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Development of surface water exposure scenarios for risk assessment of pesticides in Korea

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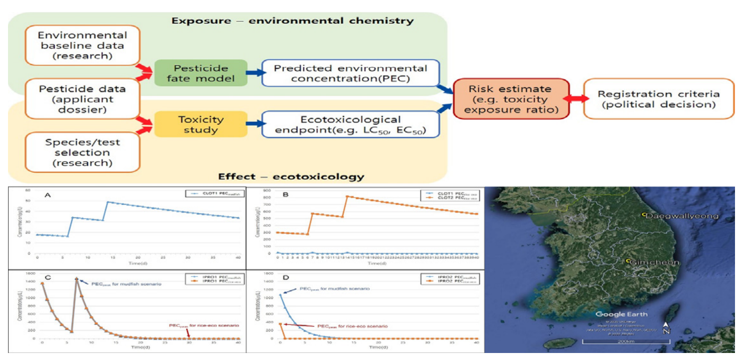
HIGHLIGHTS

- Surface water exposure scenarios were developed for pesticide registration procedure in Korea.
- The scenarios represent more realistic worst-case conditions than the current Korea's risk assessment system.
- The simulated PECs reflected the properties and the exposure routes of pesticides and meteorological conditions of Korea.
- To implement the scenarios for pesticide registration evaluation in Korea, further research on the RAC is needed.

GRAPHICAL ABSTRACT



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ABSTRACT

Surface water exposure scenarios used in the risk assessment of Korea's aquatic ecosystems, were developed to represent the 90th percentile pesticide exposure situation as a part of the country's pesticide registration procedure. The scenarios are used to estimate the pesticide concentration in the water of a rice paddy and small streams for three protection goals: (i) mudfish in rice paddies, (ii) the aquatic ecosystem of small streams located near rice paddies, and (iii) the aquatic ecosystem of small streams located near fruit orchards. The scenarios were derived taking into account major exposure routes, such as spray drift, runoff, and drainage. The scenarios were parameterized for appropriate models including the pesticide root zone model (PRZM) and the toxic substances in surface waters model (TOXSWA). A total of 17 pesticide compounds and 28 formulated products were selected to test the risk assessment using the developed scenarios. The simulated predicted environmental concentrations (PECs) fully reflected a) the exposure routes for each protection goal b) the use patterns of the products c) physicochemical properties of the pesticides, and d) meteorological conditions of Korea. However, while assessing the risks for aquatic organisms we observed that for most of the selected pesticides the calculated exposure concentrations were higher than the regulatory acceptable concentration (RAC). To implement the exposure scenarios and models for pesticide authorization in Korea, further research on the RACs is needed. We also recommend studies to develop a higher-tier model and risk-mitigation measures that can be applied to the Korean situation.

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1. Introduction

Pesticides not only protect crops from fungi, pests, and weeds, but also improve the productivity of crops by controlling their physiological functions (Hong and Kim, 2018). However, pesticides applied in agricultural fields (rice paddies, orchards), can enter surface waters via different pathways, including spray drift, drainage and runoff, which can adversely affect non-target environmental organisms that are part of the aquatic ecosystem (Park et al., 2017). Rice paddies account for 54.5% (895,729 ha) of the total agricultural area in Korea. Active ingredients of pesticides can get dissolved in the rice paddy waters and flow directly into streams or lakes via connected drainage channels (Park et al., 2003). In addition, speed sprayers are used in about 90% of Korea's orchards that results in high deposits of spray drift into the nearby streams (Hong and Kim, 2018). Therefore, as a part of the evaluation procedure for pesticide registration in Korea, risk assessment for aquatic organisms is essential for the protection of the aquatic ecosystem.

In Korea, the risk of pesticides on aquatic and terrestrial organisms is assessed in accordance with the pesticide control act (PCA, 2018). By using the information provided in the dossiers submitted by the applicants, an estimation of the associated risks is carried out taking into account the exposure and the toxicity of the pesticide (Fig. 1). The current scenarios of pesticide exposure in surface water assume that only 1% of the applied dose drains from the rice paddy to the surface water and in the case of an orchard, only 0.6% of the applied dose drifts onto the nearby stream. These assumptions need to be reconsidered since the meteorological characteristics of Korea, the physicochemical properties of the pesticides, and the concentration change (in pesticides) across multiple applications are not included in the scenarios.

The present study aims to (i) develop surface water exposure scenarios of pesticides for three protection goals in Korea, (ii) parameterize the exposure scenarios for appropriate models, (iii) test the impact of the scenarios on the risk assessments for selected pesticides registered in Korea, and (iv) discuss the directions of improvement in the current risk-assessment process of aquatic ecosystem as part of the pesticide registration procedure in Korea.

2. Materials and methods

2.1. Choice of protection goals and scenario zone

A workshop was conducted in Korea in April 2018 to discuss and agree upon the protection goals for Korea's aquatic ecosystems. The discussion was carried out between the stakeholders from pesticide industries, research institutes, test facilities and the National Institute of Agricultural Sciences (NAS). The agreed three protection goals were (i) maintaining a healthy mudfish population in the rice paddies, (ii) preserving the aquatic ecosystem of small streams located near the rice paddies, and (iii) preserving the aquatic ecosystem of small streams located near fruit orchards. The small streams were defined as first-order or second-order streams (first-order streams are smaller than second-order streams). Because in larger streams, the pesticide concentration is strongly diluted and lower than in small streams. In the aquatic ecosystem of small streams, the organisms that need protection are aquatic invertebrates, aquatic vertebrates, and algae. Since Korea is quite homogeneous in terms of agro-environmental conditions, one scenario zone was defined. NAS decided to develop scenarios to protect the 90th percentile probability in time and space, as such representing realistic worst-case conditions.

2.2. Definition of conceptual models for the three protection goals

For the first protection goal, i.e. the mudfish in rice paddies, a conceptual model was derived. Mudfish generally live in shallow water in rice paddies during the rice growing season (Han et al., 2013). The total peak concentration of pesticide in water on rice paddies was selected as the Ecotoxicological Relevant Concentration (ERC) used in risk assessment.

A conceptual model for the second protection goal (the aquatic ecosystem of small streams located near rice paddies) was also derived. In Korea, reservoirs in the upstream catchment supply water via irrigation channels to the rice paddies (MAFRA, 2006). The small streams have a continuous supply of water through these irrigation channels (Fig. 2). Twice a year the water is drained in a controlled way into the stream (RDA, 2019) through drainage channels and outlet ditches. Spraying techniques mostly used in rice paddy fields in Korea are unmanned helicopter, multi-copter (drone) and the wide area sprayer. All these methods have in common that overspray of the drainage and irrigation channels in the catchment is typical. The route of the pesticides into the stream is via overspray of the irrigation channels and subsequent drainage of the pesticide-carrying water into the stream. In the current study, runoff was not considered because the occurrence of water overflowing the dikes surrounding the paddy rice fields, is very rare. The drainage channels and dike are made with a concrete foundation. Therefore, it is assumed that the horizontal percolation through the soil occurs rarely. The only exception for this is during the monsoon season. It was assumed that foliar sprayed pesticides 100% over-spray the water in lateral irrigation channels next to the fields and then flow into the small stream. For the non-sprayed pesticides (in granule form), the compound accumulates in the water in the rice fields before its flows via drainage channels into the stream during controlled drainage. Drainage channels are usually dry, and only water flows out when controlled draining paddy water. Therefore, the dilution in the drainage channel was not considered and the concentration in the rice field was assumed to be the same as the drained concentration. And it was assumed that the peak concentration of pesticides in a small stream near the rice paddies could be calculated at the outlet ditches just before outflowing water enters the stream. Because the discharge and water volume in the stream are generally low; dilution of the pesticide is not taken into account. This changes in the monsoon season (mid-June to July-end). However, it was decided to exclude the monsoon season in the scenario selection process because during this period the aquatic ecosystem experiences a greater stress from extreme flows than from pesticide exposure. The irrigation channel has a width of 60 cm, a water depth of 20 cm, and a flow velocity of 0.04 m/s (Park et al., 2012).

Concerning the third protection goal, i.e., the aquatic ecosystem of small streams located near fruit orchards, we observed that the streams can receive pesticides through spray drift, runoff, and drainage. However, drainage was not considered to be a relevant entry route because Korean orchards have drainpipes only for poorly drained soils (RDA, 2018) which cover only 2.2% of the total orchard area (RDA, 2014). Therefore, the predicted environmental concentration (PEC) of pesticides used near orchards is the peak concentration dissolved in the water in small streams only from spray drift and from runoff.

For both the second and the third protection goals, similar the EU approach (EFSA, 2013) for aquatic organisms living in the water column of permanent edge-of-field surface waters, the concentration of the freely dissolved chemical (hence not including chemical sorbed, for example, on suspended matter or sediment) is chosen as the ERC.

2.3. Scenario selection

Scenarios are defined as fixed combinations of agro-environmental conditions, such as precipitation, soil, land use management, crops with their cropping calendar and the surface water body to be protected. For the two rice field scenarios (mudfish and small stream), a scenario selection procedure was not relevant. The vulnerability drivers for the concentration, such as the size of the water body, were fixed. Hence, calculated exposure concentrations between different locations in Korea showed no spatial variability.

For the orchard scenario preliminary calculations, using the daily precipitation amount of 20 mm or more as an indicator for the

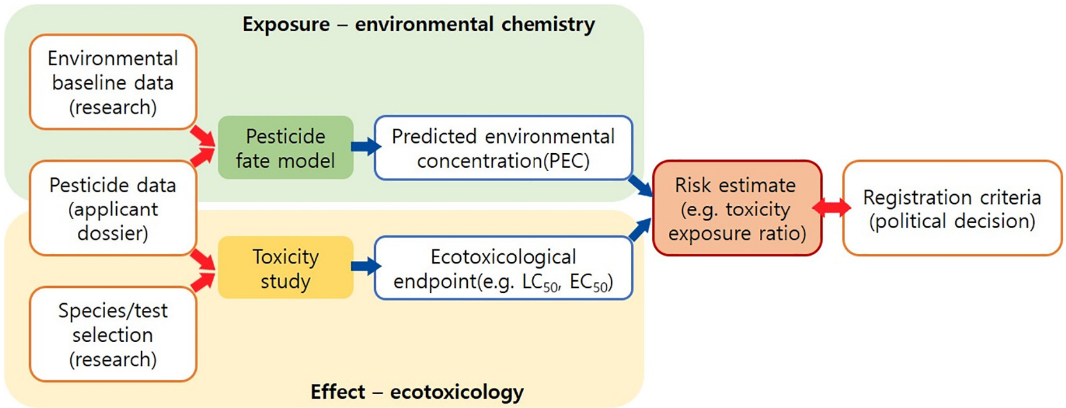

Fig. 1. Flowchart for the Environmental Risk Assessment approach.

occurrence of runoff events (Blenkinsop et al., 2008), showed that both the entry routes runoff and spray drift, are major drivers for the exposure concentration in the small stream. These calculations were done according a methodology described in Adriaanse et al. (2015). For each of the drivers a different scenario selection procedure was developed. These selection procedures comprised each three steps. The procedures are depicted in Fig. 1-1 in the S.I. (entry route runoff) and Fig. 1-2 in the S.I. (entry route spray drift).

For runoff a 90th percentile location of a meteorological station was selected. For spray drift a 90th percentile location of a stream (i.e. stream dimensions) was selected. First, considering the runoff route, it was assumed that a runoff event occurs when daily precipitation exceeds 20 mm/day (Blenkinsop et al., 2008). As a first step, for each spatial unit (i.e. one of the 43 meteorological stations; KMA, 2015) the number of days with daily precipitation exceeding 20 mm for the available years in the period 1960–2018 (the starting year and thus the total number of years used depends on the station) were ranked. Subsequently, the year corresponding to the 90th percentile was selected, thus obtaining the 90th temporal percentile. In the second step the selected values (i.e. for each meteorological station the temporal 90th percentile of the number of days with daily precipitation >20 mm) were ranked again and those meteorological stations with values around the spatial 90th percentile (so-called candidate scenario locations) were selected. In the third step, based on predefined criteria (like the location should be situated in an area with apple orchards) from the set of candidate locations the most suitable one was selected. The scenario selection location with respect to entry route spray drift results in the selection of a type of stream (i.e. dimensions of the stream). Steps taken are as follows. First, for each of the streams (19) the average (=50th percentile) wet cross sectional area of all measurements of the dry season (MOLIT, 2015; MOLIT, 2016) of two years (2016, 2017) were calculated. Note that we selected the average and not e.g. a 90th temporal percentile. The average situation was considered more robust given the large variation in wet cross sectional area and the relatively little amount of data; i.e. selecting a 90th temporal percentile and a 90th spatial percentile would have resulted in selecting a stream at the (extreme) higher end of the distribution, which we considered undesirable. In a second step the 50th percentile values of the average cross sectional area of the 19 streams were ranked again and those steams with values of the average cross sectional area around the spatial 90th percentile were selected. The ranking was done in decreasing order in order to obtain an 90th percentile vulnerable situation. After all, a stream with a smaller volume of water is more vulnerable as there is less dilution of the pesticide. In the third step based on predefined criteria from the set streams around the spatial 90th percentile the most suitable one was selected. The locations selected for runoff and spray drift were Daegwallyeong (for obtaining the meteorological data for the scenario) and Gimcheon (for obtaining the dimensions of the water course for the scenario), respectively (Fig. 3).

2.4. Selection of models and parameterization

For the both mudfish and small streams near rice paddy scenarios, a meta-model described by Peeters et al. (2008) and included in the PRIMET software tool was used. For the mudfish scenario, a PEC as result of a single application ($PEC^{1}_{mudfish}$) was calculated using the application

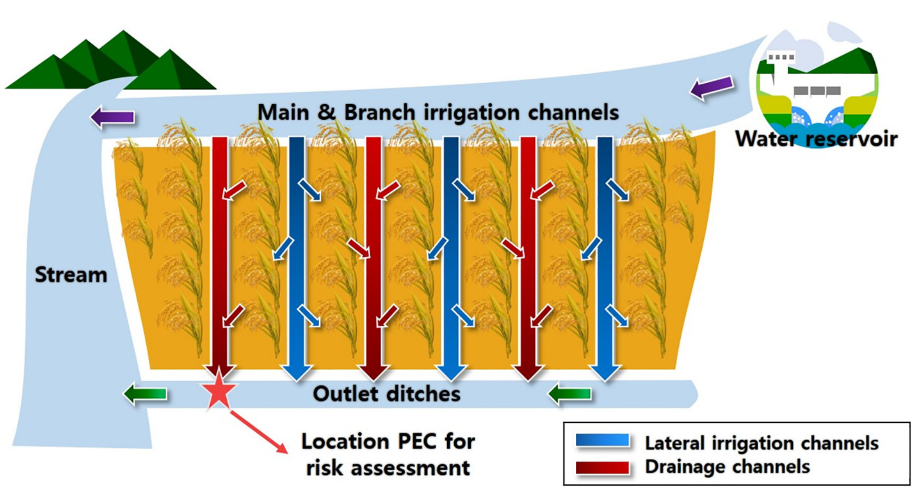

Fig. 2. Conceptual model for water flow from paddy rice fields to the small stream (Source: MAFRA, 2006).

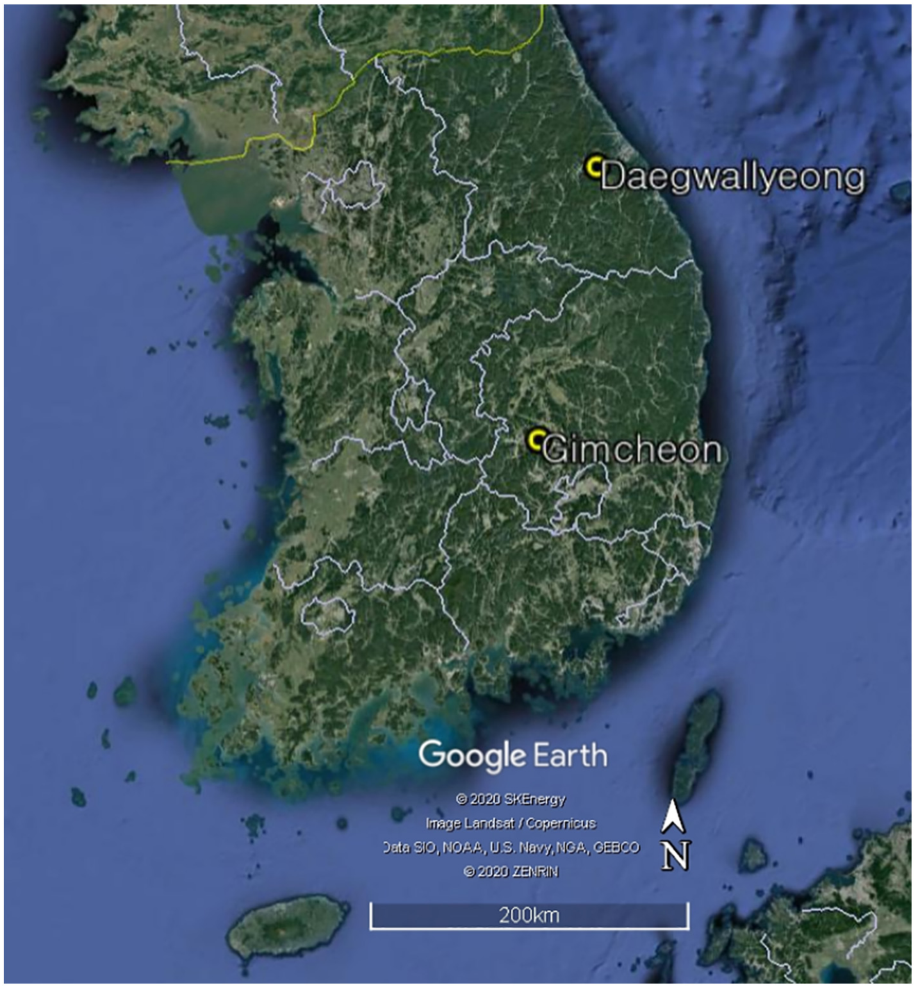

Fig. 3. Meteorological stations for selected scenario locations for runoff (Daegwallyeong) and for spray drift (Gimcheon).

rate and crop interception fraction [Eq. (1)]. The crop interception fraction was not applied to granules applied in the water or in the seedling boxes, but only to the pesticides that were foliar sprayed.

$$PEC^1{}_{mudfish} = \frac{0.1\cdot(1-CI)\cdot M}{d} \tag{1}$$

where

$PEC^1_{mudfish}$ = predicted exposure concentration for a single application (μg/L).

CI = crop interception fraction at the time of application (−).

M = application rate (g a.i./ha).

0.1 = correction factor to convert g/ha to mg/m^2

d = depth of the paddy water (m).

For the mudfish scenario, the peak concentration of pesticides in the water is calculated while ignoring losses due to the diffusion of pesticides into the soil and the adsorption of pesticides to the organic matter present in the soil. The exposure concentration was calculated from a series of applications while keeping a fixed time-interval between the applications. The calculation was carried out while considering dissipation rate k_1^* (caused by degradation in water and volatilization, supplementary information Table SI-1.1) of the pesticides [Eq. (2)].

$$PEC^n{}_{mudfish} = PEC^1_{mudfish}\frac{1-\exp(-n\cdot k_1{}^*\cdot\Delta t)}{1-\exp(-k_1{}^*\cdot\Delta t)} \tag{2}$$

where.

$PEC^n_{mudfish}$ = predicted exposure concentration for multiple applications (μg/L).

$PEC^1_{mudfish}$ = predicted exposure concentration for a single application (μg/L).

n = number of applications.

k_1^* = the overall dissipation rate coefficient accounting for degradation and volatilization (1/d).

Δt = time interval between the applications (d).

For the aquatic ecosystem of small streams near rice paddies scenario and a single foliar sprayed pesticide application, Eq. (3) was used. In Eq. (3), we take into account the instantaneous linear equilibrium sorption in suspended solids in irrigation channels for $PEC^1_{\text{rice-eco, sprayed}}$ for a single application.

$$PEC^1{}_{rice-eco,sprayed} = \frac{(0.1\cdot M)/V}{1+ss\cdot m_{om,ss}\cdot K_{om}} \tag{3}$$

where.

$PEC^1_{\text{rice-eco, sprayed}}$ = predicted exposure concentration dissolved in water for a single application for foliar sprayed pesticides (μg/L).

ss = mass concentration of suspended solids in water (kg/L).

$m_{\text{om, ss}}$ = mass fraction organic matter in suspended solids (g/g).

K_{om} = sorption coefficient of organic matter (L/kg).

For calculating $PEC^n_{\text{rice-eco, sprayed}}$ (multiple applications), Eq. (4) was used. It is similar to Eq. (2), but the dilution rate in channels was additionally accounted for calculating the overall dissipation rate k_2^* (caused by degradation in water, volatilization and dilution, Table SI-1.1).

$$PEC^{n}{}_{rice-eco,sprayed} = PEC^{1}_{rice-eco,sprayed}\frac{1-\exp\left(-n\cdot k_2{}^{*}\cdot\Delta t\right)}{1-\exp\left(-k_2{}^{*}\cdot\Delta t\right)} \quad (4)$$

where

$PEC^{n}_{\text{rice-eco, sprayed}}$ = predicted exposure concentration dissolved in water for multiple applications (μg/L).

$PEC^{1}_{\text{rice-eco, sprayed}}$ = predicted exposure concentration for a single application (μg/L).

k_2^{*} = the overall dissipation rate coefficient accounting for degradation, volatilization, and dilution (1/d).

Non-sprayed pesticides, such as granular herbicides, are not directly introduced into the irrigation and drainage channels. At the time of a controlled drainage event (mid-summer or before the harvest season), water from rice fields containing the pesticide is released via the drainage channels to the small stream. It is assumed that the pesticide concentration in the drainage channel (and thus the small stream) is similar to the pesticide concentration in the water from the rice fields at the time of this drainage event. For calculating the $PEC^{1}_{\text{rice-eco}}$ of non-sprayed pesticides, the rate of degradation and volatilization during the period between the application and the controlled drainage event was considered [Eq. (5)].

$$PEC^{1}{}_{rice-eco,non-sprayed} = \frac{(0.1\cdot M)/V}{1+ss\cdot m_{om,ss}\cdot K_{om}}\cdot\ \exp(-k_1{}^{*}\cdot\Delta t_{a-d}) \quad (5)$$

where.

$PEC^{1}_{\text{rice-eco, non-sprayed}}$ = predicted exposure concentration dissolved in water for a single application of non-spray pesticides at the time of the drainage event (μg/L).

$\Delta t_{\text{a-d}}$ = time interval between the application and the drainage (d).

In the case of multiple applications, the dissipation rate during the time interval between the last application and the drainage was considered [Eq. (6)].

$$PEC^{n}{}_{rice-eco,non-sprayed} = \frac{(0.1\cdot M)/V}{1+ss\cdot m_{om,ss}\cdot K_{om}}\cdot\frac{1-\ \exp(-n\cdot k_1{}^{*}\cdot\Delta t)}{1-\ \exp(-k_1{}^{*}\cdot\Delta t)}\cdot\ \exp(-k_1{}^{*}\cdot\Delta t_{l-d}) \quad (6)$$

where

$PEC^{n}_{\text{rice-eco, non-sprayed}}$ = predicted exposure concentration dissolved in water for multiple applications of non-spray pesticides at the time of the drainage event (μg/L).

$\Delta t_{\text{l-d}}$ = time interval between the last application and the drainage (d).

For the orchard scenario the models Pesticide Root Zone Model (PRZM), SPray drift EXposure for Upward and Sideways directed sprays (SPEXUS), and TOXic substances in Surface WAters (TOXSWA) were selected to calculate the runoff entries, spray drift deposition, and pesticide fate in the stream. The PRZM model is a one-dimensional, dynamic, compartmental model that can be used to simulate the movement of a pesticide in unsaturated soil systems within and immediately below the plant root zone (Carsel et al., 2005). For the orchard scenario in Korea, the PRZM model was used to calculate the amount of runoff water and its associated pesticide fluxes, the amount of pesticide-free subsurface drainage water, and the amount of eroded soil and its associated pesticide fluxes. The parameterization of the PRZM model for the orchard scenario is based on the EU-FOCUS R4 scenario, which represents the highest runoff potential of all the four FOCUS runoff scenarios (Adriaanse et al., 2017). Additionally, the model uses Korean crop data (RDA, 2018) and meteorological data (KMA, 2015) that spans 53 years (1966–2018), including a warm-up period of six years. The SPEXUS model is an empirical model that computes the deposits of spray drift from pesticide treatments of pome fruit orchards using wind speed, wind direction, ambient temperature, canopy density (obtained by using a phenological growth stage scale called BBCH), and the size of the orchard (Holterman et al., 2018). The SPEXUS model was parameterized for one specific scenario (Table SI-2.1), and the generated spray drift deposition (33.8%, Table SI-2.2) was used to calculate spray drift deposits that were used as inputs in the TOXSWA model. The TOXSWA model is a pseudo two-dimensional numerical model that describes pesticide fate in a water layer and its underlying sediment at the edge-of-field scale (Ter Horst et al., 2016). The TOXSWA parameterization of the EU FOCUS R4 stream scenario (FOCUS, 2001) was taken as a basis. The 100 m long Korean orchard stream is fed by a base flow of 2.78 Ls^{-1} (i.e. the average value for the FOCUS EU Runoff stream scenarios). Furthermore, the stream receives runoff water fluxes that originate from a 100 ha upstream catchment. Pesticide runoff fluxes from this upstream catchment originate from 20 ha only, i.e. the fraction of upstream catchment treated is 0.2. Furthermore, the Korean orchard stream receives lateral runoff water and pesticide fluxed from a 1 ha fully treated adjacent field. The Korean scenario the stream has a V-shaped internal cross-section and its hydrology is calibrated (see Table SI-3 for more information). The TOXSWA model parameterized for the Korean orchard stream was used to calculate the 90th percentile of pesticide concentration (in the stream) caused by spray drift and runoff over a duration of 53 years.

2.5. Crop data

Crop data for rice were gathered for different growth periods according to the BBCH scale, the date of the controlled drainage event (RDA, 2019), and crop interception data (Ter Horst et al., 2014) (Table SI-4.1). For the orchard scenario data from an apple orchard was used. Apple is the most commonly grown fruit in Korea (Statistics Korea, 2016). The crop calendar data for apple, such as the emergence date, the maturation date, the harvest date, the fallow data, the maximum rooting depth and the maximum cropping height, were obtained through personal communication with Dr. Jung-Gun Cho, National Institute of Horticultural and Herbal Science in June 2019 (Tables SI-4.2 and SI-4.3).

2.6. Pesticide data

2.6.1. Selection of pesticides

To test the risk-assessment with the scenarios, pesticides from 491 active ingredients from 1974 formulated products registered in Korea were ranked using the following three criteria: (i) ratio of the highest sales volumes (KCPA, 2016) of pesticides and their acute toxicity in fish & Daphnia (Pesticide Properties DataBase, 2007), (ii) ratio of the highest application rates (NAS, 2019) of a pesticide(s) and its toxicity, and (iii) the highest number of products with a certain active ingredient (NAS 2019). From these rankings 17 pesticide products with 10 active ingredients were selected for testing the rice paddy scenarios, and 11 pesticide products with 11 compounds were selected for the orchard scenario (Table 1).

2.6.2. Physicochemical properties of pesticides

The pesticide properties were taken from the European Food Safety Authority (EFSA) review and conclusion reports (http://www.efsa.europa.eu), the Pesticides Properties DataBase (PPDB), and The Pesticide Manual (BCPC, 2012). Data for the mudfish and rice ecosystem model included molecular mass, saturated vapor pressure at reference temperature, water solubility of the pesticides, half-life for degradation in water ($DT_{50water}$, d), and the sorption coefficient based on organic carbon (K_{oc}). For the orchard ecosystem model, the half-life for degradation in soil (DT_{50soil}), the half-life for degradation in sediment (DT_{50sed}), and their Freundlich exponent (N) were additionally collected. The K_{om} values were calculated by multiplying the K_{oc} values with 1.724 (FOCUS, 2000). All property data (Tables SI-5.1 and SI-5.2) and a protocol to select the parameters (Tables SI-6.1 and SI-6.2) are reported in the supplementary information.

Table 1
Selected pesticides with ranked categories, code names, crops and application scheme.

Pesticide	Type	Ranked categories[a] for selection	Product code	Formulation type[b]	Crop	Application rate (g a.i./ha)	Number of applications (interval(d))	Application method	Application timing
Benfuracarb	Insecticide	□, ■	BENF1	GR	Rice	720	1(−)	Water surface	10 days before transplanting
			BENF2	WG	Fruit	750	3(10)	Foliar spray	At Jun
Bentazone	Herbicide	○, ●, □, ■	BENT1	GR	Rice	3300	1(−)	Water surface	10 days after transplanting
			BENT2	ME	Rice	1600	1(−)	Foliar spray	At July–August
Carbofuran	Insecticide	○, ●	CARB1	GR	Rice	1200	1(−)	Water surface	At transplanting
			CARB2	GR	Rice	900	1(−)	Seedling box	Just after transplanting
			CARB3	GR	Fruit	1200	2(10)	Soil treatment	At May
Captan	Fungicide	□	CAPTAN	WP	Fruit	3000	5(10)	Foliar spray	At late Jun
Chlorothalonil	Fungicide	○, ●, □, ■	CHLTH	WP	Fruit	3125	5(10)	Foliar spray	At Jun
Chlorpyrifos	Insecticide	●, □, ■	CHLPF	EC	Fruit	1000	3(10)	Foliar spray	At late Jun
Clothianidin	Insecticide	☆	CLOT1	SL	Rice	30	3(7)	Foliar spray	At July–August
			CLOT2	UG	Rice	150	3(7)	Water surface	At July–August
Dithianon	Fungicide	○, □	DITHI	WP	Fruit	2344	5(10)	Foliar spray	At May
Fenitrothion	Insecticide	●, ■	FENIT	EC	Fruit	2500	2(10)	Foliar spray	At May
Fipronil	Insecticide	☆	FIPR	FG	Rice	60	1(−)	Seedling box	Before transplanting
Iprobenfos	Fungicide	○, ●, □, ■, ☆	IPRO1	GR	Rice	680	2(7)	Water surface	At July–August
			IPRO2	EC	Rice	720	1(−)	Foliar spray	At transplanting
Mancozeb	Fungicide	○, □	MANCO	WP	Fruit	3750	5(10)	Foliar spray	At May
Mefenacet	Herbicide	○, ●, ☆	MEFE	GR	Rice	1050	1(−)	Water surface	10 days after transplanting
Pendimethalin	Herbicide	○, ●	PEND1	EC	Rice	750	1(−)	Water surface	10 days after transplanting
			PEND2	GR	Rice	500	1(−)	Water surface	2 days before transplanting
			PEND3	EC	Fruit	1585	1(−)	Soil treatment	At May
Phenthoate	Insecticide	■	PHEN1	EC	Rice	570	1(−)	Foliar spray	Just after transplanting
			PHEN2	EC	Rice	570	3(7)	Foliar spray	At July–August
			PHEN3	EC	Fruit	2969	2(10)	Foliar spray	At May
Thiophanate methyl	Fungicide	○, ●, □, ■	THIO1	WP	Rice	1050	3(7)	Foliar spray	At July–August
			THIO2	WP	Rice	600	3(7)	Foliar spray	At July–August
Thiram	Fungicide	□	THIRAM	WG	Fruit	2750	5(10)	Foliar spray	At late Jun

[a] ○: highest sales volume/toxicity(fish) ratio, ●: highest sales volume/toxicity(*Daphnia*) ratio, □: highest application rate/ toxicity (fish) ratio, ■: highest application rate/ toxicity (*Daphnia*) ratio, ☆: most products.
[b] EC: Emulsifiable concentrate, FG: Fine granule, GR: Granule, ME: Microemulsion, SL: Soluble concentrate, UG: Up (self-dispersible floating) granule, WG: Water dispersible granule, WP: Wettable powder.

2.6.3. Application scheme

The data of all the selected pesticide products, including the rate of application, the maximum number of applications, the minimum interval between applications, and the general application date (Table 1), were gathered from the pesticide registration information service in Korea (NAS, 2019).

2.7. Risk-assessment for aquatic organisms

The risk-assessment for aquatic organisms was performed using the toxicity exposure ratio (TER) approach. The acute toxicity data for Fish (LC_{50}, 96 h), Daphnia (EC_{50}, 48 h), and algae (EC_{50}, 72 h) were taken from the PPDB. For the mudfish, the acute toxicity data (LC_{50}, 96 h) for each pesticide were obtained from the pesticide registration dossiers in Korea (Table 2). The acute predicted no-effect concentrations (PNECs) were calculated by dividing the toxicity value by the safety factor. In the risk assessment standard for pesticide registrations in Korea (PCA, 2018), a safety factor of 2 is applied for all species. The predicted environmental concentrations (PEC) were calculated using each model in line with the crops on which the pesticides were used. The mudfish model and the rice ecosystem model were used for rice, while the orchard ecosystem model was used for fruits. The TER for the acute risk-assessment was defined as PNEC divided by PEC_{peak} [Eq. (7)].

$$TER = \frac{PNEC;[(LC_{50}\ or\ EC_{50})/SF]}{PEC_{peak}} \tag{7}$$

where.

TER = toxicity exposure ratio (−).

$PNEC$ = predicted no-effect concentration for aquatic organisms–fish (including mudfish), Daphnia and algae (μg/L).

SF = safety factor (−).

PEC_{peak} = the maximum predicted environmental concentration for the protection goal (μg/L).

The risks associated with the pesticides were classified by the calculated TER. If the TER is lower than 1, the exposure is deemed to be higher than the PNEC. These risks are considered unacceptable. If the TER is higher than 1, the risks associated with pesticide use are considered acceptable.

3. Results and discussion

3.1. Mudfish rice field and aquatic ecosystem of small streams near rice paddies

Table 3 shows the PECs for 17 pesticide products of 10 ranked compounds as calculated for the two scenarios using on the Eq. (1)–(6).

Table 2
Acute toxicity data of selected pesticides for aquatic organisms.

Pesticide	Product code	Crop	Acute toxicity			
			Mudfish	Fish	*Daphnia*	Algae
			(LC_{50}, μg/L)	(LC_{50}, μg/L)	(EC_{50}, μg/L)	(EC_{50}, μg/L)
Benfuracarb	BENF1	Rice	10,000	2500	1.7	6700
Bentazone	BENT1	Rice	10,000	100,000	100,000	10,100
	BENT2	Rice	15,000	100,000	100,000	10,100
Carbofuran	CARB1	Rice	10,000	180.0	9.4	6500
	CARB2	Rice	10,000	180.0	9.4	6500
Clothianidin	CLOT1	Rice	10,000	104,200	40,000	55,000
	CLOT2	Rice	10,000	104,200	40,000	55,000
Fipronil	FIPR	Rice	908.0	248.0	190.0	68.0
Iprobenfos	IPRO1	Rice	17,845	14,700	1200	6050
	IPRO2	Rice	10,000	14,700	1200	6050
Mefenacet	MEFE	Rice	10,000	6000	1810	180.0
Pendimethalin	PEND1	Rice	1680	200.0	280.0	18.0
	PEND2	Rice	10,306	200.0	280.0	18.0
Phenthoate	PHEN1	Rice	3675	2500	1.7	6700
	PHEN2	Rice	3675	2500	1.7	6700
Thiophanate methyl	THIO1	Rice	10,000	11,000	5400	25,400
	THIO2	Rice	10,000	11,000	5400	25,400
Benfuracarb	BENF2	Fruit		2500	1.7	6700
Captan	CAPTAN	Fruit		186.0	7100	1180
Carbofuran	CARB3	Fruit		180.0	9.4	6500
Chlorpyrifos	CHLPF	Fruit		25.0	0.1	480.0
Chlorothalonil	CHLTH	Fruit		17.0	54.0	210.0
Dithianon	DITHI	Fruit		70.0	260.0	90.0
Fenitrothion	FENIT	Fruit		1300	8.6	1300
Mancozeb	MANCO	Fruit		74.0	73.0	44.0
Pendimethalin	PEND3	Fruit		200.0	280.0	18.0
Phenthoate	PHEN3	Fruit		2500	1.7	6700
Thiram	THIRAM	Fruit		171.0	139.0	65.0

First we will discuss the results for the mudfish scenario. The differences in the PECs of the different pesticide products are explained first of all by the difference in application scheme. For instance, the $PEC^1_{mudfish}$ of PEND1 is higher than the $PEC1_{mudfish}$ of PEND2, because the application rate of PEND1 is higher. BENF1 and IPRO2, which have both one application with the same application rate, result in a different $PEC^1_{mudfish}$ because of a different application method. BENF1 is applied to the water surface of the paddy water, whereas IPRO2 is spraying, meaning that crop interception is leading to a lower $PEC^1_{mudfish}$. A difference in the timing of the application results also in a difference in crop interception factor and thus $PEC^1_{mudfish}$ value. For instance, PHEN1 is applied after transplanting (small crop) and a crop interception factor of 0.25 is used. For PHEN2 the same application rate is used as for PHEN1. However, PHEN2 is applied after the monsoon (full grown crop) and an interception factor of 0.7 is used, resulting in a lower $PEC^1_{mudfish}$ for PHEN2 than for PHEN1. For multiple applications, the number of applications is relevant. Furthermore, the dissipation half-life (involving the processes degradation and volatilization) is responsible for a decrease in concentration in between the applications. This is illustrated by the concentration as function of time curve of CLOT1 (Fig. 4A). As result of an application the concentration increases and decreases shortly after due to dissipation, until the next application.

For the rice ecosystem scenario, the equations for sprayed and non-sprayed applications differ. First we will discuss the difference in PECs of the sprayed applications. For sprayed applications, overspray of the drainage channels is assumed and therefore the timing of the application is not relevant (i.e. unlike for the mudfish scenario, for this case crop interception is not taken into account). Next to the application rate and the effect of sorption to suspended solids, for multiple applications, the dissipation rate and the number of applications and interval between the applications, determines the PEC value for the rice ecosystem scenario. This is illustrated by the difference in $PEC^1_{rice\text{-}eco}$ of PEND1 (application rate 750 g/ha, K_{OC} 15744 L/kg) and THIO1 (application rate 600 g/ha, K_{OC} 189 L/kg). Although the application rate of PEND1 is higher than the application rate of THIO1, the $PEC^1_{rice\text{-}eco}$ of PEND1 (115 μg/L) is lower than the $PEC^1_{rice\text{-}eco}$ of THIO1 (525 μg/L). This is because of the difference is sorption to suspended solids, which is larger for PEND1 than for THIO1, leading to a lower concentration dissolved in water.

For non-sprayed applications and the rice-ecosystem scenario, the combination of residence time of pesticide in the paddy water and the DT_{50} determines the PEC_{peak}. This is illustrated by comparing the results of PEND1 and PEND2 (both granular applications). For the mudfish scenario the difference between the $PEC^1_{mudfish}$ value of pendimethalin (PEND1; 750 g/ha and PEND2; 500 g/ha) corresponds to the difference in the application rate. However, in the rice-ecosystem model, the $PEC^1_{rice\text{-}eco}$ of PEND2 was higher than that of PEND1 although the application rate of PEND1 is higher than that of PEND2. PEND1 is an herbicide used after transplanting to control young weeds; it is drained 30 days after transplanting. Given the DT_{50} of 8.1 days for pendimethalin, about 92% of the PEND1 is degraded after 30 days. PEND2 is used 2–3 days before transplanting and the water is drained immediately before transplanting. It was assumed that PEND2 was drained only 2 days after the application, which means that only about 16% of PEND2 is degraded before the contaminated paddy water was released in the drainage channel. This results in a higher PEC_{peak} of PEND2 in the drainage channel than of PEND1. For the rice-ecosystem model and granular applications, the combination of residence time of pesticide in the paddy water and the DT_{50} determines the $PEC_{peak.}$

Next, the differences in PEC due to a difference in application method, i.e. spraying applications versus non-spraying applications, will be explained by comparing results of CLOT1 (30 g/ha, $PEC^n_{rice\text{-}eco}$ is 15 μg/L) and CLOT2 (150 g/ha, $PEC^n_{rice\text{-}eco}$ is 652 μg/L). CLOT1 is sprayed (assuming overspray over the drainage channels) whereas CLOT2 is a granular and applied to the water surface. Both are applied three times after the monsoon with an interval of 7 days. The $PEC^n_{rice\text{-}eco}$ of CLOT2 is given the difference in application rate comparatively large

Table 3
DT_{50} and PEC_{peak} of pesticide in product calculated for the mudfish scenario and rice-eco scenario for selected pesticides.

Pesticide	Product code	Formulation type[a]	Application rate (g a.i./ha)	Application method and timing	Crop interception fraction	Mudfish exposure scenario			Ecosystems in small stream near rice field exposure scenario		
						DT_{50}	PEC^1	PEC^n	DT_{50}	PEC^1	PEC^n
						(d)	(a.i. μg/L)	(a.i. μg/L)	(d)	(a.i. μg/L)	(a.i. μg/L)
Benfuracarb	BENF1	GR	720	Water surface, 10 days before transplanting	–	0.47	1440	–	0.47	0.0006	–
Bentazone	BENT1	GR	3300	Water surface, 10 days before transplanting	–	130.94	6600	–	130.94	5630.84	–
	BENT2	ME	1600	Foliar spray, At July–August	0.5	130.94	1600	–	35.77	800.0	–
Carbofuran	CARB1	GR	1200	Water surface, At transplanting	–	11.36	2400	–	11.36	209.04	–
	CARB2	GR	900	Seedling box, Just after transplanting	–	11.36	1800	–	11.36	156.78	–
Clothianidin	CLOT1	SL	30	Foliar spray, At July–August	0.7	48.94	18	49.0	0.019	15.0	15.0
	CLOT2	UG	150	Water surface, At July–August	–	48.94	300	817.7	48.94	196.14	651.88
Fipronil	FIPR	FG	60	Seedling box, Before transplanting	–	89.90	120	–	89.90	117.24	–
Iprobenfos	IPRO1	GR	680	Water surface, At July–August	–	2.01	1360	1482.2	2.01	0.04	0.54
	IPRO2	EC	720	Foliar spray, At transplanting	0.25	2.01	1080	–	0.019	359.56	–
Mefenacet	MEFE	GR	1050	Water surface, 10 days before transplanting	–	740.39	2100	–	740.39	2040.37	–
Pendimethalin	PEND1	EC	750	Water surface, 10 days before transplanting	–	8.11	1500	–	8.11	115.11	–
	PEND2	GR	500	Water surface, 2 days before transplanting	–	8.11	1000	–	8.11	839.69	–
Phenthoate	PHEN1	EC	570	Foliar spray, Just after transplanting	0.25	4.39	855	–	0.019	284.93	–
	PHEN2	EC	570	Foliar spray, At July–August	0.7	4.39	342	492.9	0.019	284.93	284.93
Thiophanate methyl	THIO1	WP	1050	Foliar spray, At July–August	0.7	2.79	630	760.2	0.019	524.97	524.97
	THIO2	WP	600	Foliar spray, At July–August	0.7	2.79	360	434.4	0.019	299.99	299.99

[a] EC: Emulsifiable concentrate, FG: Fine granule, GR: Granule, ME: Microemulsion, SL: Soluble concentrate, UG: Up (self-dispersible floating) granule, WP: Wettable powder.

compared to the $PEC^n_{rice\text{-}eco}$ of CLOT1. This is because of the following reason. The dissipation half-lives differ (0.019 d for CLOT1 and 49 d for CLOT2). The reason is that the overall dissipation half-live for the sprayed pesticide (CLOT1) accounts for the effect of dilution in the stream. The flow velocity in the drainage channel is rather high (0.04 m/s) resulting in a much lower half-life than the half-life of the non-sprayed pesticide (CLOT2) which only includes the effect of degradation and volatilization. The effect on the concentration as function of time is illustrated in Fig. 4B. Whereas CLOT2 accumulates, CLOT1 quickly disappears after each application.

The results of the calculations with the mudfish scenario and the rice-ecosystem scenario were compared as well. Differences in calculated PEC_{peak} of the two scenarios are illustrated for IPRO1 (non-sprayed application) and IPRO2 (sprayed application). For IPRO1 the changes in pesticide concentration (as function time) were the same in both scenarios (Fig. 4C) because there is no difference in how the concentration as function of time (Table SI-1.2) was calculated, which included the definition of the overall dissipation rate (covering the processes of degradation and volatilization). In the mudfish scenario, the PEC_{peak} ($PEC^n_{mudfish}$) is found just after the last application whereas in the rice ecosystem scenario, the PEC_{peak} was defined as the PEC on the day of draining the rice paddy (i.e. controlled drainage after 30 days of transplanting). IPRO2 is a foliar sprayed pesticide. For both scenarios the PEC_{peak} is the result of directly spraying the water layer (for the rice-ecosystem overspray of the drainage channel is assumed). Therefore, for both scenarios the PEC_{peak} is found shortly after application. There is a clear difference in the concentration as function of time of the two scenarios (Fig. 4D). First, the PEC_{peak} for the rice-ecosystem scenario is much lower. This is due to the difference in type of PEC for the different scenarios. For the mudfish scenario the total concentration (including pesticide sorbed to suspended solids) in water is calculated, whereas for the rice-ecosystem scenario the concentration dissolved in water (so excluding pesticide sorbed to suspended solids) is calculated. Sorption to suspended solids is calculated as an instantaneous process. As the K_{OC} of Iprobenfos (IPRO1 and IPRO2) is rather large (5030 L/kg), the PEC_{peak} for the rice-ecosystem scenario is much lower than for the mudfish scenario. Secondly, the decline of IPRO2 is much larger for the rice-ecosystem scenario. For the rice ecosystem scenario IPRO2 has a smaller overall dissipation half-life because next to degradation and volatilization, dilution is accounted for as well. For the mudfish scenario only degradation and volatilization contribute to dissipation of IPRO2 in the water layer.

The results of the simulations obtained for the two scenarios illustrate that the PEC value is determined by the physiochemical properties of the pesticides, the application scheme of the products, and the exposure routes.

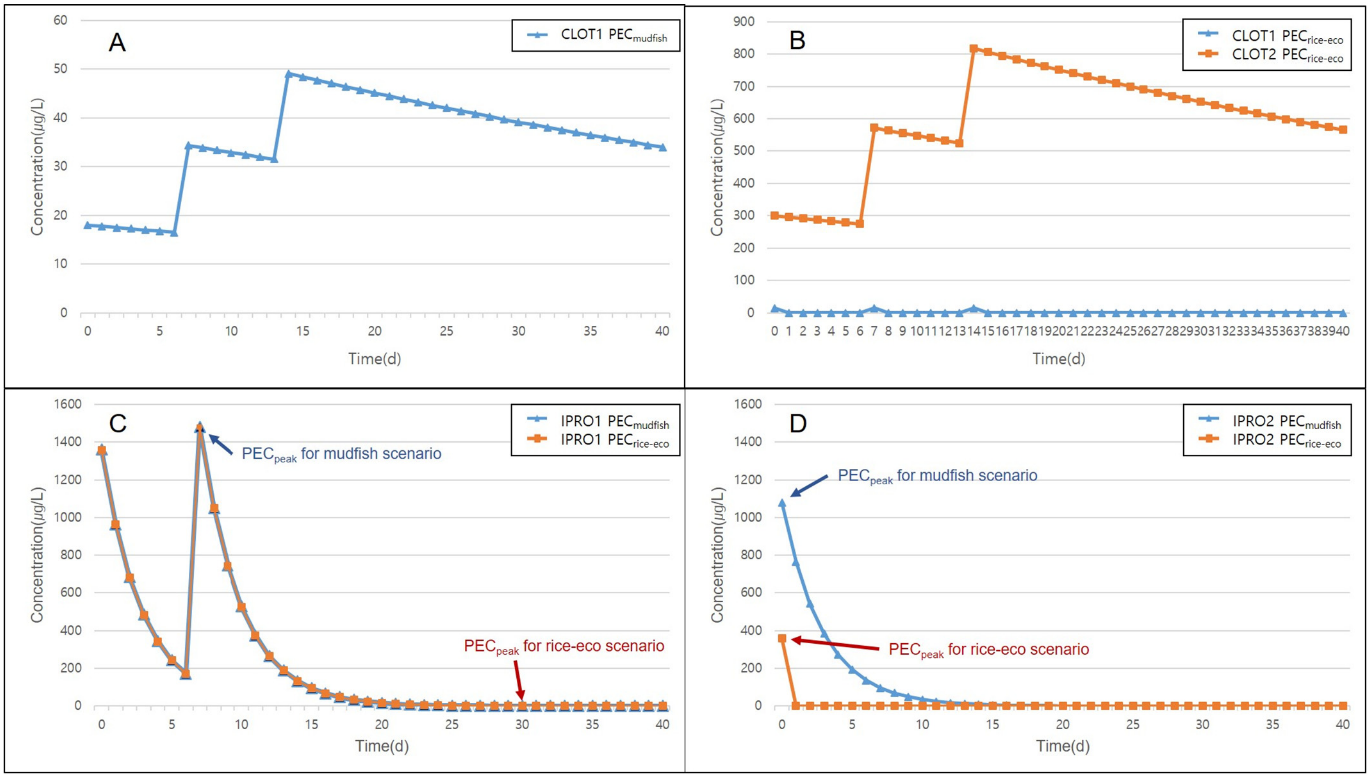

Fig. 4. Concentration as a function of time (PECs) calculated for the mudfish and rice-eco scenarios; (A) $PEC_{mudfish}$ of CLOT1, (B) $PEC_{rice\text{-}eco}$ of CLOT1 and CLOT2, (C) $PEC_{mudfish}$ and $PEC_{rice\text{-}eco}$ of IPRO1, and (D) $PEC_{mudfish}$ and $PEC_{rice\text{-}eco}$ of IPRO2.

3.2. Orchard model simulations

Table 4 presents the PEC_{peak} for 11 ranked pesticides used in orchards with calculations obtained from the PRZM and TOXSWA models, with collected meteorological data spanned across 47 years (1972–2018). The results show that, in general, the PEC_{peak} was higher when the application rate of the product was higher, except for the cases of pendimethalin and carbofuran (PEND3 and CARB3) (Fig. 5).

The PEC_{peak} of PEND3 was very low and tended to remain constant for all years. PEND3 is an herbicide sprayed at the soil surface. Therefore, instead of the spray drift percentage of 33.8% from the SPEXUS model, a percentage 1.43% was used (FOCUS drift calculator for crop <50 cm). Given the high K_{oc} (15,711 L/kg) of pendimethalin, large part of the compound was sorbed to the soil, which resulted in very small compound masses in the runoff to the stream. Therefore, all peak concentrations were the result of the spray drift event and occurred on the pesticide application dates.

The PEC_{peak} of CARB3 was also very low but fluctuated throughout all periods. CARB3 is a granular product, hence there is no spray drift onto surface water. Therefore, only runoff events determined the peak concentrations. Fig. 6 shows the daily precipitation, the runoff volume and the peak concentration in the stream of CARB3 for 47 years. All peak concentrations occurred on the date of the first runoff event that occurred after the application. The peak concentrations were particularly high when runoff occurred immediately after the application of the pesticides i.e., in 1974, 1981, 2003, and 2011.

Except for CARB3, all peak concentrations occurred on the day of the application. Pesticides with the same application date showed similar concentration changes (Fig. 5): MANCO, PHEN3, FENIT, DITHI (May); CAPTAN, THIRAM, CHLPF (late June); and BENF2, CHLTH (June). In years with high water levels in the stream on the application date, concentrations of all pesticides were lower than in other years because the peak concentration from spray drift is determined only by the water level.

Table 4
PEC_{90th} calculated by the TOXSWA model using the orchard scenario for selected pesticides.

Pesticide	Product code	Formulation type[a]	Application rate (g a.i./ha)	Application method	Application timing	PEC_{90th} (a.i. µg/L)
Benfuracarb	BENF2	WG	750	Foliar spray	At Jun	290.1
Captan	CAPTAN	WP	3000	Foliar spray	At late Jun	1169.5
Carbofuran	CARB3	GR	1200	Soil treatment	At May	35.47
Chlorpyrifos	CHLPF	EC	1000	Foliar spray	At late Jun	387.1
Chlorothalonil	CHLTH	WP	3125	Foliar spray	At Jun	1217.8
Dithianon	DITHI	WP	2344	Foliar spray	At May	911.1
Fenitrothion	FENIT	EC	2500	Foliar spray	At May	974.4
Mancozeb	MANCO	WP	3750	Foliar spray	At May	1461.5
Pendimethalin	PEND3	EC	1585	Soil treatment	At May	26.0
Phenthoate	PHEN3	EC	2969	Foliar spray	At May	1156.6
Thiram	THIRAM	WG	2750	Foliar spray	At late Jun	1064.2

[a] EC: Emulsifiable concentrate, GR: Granule, WG: Water dispersible granule, WP: Wettable powder.

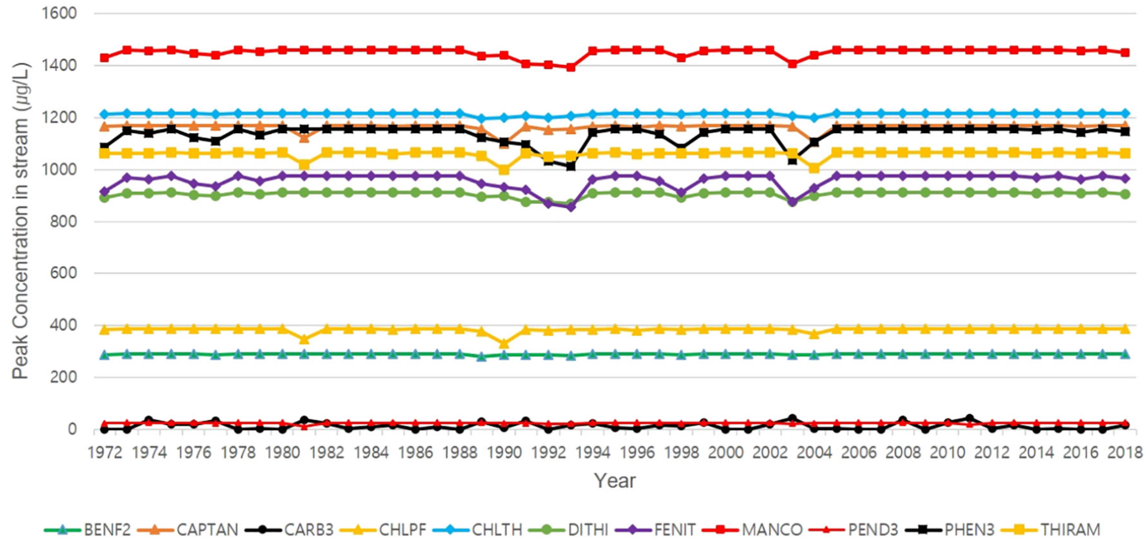

Fig. 5. PEC_{peak} for selected 11 pesticides calculated by the TOXSWA model for 47 years for the small stream orchard scenario.

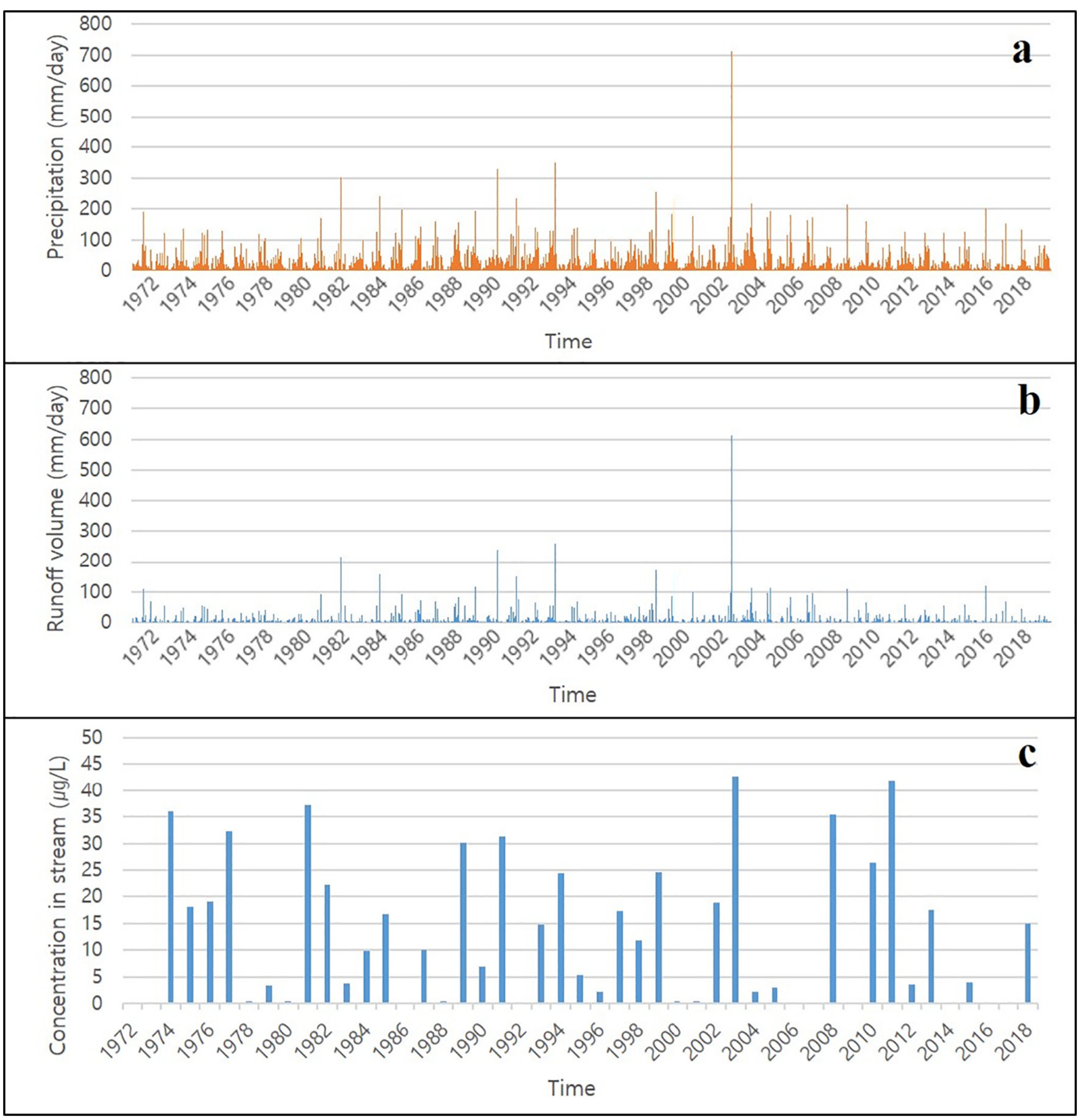

Fig. 6. Precipitation (a), runoff volume (b) and concentration in stream (c) of CARB3 for 47 years.

Using a computational fluid dynamics model, Hong and Kim (2018) predicted the spray drift rate of speed sprayer to be 28.3%–37.8%. This is similar to the simulation results (33.8%) of the SPEXUS model used in the present study.

We observed that the PECs obtained from the simulations with the orchard scenario and selected models reflected various application methods, properties of pesticide compound, and meteorological conditions in Korea.

3.3. Results of risk assessment for aquatic organisms

For the risk assessment of 28 pesticide products on fish (including mudfish), Daphnia and algae, TER values were calculated using the safety factor (SF) according the Korean standard (Table 5).

For 12% (2/17) of the tested products, the risks calculated for mudfish were unacceptable. For the rice ecosystem scenario, the risks for fish, Daphnia and algae were unacceptable for 24% (4/17), 41% (7/17), and 29% (5/17) of the products, respectively. In case of the orchard scenario, the risks of 64% (7/11), 82% (9/11) and 73% (8/11) products were unacceptable for fish, Daphnia and algae, respectively. These results are for pesticides that are specifically selected for this study because they are expected to pose the highest risks for the aquatic ecosystem based on the pesticide sales volume, the application rate, the number of products, and the toxicity. Hence, despite the fact these pesticides are registered and used in Korea, the risks, as a result of this study were observed to be significantly higher than estimated at the time of the registration procedure. The reason for this is that the drainage rate (1% of the applied dose from rice fields to streams) and the drift rate (0.6% of the applied dose in orchards to streams) of the current exposure scenarios in the risk assessment were set to be lower than those of this study. Furthermore, multiple applications are not part of the current assessment. The current risk assessment methods are not protective and it is therefore advised to implement improved exposure scenarios.

Using TER approach of this study, the regulatory acceptable concentrations (RAC) is in fact the PNEC, which is determined by the value of the toxicity endpoint and the Safety Factor (SF). Toxicity data of 96 h LC_{50} for fish was used in this study. Currently, the risk is assessed with 48 h LC_{50} according to the pesticide control act in Korea. In Park et al. (2017), for 44% of all pesticides registered in Korea, it was found that acute fish toxicity persisted from 48 h to 96 h. Therefore, for a more appropriate risk assessment to protect fish, it is necessary to change the acute toxicity endpoint for fishes to 96 h LC_{50}. And it is not certain that Korea's risk assessment criteria (SF of 2) is sufficiently protective for aquatic organisms regarding the use of pesticides. Further research, like e.g. done by Brock et al. (2015), will contribute to answer this question.

Table 5
TERs of selected pesticides for aquatic organisms.

Pesticide	Product code	Crop	TER values for Korean SF[a]			
			Mudfish	Fish	*Daphnia*	Algae
Benfuracarb	BENF1	Rice	3.47	2,083,333.3	1416.67	5,583,333.3
Bentazone	BENT1	Rice	0.76	8.88	8.88	0.90
	BENT2	Rice	4.69	62.50	62.50	6.31
Carbofuran	CARB1	Rice	2.08	0.43	0.02	15.55
	CARB2	Rice	2.78	0.57	0.03	20.73
Clothianidin	CLOT1	Rice	101.91	3473.33	1333.33	1833.33
	CLOT2	Rice	6.11	79.92	30.68	42.19
Fipronil	FIPR	Rice	3.78	1.06	0.81	0.29
Iprobenfos	IPRO1	Rice	6.02	13,611.1	1111.11	5601.85
	IPRO2	Rice	4.63	20.44	1.67	8.41
Mefenacet	MEFE	Rice	2.38	1.47	0.44	0.04
Pendimethalin	PEND1	Rice	0.56	0.87	1.22	0.08
	PEND2	Rice	5.15	0.12	0.17	0.01
Phenthoate	PHEN1	Rice	2.15	4.39	0.003	11.76
	PHEN2	Rice	3.73	4.39	0.003	11.76
Thiophanate methyl	THIO1	Rice	6.58	10.48	5.14	24.19
	THIO2	Rice	11.51	18.33	9.00	42.33
Benfuracarb	BENF2	Fruit	–	1.15	0.36	3.79
Captan	CAPTAN	Fruit	–	0.08	3.04	0.50
Carbofuran	CARB3	Fruit	–	2.54	0.13	91.63
Chlorpyrifos	CHLPF	Fruit	–	0.03	0.0001	0.62
Chlorothalonil	CHLTH	Fruit	–	0.007	0.02	0.09
Dithianon	DITHI	Fruit	–	0.04	0.14	0.05
Fenitrothion	FENIT	Fruit	–	0.67	0.004	0.67
Mancozeb	MANCO	Fruit	–	0.03	0.02	0.02
Pendimethalin	PEND3	Fruit	–	3.85	5.38	0.35
Phenthoate	PHEN3	Fruit	–	1.08	0.0007	2.90
Thiram	THIRAM	Fruit	–	0.08	0.07	0.03

[a] SF (Safety Factor): 2 for mudfish, fish, *Daphnia* and algae.

4. Conclusions

In the present study, pesticide exposure scenarios for surface water were developed for the risk-assessment of aquatic ecosystems as part of the pesticide authorization procedure in Korea. Using the PECs calculated with the models and the scenarios, their corresponding collected toxicity data and two different sets of safety factors (Korean and EU specific values), TER values were calculated for 28 selected pesticides that seemed likely to pose the highest risk. Based on the calculated TER values, most of the selected pesticides posed unacceptable risks to aquatic organisms. Risks were lower using the Korean safety factor because the Korean safety factor is up to 50 times lower than the European safety factor. To determine regulatory acceptable concentrations (RACs), the choice of the safety factor is crucial. Therefore, for Korea, further research on the appropriateness of the regulatory acceptable concentrations (RAC) should be conducted.

For the conservative tier-1 risk assessment to protect the aquatic ecosystem, it is suggested to implement the developed exposure scenarios and models in the pesticide authorization procedure in Korea. In the orchard scenario, the spray drift rate was calculated with the SPEXUS model based on the situation in Dutch orchards. It is recommended to initiate research to determine the spray drift rates in Korean orchards. And in this study we use validated models but we use them for scenarios that needed to be protective for 90% of all cases in Korea. The scenarios are used in a regulatory context with the objective to protect the aquatic environment. For the validation of the results of the PECs, it is recommended to setup the monitoring programs of which the results are feedback in to the registration procedure.

In addition, future studies should also seek to develop a higher tier exposure model taking into account the fluctuating water levels in paddy rice fields (in the mudfish scenario) due to percolation and evaporation. By which the risk-assessment procedure in Korea can be improved by expressing conditions closer to reality. Options for risk-mitigation that accept the use of spray-drift reducing equipment and application techniques are also needed. Furthermore, to protect the aquatic ecosystem in Korea, it is recommended to include other risk indicator species, such as aquatic invertebrates and aquatic macrophytes in to the risk assessment as part of the Korean pesticide registration procedure.

CRediT authorship contribution statement

Jin A. Oh: Data curation, Investigation, Writing – original draft, Writing – review & editing. **Wim H.J. Beltman:** Data curation, Investigation, Writing – review & editing. **Mechteld M.S. Ter Horst:** Data curation, Investigation, Writing – review & editing. **Seong Nam Ham:** Investigation. **Yeon Ki Park:** Conceptualization, Writing – review & editing. **Ji Young Shin:** Investigation. **Kee Sung Kyung:** Writing – review & editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.144790.

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