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ORIGINAL PAPER

Ecotoxicological risk assessment of 14 pesticides and corresponding metabolites to groundwater and soil organisms using China-PEARL model and RQ approach

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Abstract Global use of pesticides brings uncertain risks to human and nontarget species via environmental matrix. Currently, various models for exposure risk assessment are developed and widely used to forecast the impact of pesticides on environmental organisms. In this study, five commonly used insecticides, seven herbicides and three fungicides were chosen to analyze the subsequent risks in groundwater in simulated scenarios using China-PEARL (Pesticide Emission Assessment at Regional and Local Scales) model. In addition, their exposure risks to soil organisms were characterized based on risk quotient (RQ) approach. The results indicated that 23.3% of the total 528 predicted environmental concentrations (PECs) of pesticides and respective metabolites in groundwater from six Chinese simulated locations with ten crops were above 10 μg L^{-1}. Furthermore, acceptable human risks of pesticides in groundwater were observed for all simulation scenarios (RQ < 1). Based on the derived PECs in soil short-term and long-term exposure simulation scenarios, all compounds were evaluated to be with acceptable risks to soil organisms, except that imidacloprid was estimated to be with unacceptable chronic risk (RQ = 27.5) to earthworms. Overall, the present findings provide an opportunity for a more-comprehensive understanding of exposure toxicity risks of pesticides leaching into groundwater and soil.

Jiangong Jiang and Zhixin Liu have contributed equally to this work.

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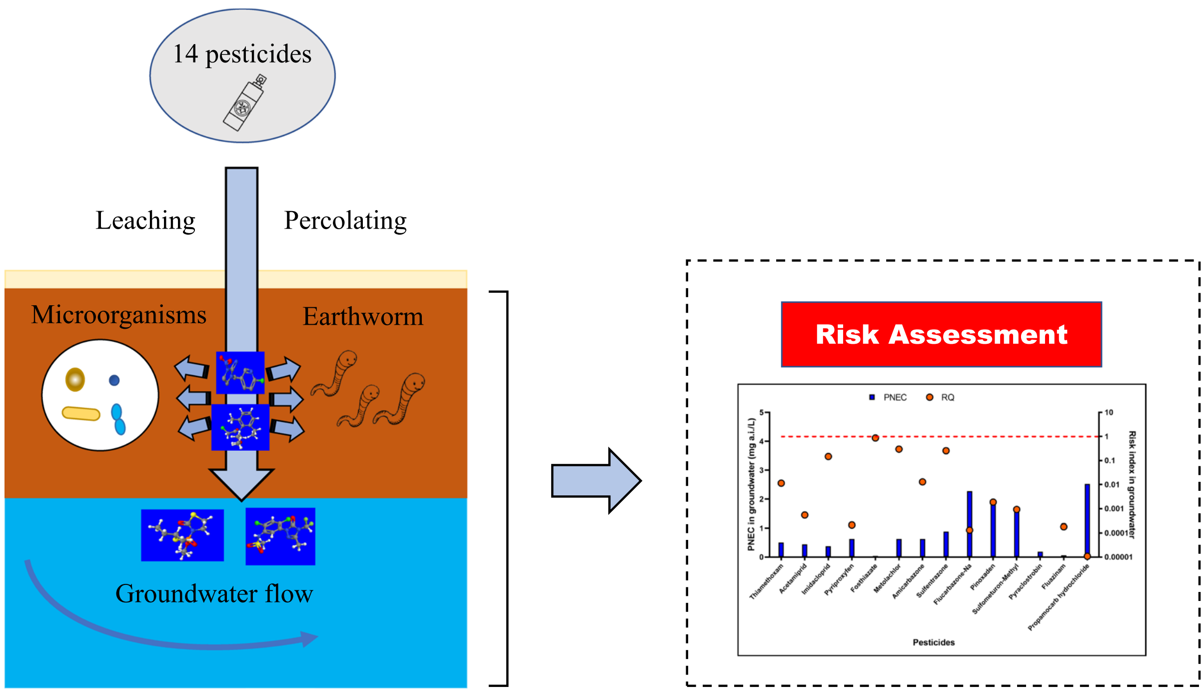
Graphical abstract



Keywords Predicted environmental concentrations · Exposure toxicity risks · Simulation models · Earthworm · Soil microorganism

Introduction

Over the past century, pesticides had played a vital role in protecting plants from insect pests and diseases, ensuring adequate crop yields and benefiting public health worldwide (Popp et al., 2012). However, most of the applied pesticides were inevitably transported to the groundwater by leaching (Gilliom, 2007). Groundwater is the major resource for agriculture, industrial and public supply. However, its property of sensitivity and stability make it easily be contaminated and the consequence will persist for long (Ouedraogo et al., 2016; Zhang et al., 2019). Of all possible pollutants, agricultural pesticide is currently recognized as a significant substance that causes the pollution of groundwater and thus seriously impacts the microorganism communities, aquatic organisms and human beings (Di Lorenzo et al., 2018; EUROSTAT, 2016; González-Rodríguez et al., 2011; Mauffret et al., 2017). Recent researches had proved that long-term intake of pesticide-contaminated groundwater was significantly related with human health damage and even cancer (Polanco Rodríguez et al., 2017). Understanding potential risks of pesticide-contaminated water to human health and revealing relevant mechanisms were beneficial to address these global concerns.

Furthermore, residues of pesticides and metabolites in soil could pose high toxicity risks to soil organisms, such as earthworms and microorganisms. As one of the major terrestrial invertebrate species, earthworm can improve physical, chemical as well as biological properties of the soil via feeding and digging activities. Considering the vulnerable individual-level sensitivity to pollutants and specific biological traits, earthworm is an ideal indicator for soil contamination which can provide a safe threshold for the protection of soil fauna (Edwards, 2004). Among artificially raising species, *Eisenia* *fetida* was often chosen as a general test organism in global ecotoxicology studies and soil environment risk assessment attributed to its short generations and high fecundity (Li et al., 2020a, 2020b). Another important indicator to evaluate soil ecological fitness is microorganism community, which benefits plants by detoxifying environmental pollutants, enhancing nutrition availability, mediating the hormonal balance and suppressing soil-borne pathogens (Bulgarelli et al., 2013). Accumulation of pesticides and their bioactive metabolites in soil may cause irreversible impairment on earthworms via dermal exposure and alimentary canal ingestion (Vijver et al., 2003). Meanwhile, pesticide exposure may decrease the biomass, bioactivity and diversity of soil microorganisms, indirectly leading to the reduction of soil fertility, and ultimately influencing the crop production (Fournier et al., 2020; Muñoz-Leoz et al., 2011). Thus, understanding the potential risks of pesticides to earthworms and microorganisms is an essential prerequisite to ensure the soil function and ecological benefits.

Many countries have set up guidelines or propose stimulating models to assess the risks of pesticides to human health through leaching into groundwater and exposure risks to soil organisms (European Commission, 2006; EFSA, 2017; Li, 2018; Li & Jennings, 2018). Recently, there are three methods available for the assessment of pesticide risk to groundwater, i.e., graded index, statistical analysis and process simulation method (Yang et al., 2017). Compared with the other two methods, process simulation requires more information, such as the agricultural application modes, dosages and frequency of pesticides in typical scenarios (Rico et al., 2016). Thus, results derived from this method could substantially predict the leaching risk for pesticides in agricultural regions. Many countries have developed process simulation models for groundwater risk assessment in specific regions. For example, U.S. Environmental Protection Agency (EPA) and Canada have jointly developed the exposure model SCI-GROW (Screening Concentration in Ground Water) and PRZM-GW (Pesticide Root Zone Model-Ground Water), which allows users to set specific scenarios for the groundwater risk assessment by adjusting the data related to the weather, soil texture and crop types. The European Union (UN) developed the model PEARL (Pesticide Emission Assessment at Regional and Local Scales) containing 10 types of the surface water and 9 kinds of groundwater standard scenario for the groundwater risk assessment. Unlike PRZM-GW, this model did not need to set specific parameters and covered the major agricultural environments and thus could effectively and representatively assume the exposure groundwater risks. Based on the PEARL model, China-PEARL model was developed by the Sino-Dutch Pesticide Risk Assessment Project (PERAP) to calculate the predicted environmental concentrations (PECs) of pesticides and degradation product leaching into groundwater in Northern China. Standard scenarios of six locations in Norther China was set in this model and established with meteorological, soil and crop datasets for further calculation. These groundwater scenarios represent for 99% vulnerability to pesticide leaching; thus, they could be used in groundwater risk assessment. By incorporating the data of pesticide physiochemical property and application data, this model could predict the average and 90th concentration of every year in 20 years. And now it has been regarded as the referenced model in evaluating the exposure risk of pesticides into groundwater by risk quotient (RQ) method (Geng et al., 2017; MAPRC, 2016). With regard to soil organisms, the current regulations and monitoring studies of pesticide residues in soil are incomplete in contrast to that for groundwater; besides, they mainly focused on the persistent and obsolete pesticides (Chiaia-Hernandez et al., 2017; Qu et al., 2016). The recommended approach for the evaluation of the ecotoxicity risk of pesticides in soil was to compare the calculated toxicity exposure ratios (TER) or risk quotient (RQ) values (Silva et al., 2019). Identifying the potential risks of currently used pesticides and their metabolites to groundwater and soil organism is urgently necessary.

This study aims to elucidate the potential exposure risks of 14 commonly used pesticides to human health and soil organisms. The risks were characterized based on RQ method, which combined the predict environment concentrations (derived from Chinese models) and predicted no effect concentrations (calculated by available ecotoxicological data and adjusted factors). These results may provide reference for the regulation of pesticide application for sustainable crop production.

Table 1 Simulated scenarios for 14 pesticides and the metabolites

Target crop	Scenario location	Pesticide	Application type[a]	Total cases
Maize	Summer maize: Shangqiu,Weifang, Wugong	Acetamiprid, pyriproxyfen, metolachlor, amicarbazone, sulfentrazone, sulfometuron-methyl, propamocarb hydrochloride	To the crop canopy	15 (18)
		Thiamethoxam, imidacloprid	Incorporation	6 (6)
		Metolachlor, sulfentrazone	To the soil surface	6 (6)
	Spring maize: Tongxin,Urumqi, Xinmin	Acetamiprid, pyriproxyfen, amicarbazone, sulfometuron-methyl, propamocarb hydrochloride	To the crop canopy	15 (18)
		Thiamethoxam, imidacloprid	Incorporation	6 (6)
		Metolachlor, sulfentrazone	To the soil surface	6 (6)
Wheat	Spring wheat: Tongxin,Urumqi, Xinmin	Acetamiprid, pyriproxyfen, metolachlor, sulfentrazone, flucarbazone-Na, pinoxaden, sulfometuron-methyl, propamocarb hydrochloride	To the crop canopy	18 (24)
		Thiamethoxam, imidacloprid	Incorporation	6 (6)
		Metolachlor, sulfentrazone	To the soil surface	6 (6)
	Winter wheat: Shangqiu,Weifang, Wugong	Acetamiprid, pyriproxyfen, metolachlor, sulfentrazone, flucarbazone-Na, pinoxaden, sulfometuron-methyl, propamocarb hydrochloride	To the crop canopy	18 (24)
		Thiamethoxam, imidacloprid	Incorporation	6 (6)
		Metolachlor, sulfentrazone	To the soil surface	6 (6)
Soybean	Xinmin, Wugong, Weifang Shangqiu	Acetamiprid, pyriproxyfen, sulfometuron-methyl, propamocarb hydrochloride	To the crop canopy	16 (24)
		Thiamethoxam, imidacloprid	Incorporation	8 (8)
		Metolachlor, sulfentrazone	To the soil surface	8 (8)
Cotton	Wugong, Weifang, Shangqiu, Urumqi	Acetamiprid, pyriproxyfen, sulfometuron-methyl, propamocarb hydrochloride	To the crop canopy	16 (24)
		Thiamethoxam, imidacloprid	Incorporation	8 (8)
		Metolachlor, sulfentrazone	To the soil surface	8 (8)
Vine	Wugong	Acetamiprid, pyriproxyfen, sulfometuron-methyl, pyraclostrobin, propamocarb hydrochloride	To the crop canopy	5 (8)
	Wugong	Thiamethoxam, imidacloprid, fosthiazate	Incorporation	3 (2)
		Metolachlor, sulfentrazone	To the soil surface	2 (2)
	Tongxin	Fosthiazate	Incorporation	1
Apple	Weifang	Acetamiprid, pyriproxyfen, sulfometuron-methyl, pyraclostrobin, propamocarb hydrochloride	To the crop canopy	5 (8)
		Thiamethoxam, imidacloprid	Incorporation	2 (2)
		Metolachlor, sulfentrazone	To the soil surface	2 (2)
Tobacco	Shangqiu	Acetamiprid, pyriproxyfen, sulfometuron-methyl, propamocarb hydrochloride	To the crop canopy	4 (6)
		Thiamethoxam, imidacloprid	Incorporation	2 (2)
		Metolachlor, sulfentrazone	To the soil surface	2 (2)
Potato	Urumqi, Tongxin	Acetamiprid, pyriproxyfen, sulfometuron-Methyl, fluazinam, propamocarb hydrochloride	To the crop canopy	10 (14)
		Thiamethoxam, imidacloprid	Incorporation	4 (4)

Table 1 (continued)

Target crop	Scenario location	Pesticide	Application type[a]	Total cases
		Metolachlor, sulfentrazone	To the soil surface	4 (4)
Sugar Beet	Xinmin	Acetamiprid, pyriproxyfen, sulfometuron-methyl, propamocarb hydrochloride	To the crop canopy	4 (6)
		Thiamethoxam, imidacloprid	Incorporation	2 (2)
		Metolachlor, sulfentrazone	To the soil surface	2 (2)
Alfalfa	Urumqi	Acetamiprid, pyriproxyfen, sulfentrazone, propamocarb hydrochloride	To the crop canopy	4 (6)
		Thiamethoxam, imidacloprid	Incorporation	2 (2)
		Metolachlor, sulfentrazone	To the soil surface	2 (2)

[a]To the crop canopy: Foliar spray of the pesticide, and the interception fraction calculated by model. To the soil surface: Direct spray of the pesticide to the soil

Incorporation: Pesticide used as soil treatment or seed coating

Materials and methods

Pesticides under evaluation

This work evaluated a total of 14 pesticides, containing five insecticides, six herbicides, three fungicides and 15 corresponding toxic relevant metabolites, which were currently registered for commercial use but lacked complete environmental exposure toxicity risk in China (Table S1). Input parameters about the physicochemical and environmental properties (molar mass, water solubility, saturated vapor pressure and half-life in aerobic soil, etc.) of them were summarized based on PPBD database (Pesticide Properties DataBase) and EFSA (European Food Safety Agency) reports, as shown in Table S2. The toxicity data for human health and soil organisms, and relative parameters were included in Table S3, according to guideline of Ministry of Agriculture of the People's Republic of China (MAPRC, 2015) and PPBD database. The application data used in assessment models were based on the Institute for the Control of Agrochemicals of the Ministry of Agriculture (ICAMA) pesticide database and the maximum recommended dosage was chosen to simulate the worst exposure scenario (ICAMA, 2021). Table 1 reports the parent pesticides and the simulated locations, crops and number of cases for the prediction of effective concentrations in groundwater.

Modelling system

We used China-PEARL model (v.2.1.2) to predict the pesticide exposure under agricultural conditions. This model could simulate the environmental fate of multiple pesticide applications in Northern China, for instance evapotranspiration and degradation on the surface of the plant and in the soil, penetration into the plant, leafy interception, wash-off by rainfall from leaves, root uptake, photocatalysis transformation, adsorption and transportation in the soil horizon and downward movement into groundwater. Considering the scientificity and feasibility, the model was thus recommended to predict pesticide concentration into groundwater following the guidelines for pesticide environmental risk assessment in China (MAPRC, 2016). Additionally, the PEC_{soil}_SFO_China (xls) model was employed to predict pesticide concentration according to the guidelines for pesticide environmental risk assessment in China (MAPRC, 2017).

Simulation application scenarios for the determination of groundwater risk

The concept model for simulating the scenarios of pesticides application was generated based on the guidelines of Forum for the Co-ordination of Pesticide Fate Models and Their Use (FOCUS) of European Union (Boesten et al., 1995). The conceptual standard scenarios were representatively chosen for the worst realistic scenario cases. In the China-PEARL model, six locations from northern China were selected, including Tongxin and Urumqi in the

North-west China zone; Xinmin in the North-east China zone; Weifang, Wugong and Shangqiu in the North China zone (Fig. S1). The 99th percentile vulnerability of environmental abiotic characteristics was defined according to the annual average value for rainfall and temperature, and a 10th percentile value for soil organic matter content. A total of eight dry-land crops were studied as representative crops, namely alfalfa, apple, cotton, maize, soybean, tobacco, vine and wheat.

Predicted environmental concentration

The PECs of 14 pesticides and their metabolites were calculated using China-PEARL pesticide leaching model at a 1 m depth for each case on the basis of the annual application(s) of the respective pesticide for 20 years (Table S2). The PEC represents the 90th percentile of all the 20 annual average concentrations of the target pesticides. The application types of pesticides in this study contains foliar spray (input as spraying to the crop canopy) and soil treatment (input as incorporation). The spray interception data used by FOCUS were adapted for the China-PEARL model calculation. The wash-off factor was set at 100 m^{-1}. To calculate the PECs of metabolites with China-PEARL, metabolites were simulated as an applied substance. The application rate of the metabolite was calculated on the basis of the application rate of the parent corrected for the difference in molar mass and the maximum percentage of metabolite occurrence fraction in the soil degradation studies (PPDB, 2020). The application rate of the metabolite was calculated by Eq. (1),

$$R_m = \frac{R_p \times F_{max} \times M_m}{100 \times M_p} \tag{1}$$

where R_m = application rate of the metabolites (g a.i. hm^{-2}); R_p = application rate of the parent pesticide (g a.i. hm^{-2}); F_{max} = the maximum occurrence fraction for the metabolite; M_m = the molar mass of the metabolite (g mol^{-1}) and M_p = the molar mass of the parent pesticide (g mol^{-1}).

The PECs for pesticides in soil were generated from PEC_{soil}_SFO_China (xls) model based on the maximum application dosage and frequency. The model returns PEC_{accu} (accumulated concentration), PEC_{twa} (Time weighted average concentration) and PEC_{max} (Max predicted environmental concentration) to estimate the potential risks to soil organisms. However, PEC_{accu} and PEC_{twa} were chosen in the calculation when the DT_{50} of the pesticide exceeded 180 days. PEC_{max} was used in the calculation when (1) the ecotoxicity endpoints used was from a specific life stage of test organisms; and (2) Acute LC_{50}/No observed effective concentration (NOEC) < 10.

Predicted no effect concentration

The predicted no effect concentration (PNEC) of pesticides for human in drinking water was estimated by Eq. (2),

$$\text{PNEC} = \frac{\text{ADI} \times \text{BW} \times P}{C} \tag{2}$$

where ADI = acceptable daily intake of the pesticide (mg kg^{-1} bw day^{-1}) according to the guidelines of MAPRC (MAPRC, 2015); BW = body weight (kg) (a default value of 63 kg is used in this study); P = the fraction of the ADI accounting for drinking water (a default value of 0.2 is used) and C = the daily drinking water consumption (L day^{-1}) (here, a default value of 2 L day^{-1} is used).

The PNEC (mg kg^{-1} dw soil) of pesticides for soil organisms was estimated by Eq. (3),

$$\text{PNEC} = \frac{\text{Endpoint}}{\text{UF}} \tag{3}$$

where Endpoint = the toxicological endpoint value in the experiment (mg/kg dw soil), such as LC_{50}, EC_{25}, and NOEC; UF = uncertain factors, which is 10 when being used to calculate acute toxicity risk of pesticides to earthworm; UF is 5 when being used to calculate chronic toxicity risk of pesticides to earthworm; UF is 1 when being used to calculate acute toxicity risk of pesticides to soil microorganism (MAPRC, 2017).

Risk assessment

A risk quotient (RQ) approach was used to assess the exposure risks of pesticides leaching into drinking water and calculated by Eq. (4),

$$\text{RQ} = \frac{\text{PEC}}{\text{PNEC}} \tag{4}$$

where the PEC values were estimated based on the China-PEARL model and compared with the PNEC. If RQ > 1, the risk of a pesticide to groundwater safety is recognized unacceptable. If RQ ≤ 1, this case is considered acceptable.

When the pesticide is without relevant toxicological metabolite(s), the RQ is calculated by Eq. (5),

$$RQ = \frac{PEC_p}{PNEC_p} \quad (5)$$

where PEC_p and $PNEC_p$ = the predicted environmental concentration (μg L^{-1}) and no environmental concentration (μg L^{-1}) for the parent molecule, respectively.

When the pesticide has toxicological relevant metabolite(s) with ADI data, the total risk is calculated by the RQ sum of the parent and its metabolites. The RQ is calculated by Eq. (6),

$$RQ = \frac{PEC_p}{PNEC_p} + \sum_i^n \frac{PEC_{m,i}}{PNEC_{m,i}} \quad (6)$$

where $PEC_{m,i}$ and $PNEC_{m,i}$ = the predicted environmental concentration (μg L^{-1}) and no environmental concentration (μg L^{-1}) for the metabolite i, respectively.

When the pesticide has toxicological relevant metabolites without ADI data or metabolites whose relevancy is unknown, these metabolites are summed up to the parent and compared to the parent's PNEC. The RQ is calculated by Eq. (7),

$$RQ = \frac{PEC_p + \sum_i^n PEC_{m,i}}{PNEC_p} \quad (7)$$

To assess the potential exposure risks of pesticides to soil organisms. The risk quotient (RQ) approach was calculated by Eq. (8),

$$RQ = \frac{PEC}{PNEC} \quad (8)$$

where the PEC values were estimated based on the PEC_{soil}_SFO_China (xls) model and compared with the PNEC. If RQ > 1, the ecotoxicological risk of a pesticide to earthworm or microorganism is recognized unacceptable. If the RQ = 1, there is a possibility of risk at this situation. If RQ < 1, the case is considered acceptable.

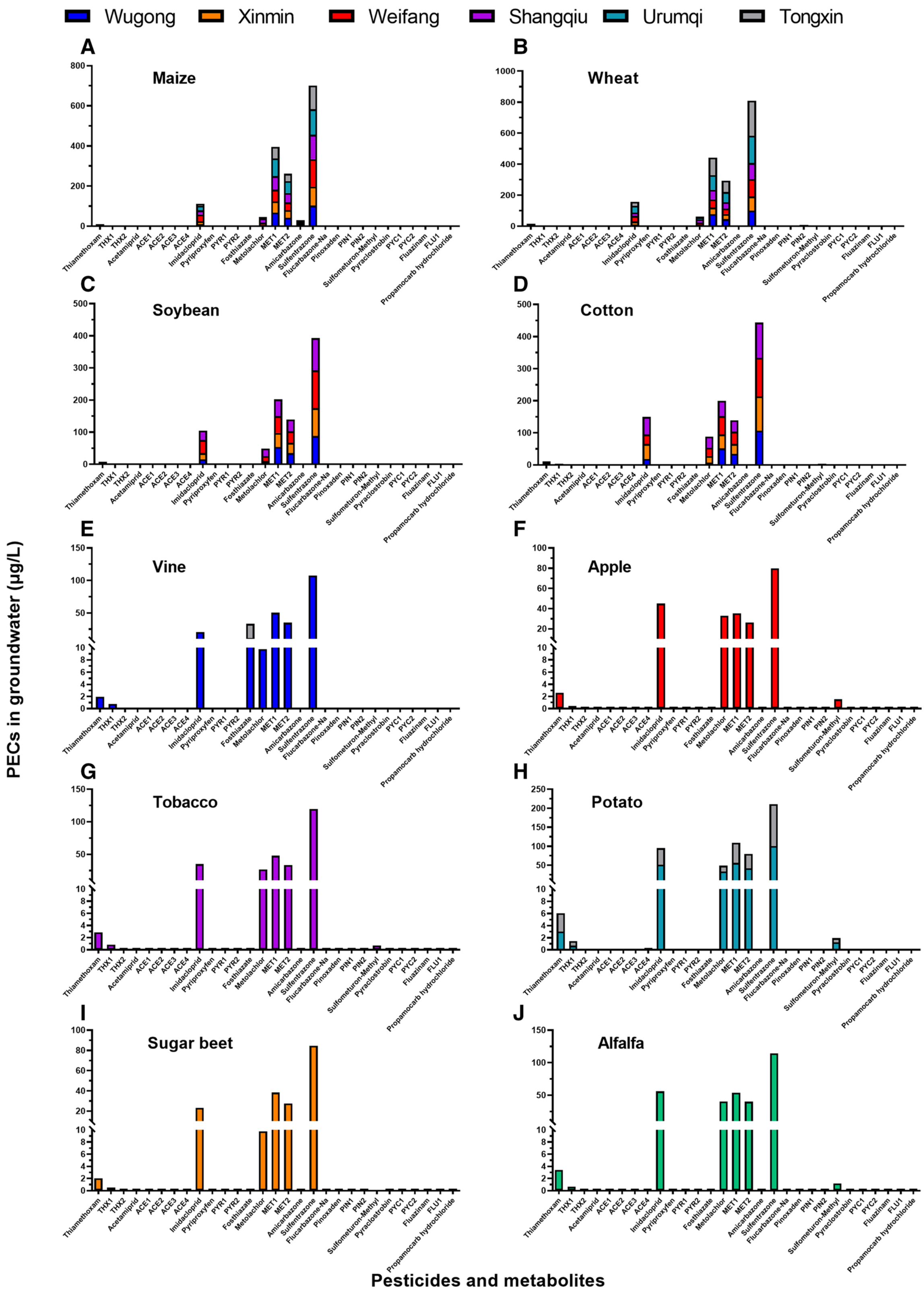
Results and discussion

PECs of pesticides and metabolites in groundwater

The samples were collected from ten crops at six locations. A summary description of the PECs of 14 parent pesticides and 15 metabolites in groundwater is presented in Fig. 1. Totally, 240 cases for parent pesticides and 288 cases for their metabolites were estimated. In the cases of arable crops (Maize, wheat, soybean and cotton), the highest PECs (≥ 10 μg L^{-1}) were found for imidacloprid, sulfentrazone, metolachlor, MESA and MOXA, compared with other compounds (Fig. 1a–d). Parent pesticides thiamethoxam, metolachlor and sulfometuron-methyl possessed relative lower PECs (< 10 μg L^{-1}). Metabolites clothianidin, thiamethoxam urea and IM-1-5 had the lowest PECs (below 1 μg L^{-1}). Additionally, the PECs of acetamiprid, pyriproxyfen, propamocarb hydrochloride (15 of 20 cases) and pinoxaden were equivalent to 0 μg L^{-1} with application mode of spraying to canopy and to the soil surface, respectively. Moreover, metabolites IM-1-2, IM-1-4, IC-0 and 4′-OH-Pyr also had PECs of 0 μg L^{-1}.

In terms of vine cases, higher PECs were observed for imidacloprid (20.66 μg L^{-1}), fosthiazate (11.61 μg L^{-1} in Wugong and 21.79 μg L^{-1} in Tongxin), sulfentrazone (107.62 μg L^{-1}), metolachlor (9.77 μg L^{-1}), MESA (50.44 μg L^{-1}) and MOXA (35.15 μg L^{-1}), in comparison with those of sulfometuron-methyl, clothianidin, thiamethoxam urea and IM-1-5 (metabolite of acetamiprid) (below 1 μg L^{-1}) (Fig. 1E). The PECs of acetamiprid, pyriproxyfen, pyraclostrobin, propamocarb hydrochloride and their metabolites were equal to 0, except IM-1-5 and PYPAC (metabolite of pyriproxyfen) with values of 0.065 and 0.0066 μg L^{-1}, respectively.

With regard to apple, tobacco, potato, sugar beet and alfalfa, the highest PECs among test compounds were derived from sulfentrazone, with a range of 79.82–119.79 μg L^{-1} (Fig. 1f–j). In terms of parent pesticides, imidacloprid and metolachlor (23.14–55.95 μg L^{-1} and 9.77–40.44 μg L^{-1}) had higher PECs compared with those of thiamethoxam, sulfometuron-methyl and propamocarb hydrochloride which ranged from 2.05–3.39, 0.30–1.54 and $1 \times 10^{-6} - 0.027$ μg L^{-1}, respectively.


Wugong
Xinmin
Weifang
Shangqiu
Urumqi
Tongxin
A
Maize
B
Wheat
C
Soybean
D
Cotton
E
Vine
F
Apple
G
Tobacco
H
Potato
I
Sugar beet
J
Alfalfa
PECs in groundwater (μg/L)
Pesticides and metabolites
Thiamethoxam
THX1
THX2
Acetamiprid
ACE1
ACE2
ACE3
ACE4
Imidacloprid
Pyriproxyfen
PYR1
PYR2
Fosthiazate
Metolachlor
MET1
MET2
Amicarbazone
Sulfentrazone
Flucarbazone-Na
Pinoxaden
PIN1
PIN2
Sulfometuron-Methyl
Pyraclostrobin
PYC1
PYC2
Fluazinam
FLU1
Propamocarb hydrochloride

◂**Fig. 1** PECs in groundwater for parent compound and transformation product in ten scenarios from six locations. THX1 = Clothianidin, THX2 = Thiamethoxam urea, ACE1 = (E)-*N*2-carbamoyl-*N*1-(6-chloro-3-pyridyl)methyl-*N*2-cyano-*N*1-methylacetamidine (known as IM-1-2), ACE2 = N-methyl(6-chloro-3-pyridyl)methylamine (Known as IM-1-4), ACE3 = 6-chloro-nicotinic acid (known as IC-0), ACE4 = *N*-(6-chloropyridin-3-ylmethyl)-*N*-methyl-acetamidine (known as IM-1-5), PYR1 = 4-OH-Pyr, PYR2 = (RS)-2-(2-pyridyloxy)propionic acid (known as PYPAC), MET1 = metolachlor ethane sulfonic acid (known as MESA), MET2 = metolachlor oxanilic acid (known as MOXA), PIN1 = 8-(2,6-diethyl-4-methylphenyl)-tetrahydropyrazolo-1,2-*d* (known as NOA 407,854), PIN2 = 8-(2,6-diethyl-4-methyl-phehyl)-8-hydroxy-tetrahydropyrazolo(1,2-*d*)(1,4,5)*o*xadiazepine-7,9-dione (Known as NOA 447,204), PYC1 = BAS 500-6, PYC2 = Methyl *N*-(2((1-(4-chlorophenyl)-1*H*-pyrazol-3-yl)oxymethyl)phenyl)carbamate (known as BAS 500-7), FLU1 = 5-((3-chloro-5-(trifluoromethyl)-2-pyridyl)amino)-alpha,alpha,alpha-trifluoro-4,6-dinitro-*o*-cresol (Known as HYPA)

Health risk assessment of pesticides in groundwater

For all simulated cases, the health risks induced by pesticides in groundwater were considered acceptable with the maximum RQs below 1 (Fig. 2). Specifically, the greatest RQ value was found for fosthiazate owing to the lowest ADI (0.004 mg kg^{-1} bw day^{-1}, Table S3), in spite of the relatively low PECs. Imidacloprid, metolachlor and sulfentrazone had relative higher risk indexes ($0.1 < RQ < 1$) than other pesticides. Propamocarb hydrochloride was considered with the lowest risks (Maximum $RQ = 1.08 \times 10^{-5}$) to groundwater. Additionally, as the PECs of pyraclostrobin and its metabolites BF 500-6 and BF 500-7 were 0, the RQs of pyraclostrobin in the groundwater of both cases (Wugong-Vine and Weifang-Apple) were estimated to be 0.

PECs of pesticides and metabolites in soil

On the basis of available physiochemical data, China-PEARL modelling-derived PECs are calculated and presented in Fig. 3. Among all of the assessed compounds, the highest PEC in soil was derived for fosthiazate (4.01 mg L^{-1}) in acute exposure scenario. Regarding parent pesticides, metolachlor, pyraclostrobin and propamocarb hydrochloride generated higher PEC_{acute} values (> 1 mg L^{-1}) than others. As for metabolites, BF 500-6 posed the highest PEC_{acute} of 0.57 mg L^{-1}. In chronic exposure scenario, five pesticides and two metabolites could generate PECs based on available information, i.e. thiamethoxam, fosthiazate, metolachlor, sulfometuron-methyl, pyraclostrobin, IM-1-4 and IC-0. Among them, metabolite IC-0 had the highest $PEC_{chronic}$ of 0.98 mg L^{-1}.

Exposure risk assessment of pesticides to earthworm and soil microorganism

Both of the acute and chronic risks of pesticides and metabolites to soil organism are summarized in Table 2. Acceptable acute risks to earthworms were identified for most of the test compounds with the RQ values below 1 (except for five metabolites). In chronic exposure scenario, imidacloprid was the only one of the seven pesticides showing unacceptable risk ($RQ = 27.5$) to earthworm. The RQ_{acute} value of test compounds ranged from 0.0185 to 0.569, indicating that the exposure risks were considered acceptable ($RQ_{acute} < 1$) to soil microorganism.

Discussion

In 193 of 528 simulated cases, the PECs of pesticides or transformed products were equal to 0 μg L^{-1}. As high as 65.9% of the total cases generated PECs below 1 μg L^{-1}, while 23.3% of them had PECs higher than 10 μg L^{-1}. The sum of some pesticides and corresponding metabolites posed high PECs (> 100 μg L^{-1}), such as sulfentrazone and metolachlor. The chosen locations for simulation represent an overall 99th percentile vulnerability of the standard for the northern dry farming scenarios of China. The model requires the physicochemical properties and application information of pesticides and metabolites, thus the content of organic matter, adsorption coefficient ($K_{om} = 0.58 \times K_{oc}$, organic carbon normalized apparent partition coefficient), aerobic half-life (DT_{50}) and application mode may be main factors contributed in the PECs discrepancy. High PECs mean that the specific pesticide possess great leaching potential to groundwater through the soil layer. The greatest leachability of sulfentrazone was probably attributed to its certain water solubility (1600 mg L^{-1} at pH 7.5), the weak soil sorption power (K_{oc} of 43 L kg^{-1}) and long persistent nature in soil ($DT_{50} = 400$ days). This result paralleled with a previous two year's case study which indicated that sulfentrazone had leaching

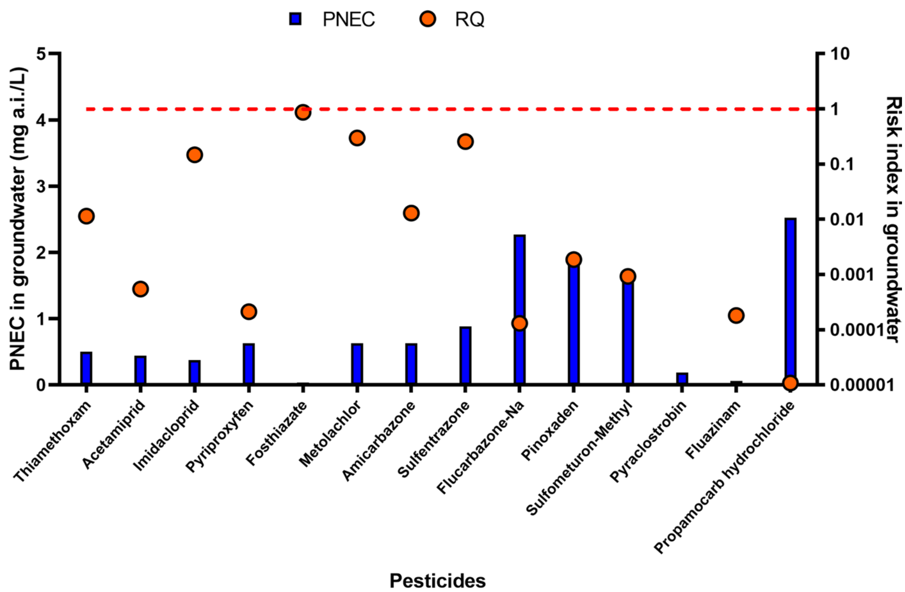


Fig. 2 PNEC and maximum summed RQ of 14 pesticides for human health in groundwater

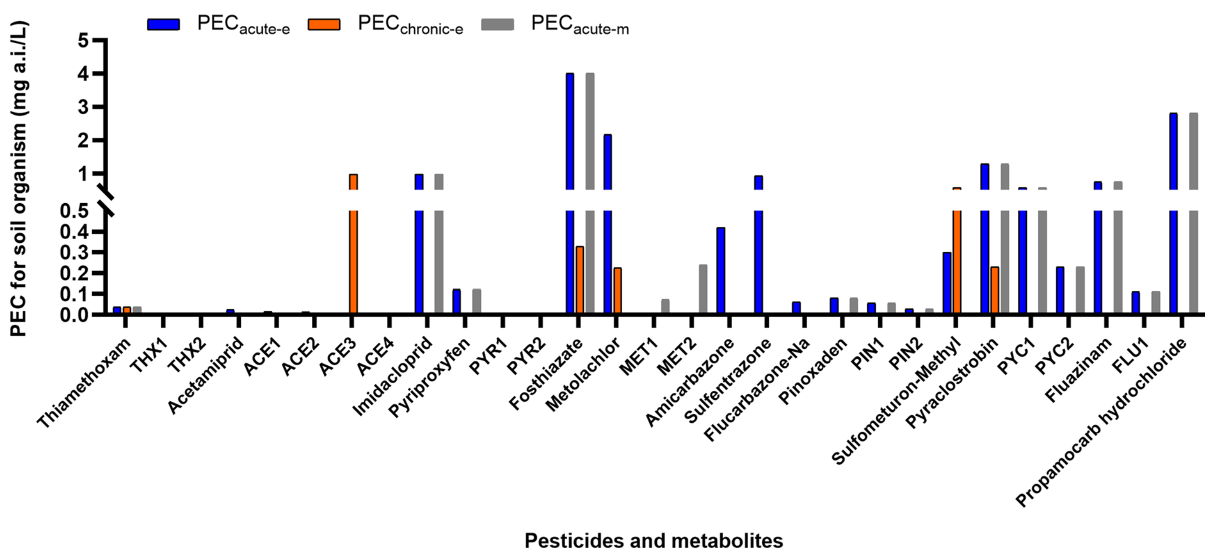


Fig. 3 PECs of 14 pesticides in soil for earthworms and microorganisms. $PEC_{acute\text{-}e}$ and $PEC_{chronic\text{-}e}$ represent PECs for earthworms in short-term and long-term exposure scenario, respectively. $PEC_{chronic\text{-}m}$ represent PECs for microorganisms long-term exposure scenario

potential in corn and soybean rotational field, with the highest concentration of 21.6 μg L^{-1} in groundwater (Thorngren et al., 2017). The difference between our simulated PEC and this actually environmental concentration may be attributed to the high application dosage (approximately threefold greater than that of Thorngren et al., 2017) and the worst-case scenario settings in the model. Another pesticide with high leaching risk was imidacloprid, with the PECs ranging from 9.96 to 55.95 μg L^{-1}. The high leaching ability of imidacloprid into groundwater lie in its physicochemical traits (water solubility of 607 mg L^{-1}, K_{oc} of 210 L kg^{-1} and DT_{50} of 187 days) and the application type of soil treatment. This result was consistent with a previous report which proposed a similar range (3.90–33.29 μg L^{-1}, incorporation

Table 2 PNEC and RQ of 14 pesticides and metabolites for earthworm and soil microorganisms

Compound	Earthworm				Soil microorganism	
	$PNEC_{acute}$ (mg/kg dw soil)	RQ_{acute}	$PNEC_{chronic}$ (mg/kg dw soil)	$RQ_{chronic}$	$PNEC_{acute}$ (mg/kg dw soil)	RQ_{acute}
Thiamethoxam	10	0.00372	1.07	0.0348	2.67	0.0139
THX1	–	–	–	–	–	–
THX2	–	–	–	–	–	–
Acetamiprid	0.366	0.0683	–	–	–	–
ACE1	100	0.000149	–	–	–	–
ACE2	100	0.000127	–	–	–	–
ACE3	100	0.00002	–	–	–	–
ACE4	100	0.000011	12.5	0.000488	0.267	0.0936
Imidacloprid	1.07	0.914	0.0356	27.5	2.67	0.366
Pyriproxyfen	100	0.0012	–	–	1.5	0.08
PYR1	–	–	–	–		
PYR2	20	0.0001	–	–		
Fosthiazate	20.9	0.192	–	–	53	0.0756
Metolachlor	14	0.154	–	–		
MET1	–	–	2	0.164	3.92	0.0185
MET2	–	–	11.12	0.0203	3.12	0.077
Amicarbazone	10	0.0421	–	–		
Sulfentrazone	10	0.0924	–	–		
Flucarbazone–Na	100	0.0006	–	–		
Pinoxaden	100	0.0008	–	–	0.4	0.2
PIN1	100	0.000567	–	–	0.4	0.142
PIN2	100	0.000287	–	–	0.066	0.435
Sulfometuron–Methyl	10	0.03	–	–		
Pyraclostrobin	56.7	0.0226	–	–	3.3	0.389
PYC1	100	0.00569	200	0.00285	1	0.569
PYC2	100	0.0023	160	0.00144	0.5	0.459
Fluazinam	10	0.0746	–	–	2.27	0.328
FLU1	50	0.00223	–	–	0.38	0.293
Propamocarb hydrochloride	66	0.0425	–	–	28.9	0.0971

mode) for PEC of imidacloprid in groundwater (Geng et al., 2017). Given the potent systemic characteristic in plant tissues and excellent efficacy in managing piercing-sucking insect pests, imidacloprid was commonly applied as soil and seed treatment agents in the past few decades and thus contributed to the contamination of water resource (Goulson, 2013). Currently, environmental monitoring research reveals that imidacloprid was frequently detected in groundwater. A research carried out in Wisconsin showed that 162 (31%) of total 527 well water samples (including groundwater monitoring wells and private potable well) were tested positive with a maximum detection of 4.54 μg L^{-1} for imidacloprid during 2011–2017 (Bradford et al., 2018). Fosthiazate also had high mobility and apparent leaching potential owing to the low K_{oc} (59 L kg^{-1}) and certain water solubility (9447 mg L^{-1}) (Karpouzas et al., 2007). Herbicides including amicarbazone, flucarbazone-Na, sulfometuron-methyl were considered with moderate leachability among all compounds, with the PECs ranging below 10 μg L^{-1}. Propamocarb hydrochloride was predicted to be with no leaching potential.

Metabolites had much different leaching potential in comparison with the parent compounds. This phenomenon was also largely attributed to the significantly different physicochemical properties of parent compounds and metabolites. For example, the PECs of clothianidin and thiamethoxam urea were approximately severalfold and about 30-fold lower than their parent compound thiamethoxam due to weaker water solubility and faster degradation. On the contrary, MESA and MOXA posed ten-fold greater PECs than parent pesticide metolachlor, due to their relatively low soil sorption power (K_{oc} of 7 and 12 L kg^{-1}, respectively) and long persistence (DT_{50} of 235 and 152.5 days, respectively). The predicted result was consistent with a recent case study by Rose et al. (2018) who reported that MESA and MOXA were more frequently detected in shallow groundwater than the parent (Maximum concentration = 0.1 μg L^{-1}), with a maximum concentration of 16 and 10 μg L^{-1}, respectively. Nonetheless, the two metabolites along with parent metolachlor were monitored in multiple hydrologic compartments, raising concerns to non-target species and human health (Chen et al., 2019; Kock-Schulmeyer et al., 2014; Mccarty et al., 2014).

However, all of the tested pesticides were evaluated to be safe to the groundwater at the highest recommended application amount in northern China. Therefore, no further assessment procedure and risk measures are needed for the present pesticides. But pesticides with certain leaching potential (such as imidacloprid, fosthiazate, metolachlor, and sulfentrazone) posed higher risk quotients, although they did not trigger the safety threshold value. Similar results were found by Geng et al. (2017) who characterize the RQ of imidacloprid below 1 under foliar spray conditions and incorporation. Regarding metolachlor and sulfentrazone, although the sum of metolachlor and main metabolite PECs were high, they exhibited relatively low toxicity relevancy (ADI = 0.1 and 0.14 mg/kg bw, respectively) for drinking water which may be the major reason accounting for their acceptable risks (Reemtsma et al., 2013). Other models also delivered the similar results, for example, Wen and Li (2014) reported that the leachable pesticides metolachlor and imidacloprid applied on soybean and maize in China showed acceptable risks to groundwater using the PRZM-GW model. Xiong et al. (2004) also found that imidacloprid were safe to the groundwater of seven target plant scenarios by incorporate the groundwater level, meteorological data, irrigation amounts and soil property in the PEARL model. Besides, evidences have proved that PEARL model was a promising tool for predicting the leaching potential of pesticides when compared to the field data. For example, Marín-Benito et al. (2014) found that PEARL predicted the observed concentrations of s-metolachlor and mesotrione better than MACRO and PRZM in an irrigated maize field. Tiktak et al. (2011) tested the PEARL model against field leaching data and proved that PEARL could calibrate the degradation and drainage of bentazone and imidacloprid well.

The environment conditions of six default locations in standard scenarios were the major factors for the China PEARL model uncertainty and sensitivity, namely meteorological average and soil properties. The vulnerability order for the six representative sites were Wugong < Xinmin < Tongxin < Shangqiu < Weifang < Urumqi (Geng et al., 2017). Our results of the PECs for most pesticides in groundwater corroborated this trend (Fig. 1). However, the current version of this model was limited to the northern parts of China, more representative districts of different parts should be covered in the future updated versions. The plants in standard scenarios should be also expanded from the major arable plants to more vegetables and trees, which may make China-PEARL model entirely appropriate for environmental risk assessment for pesticide registration in China.

The PEC of pesticide and metabolites in soil varies from the application type, crop type and chemical parameters under worst-case conditions. In our study, pesticides used as soil and seed treatment were often with long persistence in soil, such as imidacloprid and fosthiazate, easily resulting in relatively high PECs in soil. These findings are in agreement with current studies. For instance, in a European report, imidacloprid was the only detected neonicotinoid insecticide in agricultural soils, though it had been banned since 2013 (Silva et al., 2019). Fosthiazate was also proved to be persistent among nematicides, even though received degradation enhancement treatment (Osborn et al., 2010). Specifically, propamocarb hydrochloride had the slowest degradation among all tested fungicides (PEC = 2.8 mg L^{-1}), though applied as spraying to the canopy, which is probably owing to the stability of chemical structure, the high soil adsorption ability (K_{oc} of 705.9 L kg^{-1}), high application frequency (3 times in a 7-day interval) and dosages (1083 g h m^{-2}) (Chen et al., 2017).

In the short-term ecotoxicity exposure scenario, all pesticides and respective metabolites were evaluated with acceptable risks to earthworms and microorganisms in agricultural soil. However, unacceptable chronic exposure risk to earthworms was estimated for imidacloprid, since it was highly reproductive toxic with a low NOEC of 0.178 mg kg^{-1}. Similar with our results, the sublethal exposure of imidacloprid leads to reduction in the growth rate, reproduction, enzyme bioactivity and gene expression of the earthworm *Eisenia fetida* (Wang et al., 2019). Additionally, although fosthiazate as well as propamocarb hydrochloride had relatively high PECs in soil, their risks were evaluated within safe margin due to their low ecotoxicity to earthworms and microorganisms (PPDB, 2020; Wada & Toyota, 2008). Similar results were also concluded by Jiang et al. (2019) who found that application of fosthiazate on greenhouse tomato and cucumber induced no unacceptable risks based on the RQ index.

Conclusion

Our study elucidated possible fate of 14 pesticides and corresponding transformed products in soil and groundwater, based on the computer simulation programs. By applying risk quotient protocols, we found that pesticide exposure risks into groundwater and soil varied by factors including recommended application type, physicochemical characteristics and environmental conditions. The selected pesticides in this research were safe to groundwater and soil organisms, except imidacloprid (unacceptable chronic risk to earthworm). Our results derived from China-PEARL model corroborate with the experimental data. Besides, PEARL model possessed better efficiency in simulating the pesticide concentration than PRZM and MACRO. Thus, the China-PEARL model was suitable for groundwater health risk assessment but not complete, more standard scenarios of different representative locations and target plants should be added in updates. Additionally, via collecting the ecotoxicity data from database available, gaps were revealed in ecotoxicity of pesticides and metabolites to soil microorganisms. More effort is still needed for understanding the effects of pesticides and metabolites to soil organisms in order to fill the data gaps.

Author contributions JJ, BL and WM contributed to conceptualization; JJ provided methodology and software; JJ, ZL, XZ, XY, XL, LK, DX, and SY performed data curation and original draft preparation; WM, SY and RL performed visualization and investigation; WM carried out supervision; JJ, ZL, and WM performed writing—reviewing and editing.

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Declarations

Conflict of interest The authors declare no competing interests.

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