Development and Evaluation of the KOrea Insecticide Exposure Model (KOIEM) for Managing Insecticides

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The KOrea Insecticide Exposure Model (KOIEM) was developed to facilitate ecological risk-based management of Korean insecticides. KOIEM, applied as a multimedia fate model, evaluates water, soil, air, and vegetation compartments based on three water-body types (streams, ditches, and ponds). Deltamethrin, a pyrethroid insecticide, was used to evaluate and create the model parameters. After exposure of both the stream and the ditch to deltamethrin, the KOIEM-predicted concentrations and the observed levels were in agreement. The model was also evaluated using the accuracy factor (AF), which was 4.32 and 0.35 for the stream and ditch, respectively. Ecological risk assessment was also performed to evaluate the application of KOIEM for four popular South Korean insecticides (cypermethrin, deltamethrin, diazinon, and permethrin). Despite the insecticides having low PECs in water, their risk quotients were typically above 1.0. Thus, KOIEM modification would be required in further studies to account for spatial variation.

Key Words : Insecticide, Multimedia fate model, Ecological risk assessment, KOIEM

Introduction

Mathematical modeling can be a useful tool for global regulation of pesticides. Many of the existing pesticide exposure models have been developed to support environmental risk assessment and do therefore typically provide conservative estimates, traditionally termed realistic worst cases. Several environmental exposure models for pesticide application have been developed. The GENeric Estimated Environmental Concentration (GENEEC)¹ model is tier one screening model for pesticide aquatic ecological exposure model, which calculates from runoff from a treated agricultural field adjacent static water body. The EXposure Analysis Modeling System (EXAMS)² and FOrum for the Co-ordination of pesticide fate models and their USe (FOCUS)³ are termed pesticide fate models, and are applied to monitor agricultural exposure to pesticides. The pesticide paddy field (PADDY) model⁴ and the pesticide concentration in paddy field (PCPF-1) model⁵ were both developed in Japan to predict the environmental fate of pesticides in rice paddy systems. The rice water quality (RICEWQ) model,⁶ developed in the United States, calculates chemical dissipation within the paddy, as well as pesticide leaching. Multimedia fate and multi-pathway human exposure mass balance models such as CalTOX 4.07 and IMPACT 20028 are used for pesticide risk assessment at a regional scale.⁹ However, no environmental exposure models have been developed that focus on insecticides, and the implications of insecticides are often ignored because of their low concentrations in aquatic systems.

Pyrethroids (PYRs) and organophosphorous pesticides

(OPs), families of synthetic insecticides, are widely used in Korea to control a variety of insects and prevent epidemics.¹⁰ PYRs are extremely hydrophobic with octanol-water partition coefficients (Kow) between 10^6 and 10^7 , and water solubilities of only a few µg/L.¹¹ PYRs are an important class of pesticides because they rapidly paralyze insects, have low mammalian toxicity relative to other pesticides, and are less persistent in the environment.¹² However, PYRs are neurotoxic and lethal to fish at concentrations 10 to 1000-fold lower than the corresponding toxic concentrations in mammals and birds.¹³ Accordingly, model development has been focused for PYRs as target insecticides.

In this study, we first intended to develop a region-specific insecticide exposure model based on Korean topography. We investigated the environmental fate of insecticides in various medias including water, soil, and air, and assessed ecological risk using a multimedia fate model. The major objectives of this study were to (1) develop the KOrea Insecticide Exposure Model (KOIEM) for use in the Korean environment, (2) evaluate KOIEM by comparing the predicted model results to actual environmental monitoring data for a insecticide, then (3) apply KOIEM to assess the ecological risk of several insecticides used in Korea.

Model Development

Model Description. The KOrea Insecticide Exposure Model (KOIEM), a multimedia fate model for estimating insecticide concentrations, was developed for three waterbody types (streams, ditches, and ponds). KOIEM simulates the fate and transport of insecticides sprayed in the air and

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transported into the water through soil and vegetation.

Based on the assumptions and mechanisms of the model, mass balance in the model area can be described by a set of differential equations, one for each compartment. By solving the set of mass balance equations, the model provides the concentration of insecticides in each compartment, as well as various cross-media fluxes. This model can obtain timedependent concentrations of unsteady-state solutions. The numerical solution was obtained using Euler's method¹⁴ to solve the set of ordinary differential equations described above. The computer code was written in VISUAL BASIC using the Microsoft Visual Studio v.2008 platform.

Model Scope. The study areas were the Banseok stream $(L \times W = 200 \text{ m} \times 30 \text{ m})$, the Jukdong ditch (600 m × 4 m), and the Jukdong pond (40 m × 2.5 m), located in Daejeon, South Korea (Fig. 1). As shown in Figure 2(a), the Banseok



Figure 1. Location of the study area in South Korea (★: Banseok stream; ▲: Jukdong ditch and pond).

stream consists of three zones (i.e., a spray zone, the adjacent zone, and water), since its width is longer than the maximum spray distance. The average discharge of the stream $(0.4 \text{ m}^3/\text{sec})$ is greater than those of the ditch and pond.

The Jukdong ditch and pond only include a spray zone, because their widths are shorter than the maximum spray distances. In addition, the insecticide is sprayed directly to the water surface. As the pond composed some part of the ditch, despite the similar spatial compositions of the ditch and pond, there are differences in their sizes ($W \times L$) and water discharges (ditch: 0.01 m³/sec, pond: 0.0001 m³/sec).

Insecticide application was carried out on both sides of the stream and one side of the ditch and pond (Fig. 2(b) and (c)). Spatial distribution of the land surface type was classified as bare soil and vegetation covered soil, in which short weeds were the dominant. The height of the air compartment was assumed to be 100 m, accounting for spatial mixing. The effective depth of the soil compartment was assumed to be 0.1 m. The measured depth of the water compartment for the stream, ditch, and pond was 0.25, 0.1, and 0.1 m, respectively. Each compartment was assumed to be a "mixed box", in which all environmental properties and chemical concentrations are uniform throughout the compartment.

Model Process. The environmental transport processes considered in this model can be divided into intra-media and inter-media processes. Intra-media processes include (1) wind drift, (2) dispersion and advection, (3) degradation, and (4) leaching. Inter-media processes include (5) volatilization, (6) dry deposition, (7) wet deposition, (8) run-off, (9) uptake by plant roots, (10) wash-off from the vegetation surface, and (11) volatilization from the soil and water to the atmosphere. A schematic diagram of the model is displayed in Figure 3.



Figure 2. Spatial scope of the model in this study: (a) Stream, (b) Ditch and (c) Pond.

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Figure 3. Conceptual diagram of the model in this study.

Wind Drift: There are two approaches to estimate wind drift, a proportional approach¹⁵ and a meteorological approach.¹⁶ In this study, we used a proportional approach using empirical equations based on monitoring data because micrometeorological factors were not available in the study areas. This method, which has been widely used in the

Table 1. Input data used for deltamethrin in simulating KOIEM

EPPO¹⁷ and FOCUS models,³ provides drift as a ratio of distance to wind speed. However, it has a limited application to the Korean environment due to variable topographic and meteorological characteristics. Thus, we applied the equations suggested by Nuyttens *et al.*¹⁸

Dispersion and Advection: Air dispersion is estimated based on the Lagrangian model,¹⁹ which assumes that the dispersion has a Gaussian distribution. Additionally, pollutant dispersion and advection from cell to cell is estimated based on 30-year average (daily and monthly) meteorological data, monitored by the Daejeon Korea Meteorological Administration (KMA). The model calculates incoming and outgoing air pollutants every minute by considering dispersion and advection. In an air grid cell, only lateral dispersion is considered since the vertical distribution of pollutants is assumed to be constant within a designated range of atmospheric altitudes. Air grid cells with a specific mass of pollutants migrate based on wind speed and direction, and cell area increases from $L \times L$ to $(L + 1.54\sigma_v) \times (L + 1.54\sigma_x)$, over time, by dispersion. The lateral dispersion parameters $(\sigma_x \text{ and } \sigma_y)$ were estimated using Briggs's approach based on

	Input data	Properties	Reference
	Wind speed	30-year average daily data	KMA ^a
	Wind direction	30-year average monthly data	KMA^{a}
Meteorological data	Precipitation	30-year average daily data	KMA^{a}
	Air temperature	30-year average daily data	KMA^{a}
	Humidity	30-year average daily data	KMA ^a
	Molecular weight	505.21	21
	Vapor pressure	0.002 mPa at 20 °C	21
	Solubility	0.002 mg/L at 20 °C	21
	Henry's law constant	$12.6 \pm 4.1 \text{ Pa m}^3 \text{ mol}^{-1}$	22
Physical-chemical data	Log octanol-water partition coefficient (log Kow)	5.43	21
	Log organic carbon partition coefficient log Koc	5.56-6.21	23
	Half life in water	2-4 h	23
	Diffusivity in air	0.0099 m ² /hour	24
	Diffusivity in water	1.59E-06 m ² /hour	24
	Land cover	Grass	-
	Slope	Calculation by DEM	-
o., .c.	Soil bulk density (kg/m ³)	2,650	25
Site-specific	Porosity	0.3	Assumed
uata	Foc	0.02	26
	LAI, RAI	2.0 , 5.4	Assumed
	Water discharge (m ³ /sec)	0.4 (stream), 0.01 (ditch), 0.0001 (pond)	Monitored
	Application period	6/1-6/30	-
	Application rate	0.13 g/ ha·sec	-
	Duration time of Application	1 min 5 sec (stream), 3 min 15 sec (ditch),	
	(= waterside length/speed of spraying car)	13 sec (pond)	-
Application Scenario	Interval	7 days	-
	Number of application	4	-
	Diameter of sprayed aerosol	250 μm	-
	Width of air spray	7 m	-
	Simulation time	6 months	-

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Table 2. Measured concentrations of deltamethrin immediately after application (0 min) at the sampling sites^{*a*} ($S_0 \sim S_5$) at Banseok stream and Jukdong ditch

Site	Sampling	Concentration (µg/L)						
	time	\mathbf{S}_0	\mathbf{S}_1	S_2	S_3	S_4	S_5	
Stream	June	0.46	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>	
	July	0.13	0.15	<dl< td=""><td>-</td><td>-</td><td><dl< td=""></dl<></td></dl<>	-	-	<dl< td=""></dl<>	
Ditch	June	14.3	1.92	0.68	0.15	0.08	0.11	
	July	0.26	-	-	-	-	-	

 ${}^{a}S_{0}$ = starting point of application, S_{1} = 5 m apart from application point, S_{2} = 10 m apart from application point, S_{3} = 40 m apart from application point, S_{4} = 70 m apart from application point, S_{5} = 100 m apart from application point, < DL = concentrations below detection level of deltamethrin (0.04 µg/L)

the Pasquill stability class.²⁰ Moving cells overlap with other cells, and the pollutant mass is allocated to other cells based on the amount of overlapping air grid cell area.

Model Input Data. Model inputs included meteorological and site-specific data for the study area, physical-chemical properties of the insecticides, and application scenarios. Deltamethrin, a pyrethroid insecticide common in Korea, was chosen to parameterize and evaluate the model. Table 1 summarize the input data and application scenarios for deltamethrin. Insecticide was sprayed by control truck on both sides of the steam and to one side of the ditch and pond. It was assumed that the insecticide sprayed into the air as an aerosol was deposited onto the soil and vegetation, according to settling velocity (which is dependent on the aerosol diameter).

Field Experiments. In this study, only deltamethrin was monitored for evaluating KOIEM. Sampling of the stream and ditch was conducted in both July and August at specific time intervals, at a known distance from the initial treatment point. Samples were obtained by submerging 2-L plastic bags into the water and storing them at 4 °C until analysis. A water sample of 500 mL was taken using a separatory funnel with dichloromethane (50 mL), and the sample was shaken for 3 min. This extraction procedure was repeated 3 times. The extract was dried over sodium sulfate and evaporated in a rotary evaporator. The residue was dissolved in 1 mL of acetone and then analyzed using a gas chromatograph (Agilent 6800N with an electron capture detector: 30 m \times 0.250 mm i.d. \times 0.25 μ m J&W DB-1 column). The gas chromatography operating conditions included an injection port temperature of 250 °C, a detector temperature of 300 °C, and a carrier gas (N₂) flow of 0.6 mL/min. The column temperature was programmed to start at 150 °C with an increase of 5 °C/min to 250 °C, a hold for 2 min, followed by an increase of 2 °C/min to 300 °C, and a final hold for 2 min.

Results and Discussion

Simulation and Evaluation of KOIEM. KOIEM was evaluated by comparing the predicted and actual times required for the stream and ditch to reach their maximum



Figure 4. Model simulation results of deltamethrin according to water-body type. Predicted concentrations in water were compared with measured concentrations for (a) Stream and (b) Ditch.

concentrations of deltamathrin.

Additionally, we compared the predicted 'retention time' which means insecticide could be detected in water after application, with the observed times. As seen in Figure 4, KOIEM predicted that deltamethrin would reach a maximum value in the water bodies within 3 min (Banseok stream) or 5-6 min (Jukdong ditch) of exposure. The observed data confirmed that deltamethrin reached its maximum value within a few minutes. The predicted and observed retention times also showed very little differences. The model predicted a retention time of 19 min for the Banseok stream and 5 h for the Jukdong ditch, while the observed retention times were 10 min and 8 h, respectively.

KOIEM was evaluated for deltamathrin monitored in the stream and ditch using the accuracy factor (AF), which is defined as the ratio of predicted concentrations to measured concentrations.²⁷ Deltamethrin concentrations were measured at sites S0 through S5 in the Banseok stream and the Jukdong ditch (Table 2). For values below the detection limit, values of 0.02 μ g/L were assumed (half the detection limit). Higher deltamethrin concentrations were found in ditches compared to streams, and the concentrations gradually decreased from S0 (i.e. starting point of application) to S5 (i.e. 100 m apart from application point) (Table 2). However, the model did not account for the changes in concentrations according to space, and thus we used the average concentrations from S0 to S5 to calculate AF. In the stream, the predicted environmental concentration (PEC)



Figure 5. Comparison of Predicted Environmental Concentration (PEC) with Measured Environmental Concentration (MEC) for deltamethrin in Stream and Ditch.

was 0.38 μ g/L and AF was 4.32. For the ditch, PEC was 0.88 μ g/L and AF was 0.35. Although the AF less than 1 was not sufficient for a conservative purpose, it could predict the exposure level with an uncertainty of less than a factor of 5 (Figure 5).

The predicted KOIEM results were compared with those of existing pesticide models (GENEEC and FOCUS). The estimated maximum concentrations predicted by KOIEM were higher than those of GENEEC and FOCUS. Also, the retention time predicted by KOIEM varied from the values 1187

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predicted by GENEEC and FOCUS. GENEEC predicted that 10% of the maximum concentration remained for 21 days after exposure. FOCUS predicted that deltamethrin persisted for 7 days in the ditch and pond, and for 4 days in the stream after exposure. However, the retention times predicted by KOIEM for the stream and ditch ranged from minutes to hours. The differences between KOIEM, FOCUS, and GENEEC may be due to differences in the spraying site size and adjacent zones, water discharge, or wind speed. Accordingly, the sensitivity of KOIEM to the inputs was evaluated using the sensitivity index ($SI = (y_{+50} - y_{-50})/y$, where y is the prediction from the inputs that is not disturbed, y_{+50} and y_{-50} are the predictions from the inputs disturbed by \pm 50% of their original values, respectively).

We found that the spray amount (application rate, |SI| = 2.00), spray particle size (|SI| = 1.41) water depth (|SI| = 1.33), and discharge (|SI| = 1.04), strongly influence PECs in the water compartment (with an absolute ($|SI| \ge 1.0$). These observations indicate that application of existing pesticide models without accounting for the specific application type (i.e. the spray amount (application rate), spray particle size) and site-specific parameters (i.e. spatial structure, water depth and discharge) increases the uncertainty of model prediction.

Application of KOIEM. Ecological risk in three waterbody types was assessed using KOIEM for four insecticides that are commonly used in Korea. The model was not evaluated for the pond due to the lack of the monitoring data.

Table 3. Application scenarios of insecticides used in the simulation

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Insecticides	Application rate ¹⁰ $(g ha^{-1}sec^{-1})$	Application period ¹⁰	Duration time of application (sec)	Interval (days)	Number of application	Diameter of sprayed aerosol	Spray distance	Simulation time
Cypermethrin	8.93							
Deltamethrin	0.13		65 sec (stream)					
Diazinon	17.86	6/1~8/30	195 sec (ditch)	7 days	4	200 µm	7 m	5 yrs
Fenitrothion	44.64		13 sec (pond)					
Permethrin	1.12							

Table 4. Input parameters of in	nsecticides to	simulate I	KOIEM
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Parameters	Cypermethrin	Deltamethrin	Diazinon	Permethrin
Structure		Br Contraction	N N SHOW	c L L a C a
MW (g/mole)	416.3	505.21	304.35	391.28
WS ²⁸ (mg/L)	0.004	0.002	40	0.006
VP ²⁸ (Pascal)	4.09E-07	0.20E-5	0.01	2.91E-06
H ²⁸ (atm m ³ /mole)	4.02E-09	1.18E-09	1.10E-7	9.97E-07
Molar Volume ²⁹ (m ³ /mole)	332.8	341.2	267.7	320.1
Log Kow ²⁸	6.6	6.2	3.8	6.5
Half-life in water ²⁸ (h)	4,320	14	504	1,440
Half-life in soil ²⁸ (h)	8,640	2,400	336	672
Half-life in air ²⁸ (h)	1,176	10.8	96	9.6
Diffusivity Coefficient in air ²⁹ (m ² /hour)	0.0103	0.0099	0.0132	0.0108
Diffusivity Coefficient in water ²⁹	1.61E-06	1.58E-06	1.83E-6	1.64E-06
(m ² /hour)				

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	Average PEC _{water} (µg/L)			Data used for eco	Risk Quotient (RQ)				
Insecticides	Stream	Ditch	Pond	Species	End point	Toxicity value (µg/L)	Stream	Ditch	Pond
				Scenedesmus acutus var. acutus	EC50	112,450	2.37E-01	4.96E-01	5.53E+00
Cypermethrin	26.64	55.72	622.04	Daphnia magna	EC50	1.56	1.71E+04	3.57E+04	3.99E+05
				Oncorhynchus mykiss	LC50	10	2.66E+03	5.57E+03	6.22E+04
				Scenedesmus subspicatus	EC50	2,560	1.48E-01	3.44E-01	3.71E-01
Deltamethrin	0.38	0.88	0.92	Daphnia magna	EC50	0.64	5.94E+02	1.38E+03	1.48E+03
				Oncorhynchus mykiss	LC50	3.19	1.19E+02	2.76E+02	2.98E+02
				Pseudokirchneriella subcapitata	EC50	6,400	8.35E+00	1.79E+01	6.28E+01
Diazinon	53.44	114.44	401.70	Daphnia magna	EC50	0.00029	1.84E+08	3.95E+08	1.39E+09
				Oncorhynchus mykiss	LC50	800	6.68E+01	1.43E+02	5.02E+02
				Scenedesmus quadricauda	EC50	10,000	3.33E-01	7.05E-01	6.73E+00
Permethrin	3.33	7.05	67.29	Daphnia magna	EC50	3.5	9.51E+02	2.01E+03	1.92E+04
				Oncorhynchus mykiss	LC50	6	5.55E+02	1.18E+03	1.12E+04

Table 5. Ecological risk assessment of four major insecticides used in Korea based on KOIEM simulation results

The model evaluation results for the pond are assumed to be the same as that for the ditch due to their similar spatial compositions and input data. Application scenarios and input parameters for the insecticides are summarized in Tables 3 and 4. Many techniques have been developed to predict ecological risk.³⁰ In this study, single-point exposure and effect comparisons were adopted with the risk quotient (RQ) method. The RQ is defined as the ratio of PEC to the predicted no effect concentration (PNEC).³¹ PNEC can be estimated by applying assessment factors (depending on the quality and quantity of available toxicity data) to the toxicity value of the organism most sensitive to the toxin. In this report, PECs were obtained by averaging the concentration of insecticides in water for 1 year. PNECs were obtained using the assessment factor combined with 1,000 values from the E(L)C50 data.³² The obtained RQs are summarized in Table 5. For ponds, the RQs of all insecticides were above 1.0. For streams and ditches, despite having relatively lower RQs than ponds, most values were also above 1.0. Based on these observations, very low exposure (a few ppb levels) to common Korean insecticides may be toxic to the aquatic environment. The results have demonstrated that common insecticides may cause environmental risk in Korean aquatic environment chronically. Though currently insecticides have not been managed with exposure model distinguished from pesticide model, exposure model for chronic risk management of insecticide would be needed as a decision-making tool.

Conclusions

We developed a multimedia fate model (KOIEM) that predicts insecticide concentrations for three water-body types by considering topographical characteristics of the study area. Using this model, we predicted the path that aerosolized atmospheric insecticides would take to access the water. Despite limited monitoring, we found the AF of KOIEM in water compartments to be below 5. The target insecticide quickly reached its maximum concentration in the water. Wind drift significantly affected the concentration of insecticides in the water shortly after exposure because of the small spraying and adjacent zones in the study area.

Most models are highly sensitive to changes in spray method, spray amount, and topographic characteristics of the study area. Thus, existing pesticide models are limited when applied to other countries or areas. A long-term simulation conducted using KOIEM revealed that the insecticides could cause adverse effects in all three water-body types. The low toxicity of PYRs to mammals may be misleading in terms of ecological toxicity. It would be resulted that despite the low environmental concentrations of PYRs chronic adverse effect may be occurred in Korean aquatic environment. Further modification of KOIEM to reflect spatial variation and evaluation in other types of media (i.e. soil, air) will be useful in assessing the capability of this model as a decision making tool and the potential ecological risk of insecticide application.

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