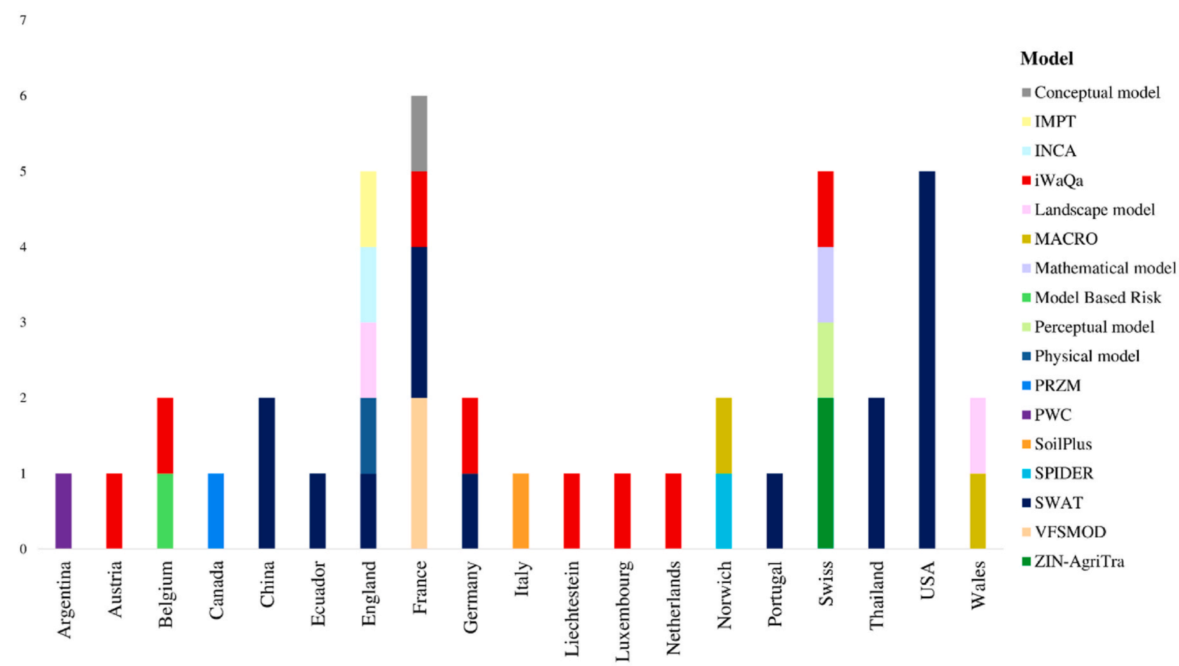

Fig. 3. Relationship between geographical area and model.

framework (Landscape scale model) to assess the distribution of pesticide risk areas. The model is based on the source-mobilization-delivery-impact model of the water pollutant transfer continuum (Lemunyon and Gilbert, 1993) and is composed of different modules. The portion of pesticides susceptible to runoff losses are computed based on the amount of applications net of soil absorption. Then, the SCS-CN (Hjelmfelt, 1991) method, included in the soil water balance model (WaSim, Hess and Counsell, 2000), was used to define the amount of pesticides mobilized by any rainfall event. Finally, the partitioning of pesticides transported in surface and drain flow pathways was determined using the Phosphorus and Sediment Yield CHaracterisation In Catchments (PSYCHIC, Collins et al., 2007). The model input data are land cover, soil, slope, pesticide application rate, climatic data and digital elevation model. The outputs concern the spatial distribution of pesticide loads mobilized and delivered to the receiving watercourses (Comber et al., 2019).

3.3. Pesticides

Regarding the pesticides, 34 different compounds were modeled.

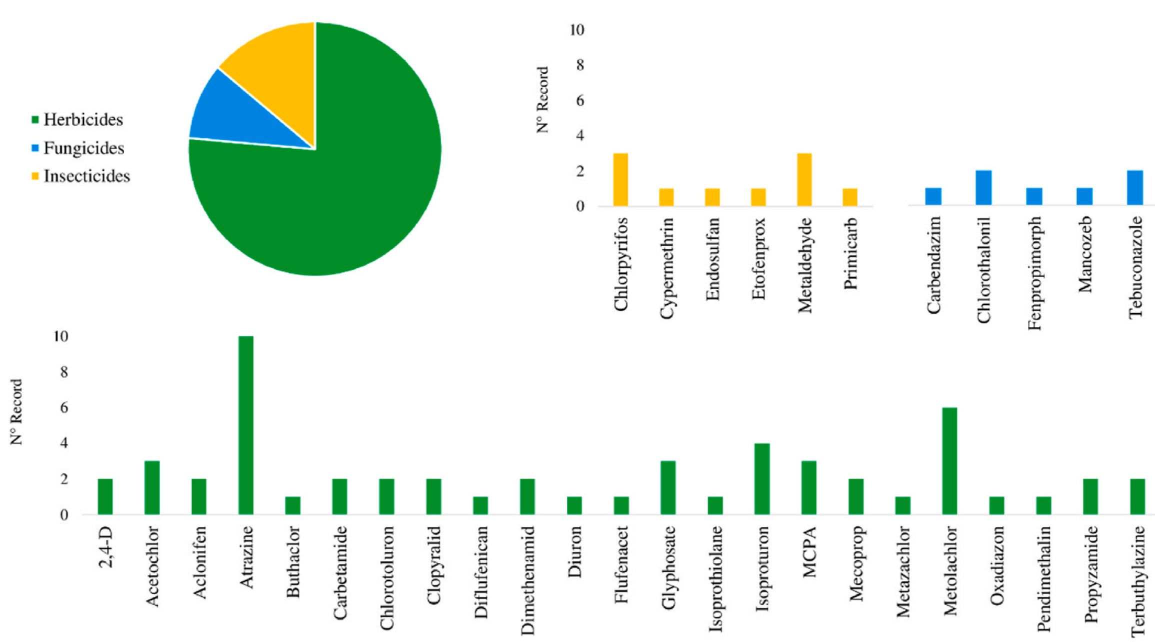

Fig. 4. Distribution of pesticides into three categories: herbicides, fungicides and insecticides.

Atrazine was the most studied (27.57%), followed by metolachlor (17.14%), isoproturon, glyphosate, acetoclhor, metaldehyde and chlorpyrifos (8.57%; Fig. 4). Pesticides were grouped into three categories: herbicides (with a frequency of 76%), insecticides (14%) and fungicides (10%) (Fig. 4). Atrazine was the most widely studied herbicide (ten records), chlorpyrifos and metaldehyde were the most commonly modeled insecticides (three records). Finally, three records were found for fungicides: chlorothalonil and tebuconazole (Fig. 4).

Isoproturon, metolachlor, and terbuthylazine were the most studied compounds (Fig. 5a). Indeed, isoproturon was investigated in nine countries, while, metolachlor and terbuthylazine were analyzed in eight studies. However, it should be noted that Austria, Belgium, France, Germany, Liechtenstein, Luxembourg, Netherlands and Switzerland were included in a single paper (Moser et al., 2018), which considered the whole Rhine basin as the study area (Fig. 5a). Other compounds investigated in more than two countries included atrazine (USA, Swiss, China and Thailand), chlorpyrifos (China, France and Italy), MCPA (England, France and Norway) and glyphosate (Argentina, Belgium and France) (Fig. 5a).

Regarding the number of studies related to a single compound, metolachlor showed the highest number of records (Berenzen et al., 2005), followed by isoproturon (Barreto et al., 2020) and atrazine (Bannwarth et al., 2014). France, Switzerland and the USA showed multiple records for the same substance because more than one study was found (Fig. 5a).

Lastly, Fig. 5b shows the relation between the single compound and the model used. SWAT is the model that simulated the highest number of pesticides, followed by IMPT and MACRO. In addition, iWaQa was also frequently used, especially for modeling isoproturon, metolachlor and terbuthylazine (Fig. 5b).

4. Discussions

4.1. General comments on the results

In this work, a dataset concerning modeling applications to simulate the fate of pesticides in surface waters was built up by analyzing 33 ISI papers (2013–2020). A set of 34 attributes, such as information about the model used, the study area, the calibration and the validation processes, the compound investigated and the results in terms of loads, concentrations or critical sources areas were retrieved from the reviewed papers. The resulting dataset is an important source of information that can be used and expanded for future studies. In addition, it can help users in selecting an appropriate model based on their objectives. Further analysis could be related to specific issues such as the modeling of the drift of the pesticide or the fate of pesticides in small or intermittent streams (Lorenz et al., 2017; Szöcs et al., 2017; Wang et al., 2019). Physical and chemical properties of pesticides and environmental factors (e.g., types of crops, soil properties, climate) influence the amount of substance that is released into the river system. Intermittent streams and spring waters tend to receive greater inputs of pesticides both because they are more interconnected with the surrounding landscape and because the dilution effect is low due to low streamflow. Therefore, proportionately higher pesticide contamination can be expected compared to large perennial rivers (Szöcs et al., 2017). However, a very limited number of studies on monitoring and modeling pesticides in small streams has been conducted and published in ISI journals (Lorenz et al., 2017; Szöcs et al., 2017).

In the papers analyzed papers, 17 different models were applied to assess the fate of pesticides. MACRO, PRZM and SWAT were already the subject of other reviews (Quilbé et al., 2006; Payraudeau and Gregoire, 2011; Mottes et al., 2013; Wang et al., 2019). Mottes et al. (2013) showed that MACRO and PRZM make it possible to apply pesticides with tillages as input, above the canopy or directly on the soil, while SWAT considers the transfer of pesticides in soils only after an aboveground application. However, PRZM and MACRO consider the effect of tillage on pesticide distribution only if tillage practices take place on the same day as the pesticide's application (Mottes et al., 2013). Gagnon et al. (2014) showed that PRZM only estimates the amount of pesticides in the surface runoff and not in the stream, leading to an overestimation. Villamizar and Brown (2017), comparing MACRO with SPIDER, noted that MACRO does not account for the sub-lateral flow routing of pesticides and may underestimate compound concentrations, for example, of Clopyralid. On the other hand, SWAT was found to be one of the best performing models for assessing pesticide contamination under different conditions and within different BMPs (Quilbé et al., 2006; Mottes et al.,

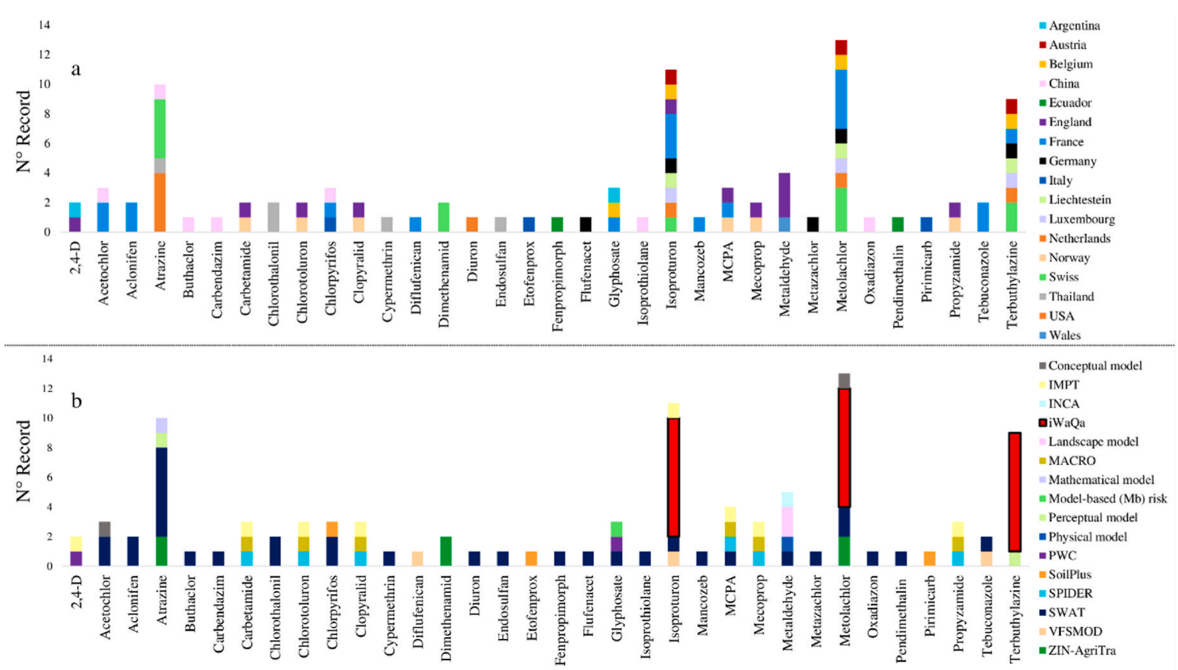

Fig. 5. Relationship between pesticides and study area (a) and between pesticides and model (b). The black rectangle indicates all the records belonging to the Rhine basin.

2013). Indeed, SWAT is one of the most widely used models globally (Wang et al., 2019). The results of this overview confirmed that SWAT is currently the most used model, both in terms of model applications (15 of 33) and in terms of geographical areas (8 of 19). This work also revealed that PRZM and MACRO are among the most commonly used models, with two case studies each. PRZM was included in the PWC model for pesticide risk assessment used by D'Andrea et al. (2020) in their study in the Pampa Region (Argentina).

ZIN-AgriTra was found in two applications, which were carried out by the same authors (Gassmann et al., 2013; Gassmann et al., 2015) and in the same study area (Ror headwater basin, Swiss). This model does not include erosion and sediment transport; hence, the concentrations of sediment related substances could be underestimated. However, the authors affirmed that ZIN-AgriTra could also be applied in other areas (Gassmann et al., 2013; Gassmann et al., 2015).

All the other models discussed in this review were applied in a single case study; thus, it is difficult to evaluate their performance in different environment conditions.

In their multi-criteria analysis, Quilbé et al. (2006) pointed out that BASIN and GIBSI are two functional models to simulate the fate of pesticides both based on the equations used by the SWAT model. However, the use of these models seems to be very limited since neither the new nor the old reviews reported applications in case studies (Payraudeau and Gregoire, 2011; Mottes et al., 2013).

Considering the global distribution of the studies, the main clusters were found in Europe, North and South America and Asia. These results are in line with what was reported by Wang et al. (2019) and Borrelli et al. (2021). In contrast with the latest reviews, this study highlighted that Europe was the continent with the highest number of model applications, while no studies were found in Africa and Australia. Moreover, it is important to underline that in some countries such as Russia, the limited number of ISI papers (or their absence) does not necessarily correspond to a lack of studies since the results have probably been published in the local language.

Another key point that emerged from our analysis concerned the calibration and validation of the models. Among the 33 studies analyzed, 24 performed the calibration, of which 17 also reported the validation. In most cases, calibration and/or validation was performed for conceptual or physically based models (e.g., SWAT, ZIN-AgriTra) (Payraudeau and Gregoire, 2011; Wang et al., 2019). The calibration techniques (e.g., manual or automatic procedures) were extremely variable and specific for each study; thus, it is difficult to find a specific trend and to make some classifications. The causes of the difference between the number of studies performing the calibration and the number of studies performing the validation depend on the limited availability of observed data (i.e. concentrations and streamflow), which often makes authors lean towards calibration only to reduce model uncertainty (Gassmann et al., 2013; Wang et al., 2019; Ammann et al., 2020; Ricci et al., 2022b). Field measurements, samplings and analytical determinations are expensive and, for this reason, monitoring is generally not carried out in developing countries (e.g., African countries) for some types of streams, such as intermittent rivers (De Girolamo et al., 2022a). In other cases, field data are missing, making model calibration and validation impossible (Gagnon et al., 2014; Carluer et al., 2017; D'Andrea et al., 2020). Indeed, several authors pointed out that limited data availability is a limiting factor in model applications (Borrelli et al., 2021; Ricci et al., 2022b; De Girolamo et al., 2022b).

4.2. *Level of pollutants in surface waters*

Regarding surface waters, the legally accepted concentrations of pesticides are very different from one country to another. This issue was already underlined by Li and Fantke (2022) who investigated the pesticide regulations for surface waters from 53 countries. The authors pointed out that large variations in pesticide regulations, standard types, and related numerical values exist and they concluded that regulatory inconsistencies accentuate the need for international collaboration on environmental management as well as specific water quality standards. The European Union (EU) regulates pesticides more tightly than China, Canada and the United States (Ouyang et al., 2017; EPA, 2022). EU directive 2013/39 (EU, 2013) identified priority substances for river ecosystems, defining the Annual Average (AA) and the Maximum Admissible Concentrations (MAC). Moreover, in 2015, the EU published a list of substances for Union-wide monitoring in the field of water policy (Watch List) (Directive, 2015/495) and in 2018 published the second Watch List, which integrated and amended the previous one (Pietrzak et al., 2019). For the non-priority substances, in contrast, no limits are provided by the EU with reference to surface waters. However, several authors point out that non-priority substances can play a key role in the ecological status of aquatic environments (Brack et al., 2018; Posthuma et al., 2020; Wolfram et al., 2021). With EU directive 2020/2184 (EU, 2020), the EU fixed the limits for pesticides in drinking waters at 0.1 μg L^{-1} for a Single Generic Pesticide (SGP) and 0.5 μg L^{-1} for the Total Of Pesticides (TOP).

In this study, to give some information about the level of pesticides reported in the papers analyzed, it was chosen to compare the concentrations with the EU surface water quality standard for the priority substances and the EU drinking water quality standard for the non-priority substances. Among the main substances, the average concentration of atrazine (0.685 μg L^{-1}; range 0.378–1.270 μg L^{-1}) was found to be slightly over the EU AA (0.6 μg L^{-1}) in the study carried out by Ouyang et al. (2017), who applied the SWAT model in the Abujiao basin (Northeast China). Ammann et al. (2020), applying a perceptual model included in the SUPERFLEX hydrological framework in the Eschibach basin (Northeast Switzerland), found atrazine concentrations at the event scale ranging from 0.02 to 40 μg L^{-1}. These values are much higher than the EU MAC (2 μg L^{-1}). Metolachlor ranged from 0 to 10 μg L^{-1} in the work carried out by Boithias et al. (2014), who applied the SWAT model in the Save River Basin (South France). Moreover, Lutz et al. (2017) found concentrations of S-metolachlor on average higher than 10 μg L^{-1}, with a peak of 64.1 μg L^{-1}, by applying a conceptual model in the Alteckendorf basin (Bas-Rhin, France). In both these studies, the concentrations reported are higher with respect to the SGP limit (0.1 μg L^{-1}). Moser et al. (2018), who studied the transport of pesticides in the Rhine Basin by applying the iWaQa transfer model, found concentrations of S-metolachlor (0.01 μg L^{-1}) lower than the SGP limit and concentrations of the isoproturon lower than the EU AA (0.3 μg L^{-1}). Morselli et al. (2018), who applied the DynAPlus model at the event scale in Northern Italy, found the peak of Chlorpyrifos (0.35 μg L^{-1}) to be higher than the EU MAC (0.1 μg L^{-1}). Bannwarth et al. (2016) studied the transport of chlorothalonil using the SWAT model in the Mae Sa basin (Northern Thailand); they reported concentration values (0.005–0.006 μg L^{-1}) below the SGP limit. Among the other substances retrieved from the dataset analysis, aclonifen (0–5 μg L^{-1}) and cypermethrin (0.006–0.008 μg L^{-1}) have exceeded the limits reported in the EU AA (aclonifen: 0.012–0.12 μg L^{-1}; cypermethrin: 0.0005–0.005 μg L^{-1}) (Boithias et al., 2014; Bannwarth et al., 2016). Similarly, concentrations of terbuthylazine (0.04–35 μg L^{-1} at event scale), isoprothiolane (0.571 μg L^{-1}), acetochlor (1.8 μg L^{-1}) and propyzamide (1.4 μg L^{-1}) were higher than the SGP limit (0.1 μg L^{-1}) (Pullan et al., 2016; Lu et al., 2017; Ouyang et al., 2017; Ammann et al., 2020).

Particular mention should be made of oxadiazon: a selective herbicide studied by Ouyang et al. (2017). Although this compound

(0.016–0.107 μg L^{-1}) slightly exceeded the SGP limit, it was the only substance found in this review that was reported in the first Watch list (EU, 2015/495). Finally, substances such as pendimethalin, fenpropimorph, metazachlor, flufenacet, chlorotoluron, carbetamide, clopyralid, dimethoate, dichlorvos and malathion showed low concentrations from below to slightly over the SGP limit (Fohrer et al., 2014; Ouyang et al., 2016; Villamizar and Brown, 2017; Cambien et al., 2020).

Based on the results of this study, it is evident that several areas are facing water quality issues relating to pesticides, confirming the study by Wang et al., 2019). Several pesticides exceed ecotoxicological thresholds. Hence, mitigation measures to reduce exposure in aquatic systems should be designed. Another key point arising from this study is that, alongside a good number of studies that standardized the representation of the results (e.g. concentrations in μg L^{-1}), there are other studies that reported only the maps of the critical source areas (Gagnon et al., 2014; Gassmann et al., 2015; Quaglia et al., 2019), the pesticide loads (Gassmann et al., 2013; Bannwarth et al., 2014; Baffaut et al., 2015; Chen et al., 2017) or the concentrations in ppb (Winchell et al., 2018). This contributes to the loss of some information about specific compounds and to making the comparison incomplete. For instance, in this work, no concentrations data were available for chlorpyrifos, diuron, tebuconazole and glyphosate.

5. Conclusions and recommendations for future works

The increased use of pesticides in agriculture is a threat to soil and water, ecosystems, and human health. The awareness of the potential risks of the excessive use of pesticides led to a social demand for quantifying their presence in the environment (i.e., soil and water resources) and for improving cropping systems in order to reduce their use.

This review summarizes the current state of knowledge on the modeling of pesticide surface waters. The results showed that water contamination with pesticides is a priority issue of global concern. Based on current published studies, it was found that modeling approaches for assessing the fate of pesticides are constantly evolving. Several models were developed that operate at the field, sub-basin and basin scale and the model algorithms work well with diverse watershed conditions, management strategies and pesticide properties. However, this review showed that data availability is still a limiting factor in model implementation; for this reason, most of the studies have been developed in Europe, North America and China. In particular, pesticide concentrations measured in the field, which are needed to calibrate models, are the main limiting factor.

The research gaps that have not been filled by the studies analyzed include the followings: (i) integration of models operating at the field and watershed scales, as well as the integration of in-pond and instream modules; (ii) specific modules for simulating physically based BMPs for managing pesticide excess; (iii) modules able to prioritize the measures for reducing pesticide losses and to develop the relative economic analysis; (iv) engagement of local stakeholders in model implementation processes.

Future development should also assess the presence and impact of the possible effects of multiple substances operating in combination on the aquatic environment around the world in the context of water supply and human safety.

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Credit author statement

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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 are attached in supplementary material S1

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.120553.

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