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Estimating Concentrations of Pesticide Residue in Soil from Pepper Plot Using the GLEAMS Model

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Abstract

BACKGROUND: Mathematical model such as GLEAMS have been developed and successfully applied to upland fields to estimate the level of pesticide residues in soil. But, the GLEAMS model rarely applied to the Korean conditions.

METHODS AND RESULTS: To evaluate pesticide transport in soil residue using the GLEAMS model from pepper plot, Alachlor, Endosulfan, Cypermethrin and Fenvalerate were applied for standard and double rate. Soil sampling was conducted and decaying patterns of pesticides were investigated. Observed climate data such as temperature and irrigation amount were used for hydrology simulation. The observed pesticide residue data of 2008 were used for parameter calibration, and validation of GLEAMS model was conducted with observed data of 2009. After calibration, the K_{oc} (Organic carbon distribution coefficient) and WSHFRC (Washoff fraction) parameters were identified as key parameters. The simulated concentrations of the pesticides except Fenvalerate were sensitive to K_{oc} parameter. Overall, soil residue concentrations of Alachlor, Cypermethrin and Fenvalerate were fairly simulated compared to those of

Endosulfan. The applicability of the GLEAMS model was also confirmed by statistical analysis.

CONCLUSION(s): GLEAMS model was eligible for evaluation of pesticide soil residue for Alachlor, Cypermethrin and Fenvalerate.

Key Words: GLEAMS, Pesticide residue, Simulation, Water quality

INTRODUCTION

Agricultural use of pesticides account for about 80% of all pesticide use in the United States (NRCS, 1997). Pesticide protects crops and ensures stable production, but pesticide has residual characteristics and causes chronic toxicity. Pesticide in soil residue could be transported by rainfall runoff and soil erosion from a watershed into water body. The extensive use of pesticides had raised public concerns about health and environmental issues. In order to reduce the environmental impact of pesticides, it is important to understand pesticide fate and transport (Yuan *et al.*, 2000).

Pesticide contamination of groundwater is a potential health and environmental issue (Wade *et al.*, 1998). Concern has been raised that the use of more pesticides on soils that exhibit high rates of water infiltration

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may accelerate leaching of pesticides into the subsurface waters underneath the agricultural croplands (Sadeghi and Isensee, 1994). In order to assess the environmental risk of pesticides, information is usually required on the likelihood of exposure of organisms to the constituents of pesticides, expressed as a predicted environmental concentrations, and the likely effects of the constituents of pesticides on aquatic and terrestrial organisms, expressed as a predicted no-effect concentrations (Chung *et al.*, 2008).

Over the last twenty years, mathematical models have been successfully applied to upland fields to estimate the level of pesticide residues outside the field where the potentially exposed organism is located (Chung *et al.*, 2008). Some commonly used models for the evaluation of non-point source pollution in upland fields are the Pesticide Root Zone Model (PRZM; Carsel *et al.*, 1984), the Root Zone Water Quality Model (RZWQM; Malone *et al.*, 2004), the Groundwater Loading Effect of Agricultural Management Systems (GLEAMS ; Leonard *et al.*, 1987). GLEAMS model was evaluated by several researches on pesticide in soil residue (Smith *et al.*, 1991; Malone *et al.*, 1999; Rekolainen *et al.*, 2000; Dann *et al.*, 2006; Connolly *et al.*, 2001; Kim and Chung., 1995). But, the model rarely applied to the Korean conditions. The objective of this study was to evaluate pesticide residue in soil using the GLEAMS model from pepper field.

MATERIALS AND METHOD

GLEAMS model description

Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) is a field scale hydrology, crop growth, erosion and chemical transport model with a complex subsurface component that can accommodate depth-variable parameters (Leonard *et al.*, 1987). GLEAMS predict the partitioning of pesticides into surface runoff, sediment, and percolation as a result of tillage, cropping, and pesticide management practices. Output data include runoff, sediment, and percolation amounts, pesticide masses in runoff, sediment, and percolation, etc. Output frequency can be by day, month, or year (Truman and Leonard, 1991).

Field experiment

The experiments were conducted at the greenhouse in Chonnam National University, Gwangju, Korea (35°10'N, 126°53'E). The experimental plot was 2.5 m² (1.5 m by 1.66 m) and pepper was selected for the experiment. Duplicates for standard (STD) and double (DBL) rate applications of four pesticides: Alachlor, Cypermethrin, Endosulfan, and Fenvalerate were used for experiment. The soil types of the experimental plots were of Pyeongtaeg series (silt loam, mixed, mesic family of Typic Endoaquepts) (National Institute of Agricultural Science and Technology, 2006). The chemical properties of the experimental plot soil are shown in Table 1.

Table 1. Physical and chemical properties of the soil in the experimental plots

Soil	grain-size distribution (%)				CEC (cmol kg ⁻¹)	pH	OM (g kg ⁻¹)	T-N (g kg ⁻¹)	NH ₄ ⁺ NO ₃ ⁻		Avail. P (mg P ₂ O ₅ kg ⁻¹)
	Clay	Silt	Sand	Soil Texture					(mg N kg ⁻¹)	(mg N kg ⁻¹)	
	20.0	21.5	58.5	Sandy Clay Loam	10.2	6.1	26.6	1.3	9.0	72.4	33.6

Agricultural activities and pesticide management

The agricultural activities including fertilizer application records are shown in Table 2. The cropping period was from the beginning of May to the end of

September. Pepper was transplanted from May 14 to May 20 and fertilizer was applied late May. Irrigation in each plot was applied and monitored in two day interval after pesticide application.

Table 2. Agricultural activities in the experimental field during the study period (2008-2009)

Date (Julian day)	Agricultural activities	Remark
2008-05-14(135)	Pepper transplanting	
2008-05-14(135)	Fertilization	
2008-06-05(157)	Pesticides application	Alachlor
2008-06-10(162)	Pesticides application	Cypermethrin Endosulfan (α , β , sulfate) Fenvalerate
2008.09.02(246)	Harvest	

2009-05-14(134)	Fertilization	
2009-05-20(140)	Pepper transplanting	
2009-06-16(167)	Pesticides application	Alachlor Cypermethrin, Endosulfan (α , β , sulfate)
2009-06-22(173)	Pesticides application	Fenvalerate
2009-09-18(261)	Harvest	

The pesticide application rate is shown in table 3. The standard application rates of Alachlor, Endosulfan, Cypermethrin, and Fenvalerate were 40, 50, 1.67 and 1.67 kg/ha, respectively in 2008 and 2009. Alachlor and Endosulfan are applied as form of granule and dustable powder. And Cypermethrin and Fenvalerate are applied as emulsifiable concentrate.

Table 3. Pesticide Management in experimental plot (2008)

Pesticide	Effective Ingredient (%)	Standard Application Rate (kg/ha)	Remark
Alachlor	5	40	Herbicide
Endosulfan	3	50	Insecticide
Cypermethrin	5	1.67	Insecticide
Fenvalerate	5	1.67	Insecticide

Soil sampling

Two samples per each soil layer were collected (0-20, 20-40, 40-60 cm). After sampling the samples were immediately transported to the laboratory and added preservatives before they were stored at 4°C prior to analysis.

Soil sample analytical method

A method using ultrawave-assisted extraction with 15% acetone in n-Hexane followed by Gas chromatography with ECD was developed for the determination of Endocrine Disrupter Pesticide residues in field Soil.

Climate data for GLEAMS model

The GLEAMS model requires input data for hydrology, topography, soil and pesticide. It also require mean daily air temperature, daily precipitation, mean monthly

maximum and minimum temperatures, solar radiation, wind speed, and dew point temperature data (Leonard *et al.*, 1987). Also, input requirements for GLEAMS include daily rainfall volumes, crop and management parameters, and intrinsic soil physical and chemical properties with depth, soil detachment and transport parameters, and pesticide properties. Meteorology data from the period 2008 and 2009 were used in this study derived from observed data of Gwangju weather station.

Soil physical parameters for GLEAMS model

An effective rooting depth of 60 cm deep was considered and divided into three horizons based on soil texture. Measured data on clay, silt, sand, and organic matter contents were used but porosity, field capacity, wilting point, and hydraulic conductivity were obtained from the GLEAMS' database (Leonard *et al.*, 1987, 1990). Table 4 show that major input parameters for hydrology submodel.

Table 4. Input parameter values for hydrology submodel

Item	Description	Input value			Remark
		1 st	2 st	3 st	
	Layer				
	Soil layer thickness (cm)	20	40	60	field data
	Porosity (cm^3/cm^3)	0.4	0.4	0.4	GLEAMS manual
	Wilting point (cm^3/cm^3)	0.18	0.18	0.18	
	Organic matter content (%)	1.29	1.29	1	soil test
	Field capacity (cm^3/cm^3)	0.3	0.3	0.3	GLEAMS manual

Pesticide parameters for GLEAMS model

Pesticide parameters derived from guideline from Korean Crop Protection Information Center for pesticide (2008) and GLEAMS model user's guide (Knisel, 1993). The major parameters were K_{oc} ; organic carbon distribution coefficient, WSHFRC; washoff fraction, SOLLIF; half-life in soil, H_2OSOL ; pesticide water solubility, HAFLIF; foliage half-life.

RESULTS AND DISCUSSION

Observed weather and irrigation amount data

Fig. 1 shows mean daily temperature variation during 2008 and 2009. Temperature ranged from 11.7°C to 29.7°C and from 14.8°C to 29°C during field experiment (may-september) period of 2008 and 2009, respectively. The experiment was conducted under housed conditions excluding rainfall. Therefore, water supplied to soil in two or three days interval by manual irrigation (Fig. 2). The applied water amount ranged 0.8-3.2 mm/day. The total applied amounts were 55.6 mm and 87.2 mm for 2008 and 2009, respectively.

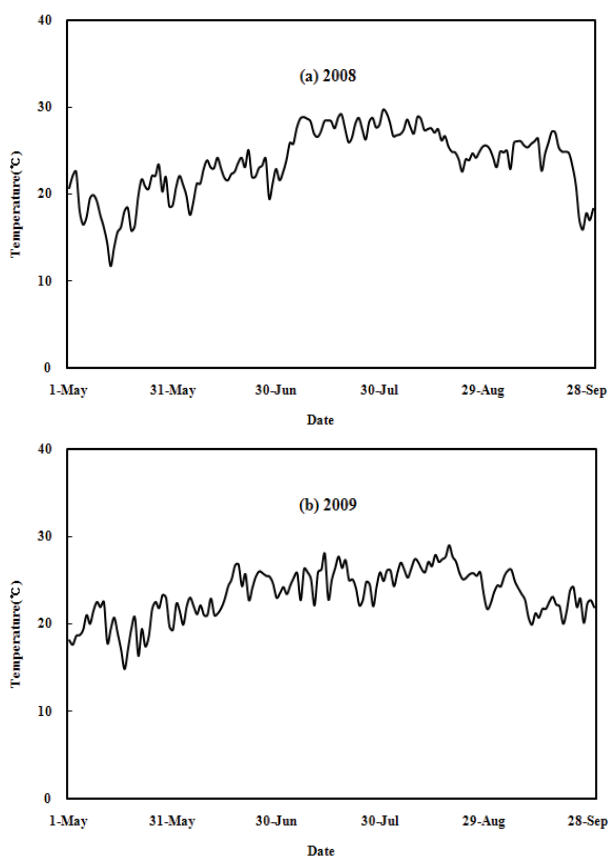


Fig 1. Changes in mean daily temperature for cropping period in 2008 (a), and 2009 (b)

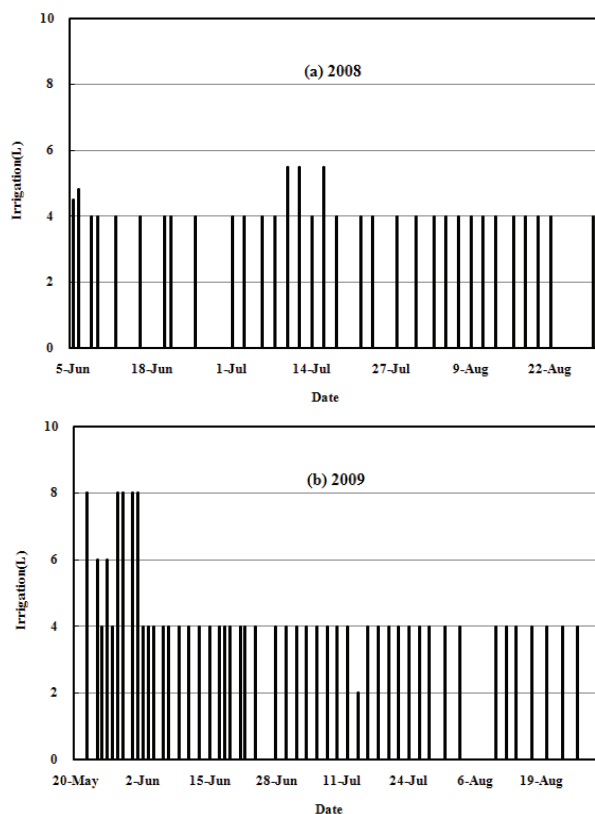


Fig 2. The amount of daily irrigation for cropping period in 2008 (a), and 2009 (b)

Parameter calibration

Calibrated parameter values in this study are given in Table 5. These parameters were used for standard and double rate conditions, together. Application rate, APRATE, is specified in units of kg/ha active ingredient (Knisel, 1993). APRATE for standard rate application conditions were 40, 1.67, 50, 1.67 kg/ha for Alachlor, Cypermethrin, Endosulfan and Fenvalerate, respectively.

Table 5. Parameter values of GLEAMS pesticide submodel after Calibration

Parameter Pesticide	APRATE (kg/ha)		K _{oc} (ml/g)	WSHFRC	SOLLIF (days)	H ₂ OSOL (mg/L)	Volatilized Rate ($\mu\text{g m}^{-2}\text{hr}^{-1}$)	HAFLIF (days)	
	STD	DBL						Foliar	Soil
Alachlor	40	80	*15 (170)	0.4	15	240	2.8	3	15
Cypermethrin	1.67	3.33	*1000 (10000)	0.4	*70 (30)	0.004	0.07	5	30
Endosulfan	50	100	*20000 (12400)	0.05	50	0.32	29.8	3	50
Fenvalerate	1.67	3.33	5300	*0.7 (0.25)	35	0.002	983.0	10	35

*After Calibration

(): Default Parameter by SCS data base in GLEAMS

K_{oc}, the organic carbon distribution coefficient, which represents adsorption capacity, affects significantly the pesticide concentrations in soil residue (Dann *et al.*, 2006). The calibrated K_{oc} value of Alachlor was smaller than those of other pesticides used in this study. The simulated concentrations of Alachlor were sensitive to K_{oc} parameter relatively, while the simulated concentrations of Fenvalerate did not affected by K_{oc} parameter. Fenvalerate usually sprayed as liquid type on foliage and assumed to have a small solubility (Khang *et al.*, 1986).

The washoff fraction, WSHFRC, which, represents fraction of pesticide on the foliage available for washoff by rainfall influenced strongly to Fenvalerate concentration in soil residue. The calibrated WSHFRC values of Endosulfan and Fenvalerate were 0.05 and 0.7, respectively. Endosulfan showed the lowest value while Fenvalerate showed the highest one.

SOLLIF, which indicate half-life in soil, was sensitive parameter for soil residue simulation except Fenvalerate, since the adsorption in soil particles of Fenvalerate was very high and the mobility of Fenvalerate was small. Previous study indicated that the observed concentrations of Fenvalerate remained constant in soil (Khang *et al.*, 1986).

The H₂OSOL which indicate pesticide water solubility were 240, 0.002mg/L for Alachlor and Fenvalerate, respectively. Alachlor showed the highest value, while Fenvalerate showed the lowest value. Nevertheless, the simulated concentrations of pesticide in soil residue did not affected by the H₂OSOL values. The simulated concentrations of Cypermethrin and Fenvalerate were sensitively responded by HAFLIF values, which indicate the foliage half-life.

The observed data of 2008 were used for parameter calibration. Fig. 3 shows the observed and simulated Alachlor residue in soil layer of 0-20 cm. The Alachlor concentrations in soil residue for standard (STD) and double (DBL) application treatment ranged 0.2-0 and 2.02-0 ppm, respectively. The simulated concentrations of Alachlor in soil residue for STD and DBL varied 0.68-0 and 1.36-0 ppm, respectively.

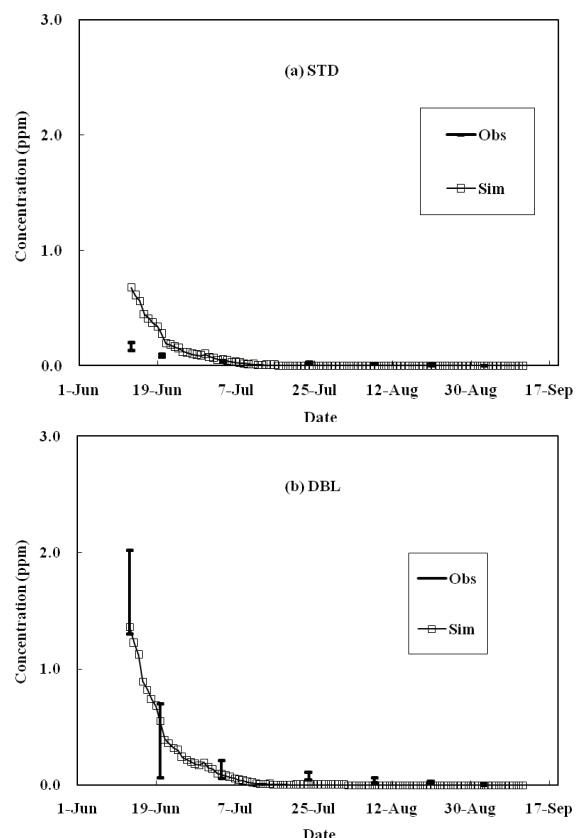


Fig 3. Observed and simulated pesticide residue in soil for Alachlor after calibration.

GLEAMS simulation after calibration

The concentrations of Alachlor in soil residue for double rate application conditions were remarkably increased compared to those of standard application plots. The GLEAMS model also indicated that the simulated concentration of Alachlor was affected by the application rate.

Fig. 4 shows the observed and simulated Endosulfan residue in 0-20 cm soil layer. The Endosulfan concentration in soil residue for STD and DBL ranged 1.27-0.03 and 2.4-0.06 ppm, respectively. The simulated concentrations of Endosulfan in soil residue for STD and DBL ranged 1.45-0.42 and 2.93-0.87 ppm, respectively.

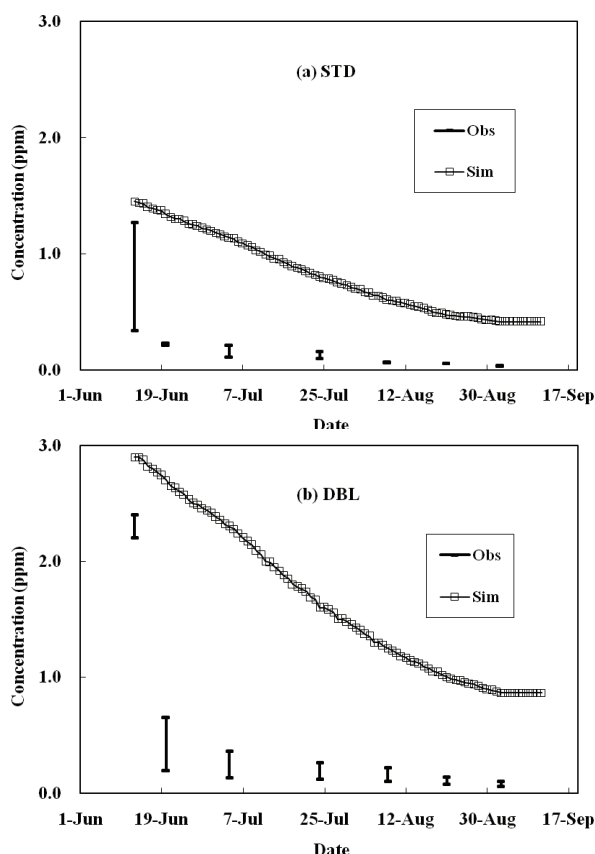


Fig 4. Observed and simulated pesticide residue in soil for Endosulfan after calibration

The observed pesticide residue in soil for Endosulfan was quickly decreased in soil layer after three days for application Endosulfan. However, the GLEAMS model did not simulate fairly decaying pattern of pesticide residue in soil layer in DBL treatment. Fig. 5 shows the observed and simulated pesticide residue in soil for Cypermethrin. The Cypermethrin concentration in soil residue for STD and DBL ranged 0.18-0.07 and 0.94-0.09 ppm, respectively. The simulated concentrations of Cypermethrin in soil residue for STD and DBL

ranged 0.14-0.05 and 0.27-0.11 ppm, respectively.

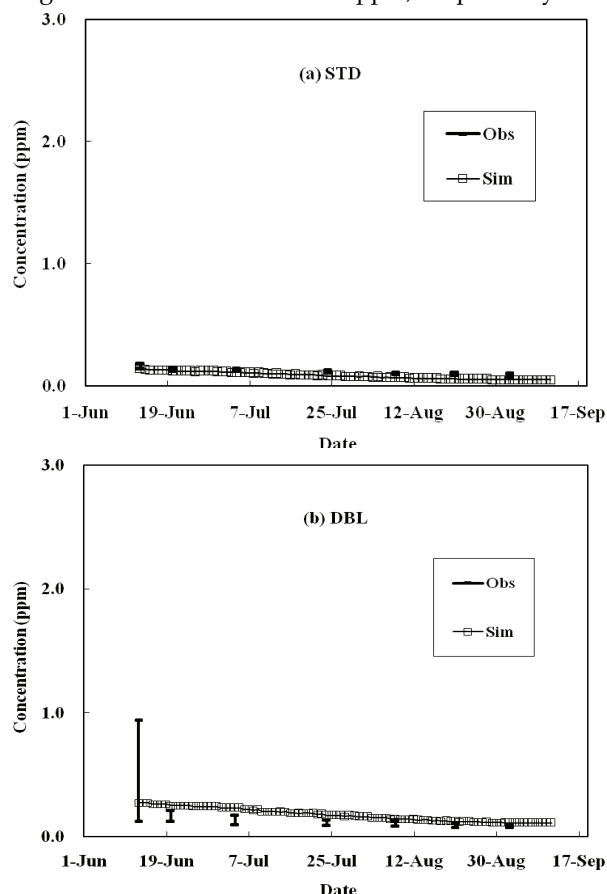
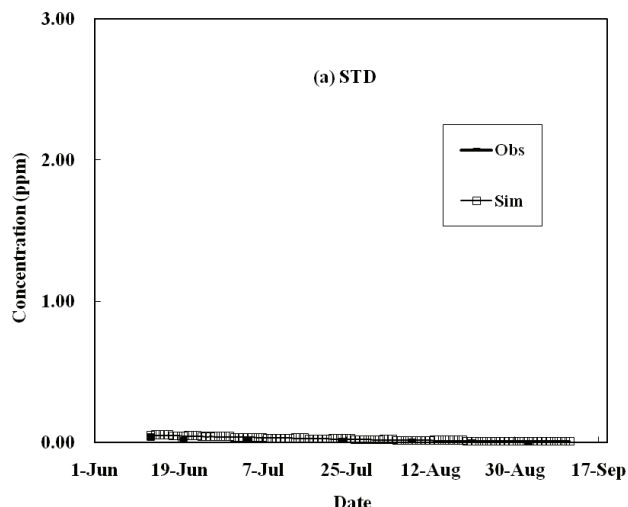


Fig 5. Observed and simulated pesticide residue in soil for Cypermethrin after calibration

Fig. 6 shows the observed and simulated pesticide residue in soil for Fenvalerate. The Fenvalerate concentration in soil residue for STD and DBL ranged 0.05-0 and 0.09-0 ppm, respectively. The simulated concentrations of Fenvalerate in soil for STD and DBL ranged 0.052-0.009 and 0.1-0.019 ppm, respectively.



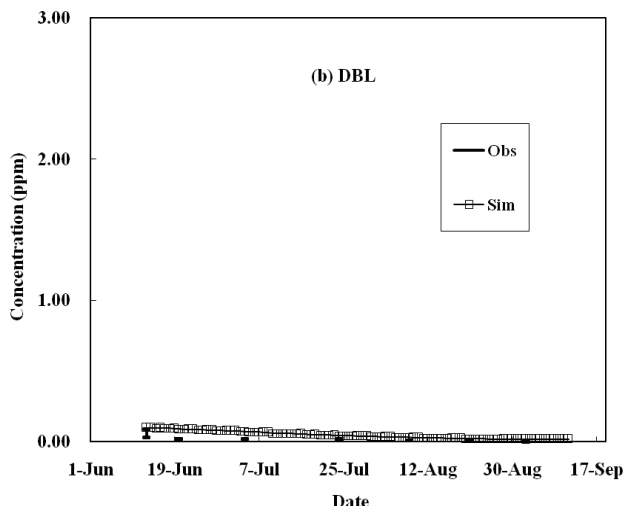


Fig 6. Observed and simulated pesticide residue in soil for Fenvalerate after calibration

The observed concentrations of Cypermethrin and Fenvalerate did not much affected by the application rate compared to others. Fenvalerate was not detected after spraying and assumed to be lost via volatilization (Khang *et al.*, 1986; Woodrow *et al.*, 2001). Also, Fenvalerate was well adsorbed in soil particle and mobility of Fenvalerate was small. Since, Fenvalerate residue in soil primarily existed on surface layer and compare to the other pesticides Fenvalerate was rapidly decomposed by microorganism and sunlight (Greenberg, 1981).

Endosulfan showed the highest concentration while Fenvalerate showed the lowest concentration in STD treatment. Similar trend was also observed for double rate application plots. The Endosulfan concentrations in soil surface layer rapidly decreased. The Endosulfan would be volatilized or resulted in decreased concentration in soil at surface layer (Woodrow *et al.*, 2001).

Validation of the GLEAMS model

Validation of GLEAMS model was conducted with observed data of 2009. Fig. 7 shows the observed and simulated pesticide residue in soil for Alachlor. The Alachlor concentration in soil residue for STD and DBL ranged 0.91-0 and 1.388-0 ppm, respectively. The simulated concentrations of Alachlor in soil residue for STD and DBL ranged 1.87-0 and 1.88-0.0002 ppm, respectively.

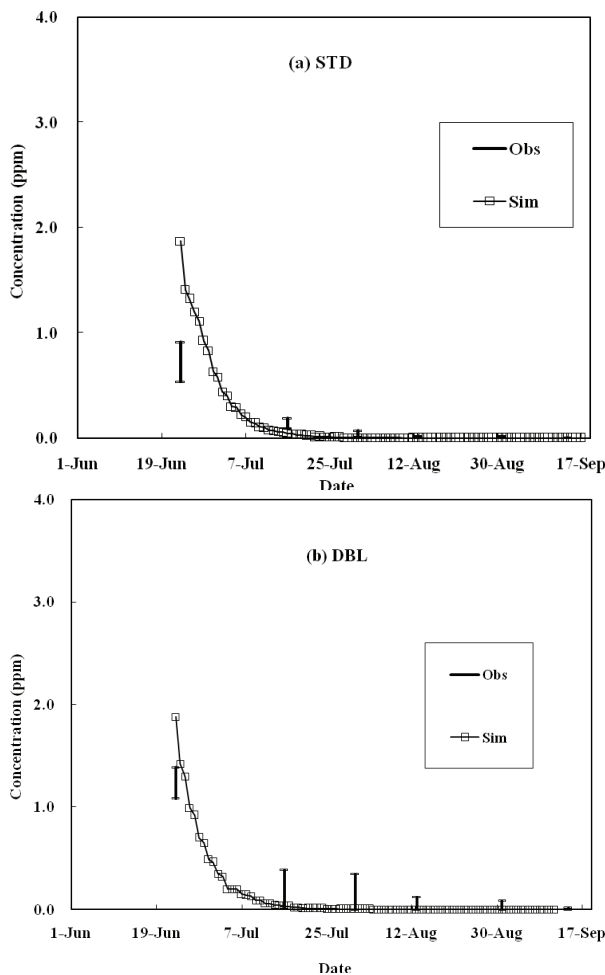
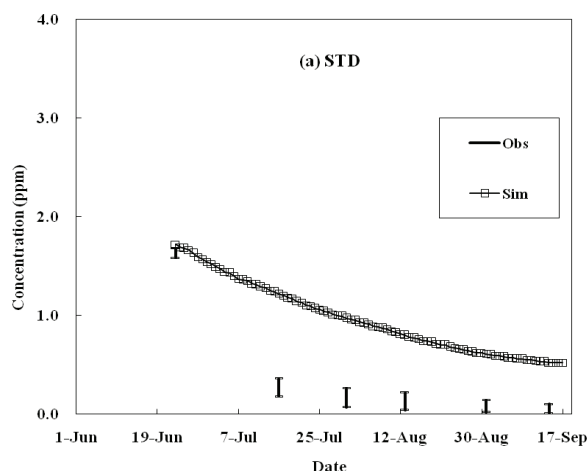


Fig 7. Observed and simulated pesticide residue in soil for Alachlor during validation period

Fig. 8 shows the observed and simulated pesticide residue in soil for Endosulfan. The Endosulfan concentration in soil residue for STD and DBL ranged 1.68-0.01 and 2.98-0.029 ppm, respectively. The simulated concentrations of Endosulfan in soil residue for STD and DBL ranged 1.72-0.52 and 3.45-1.08 ppm, respectively.



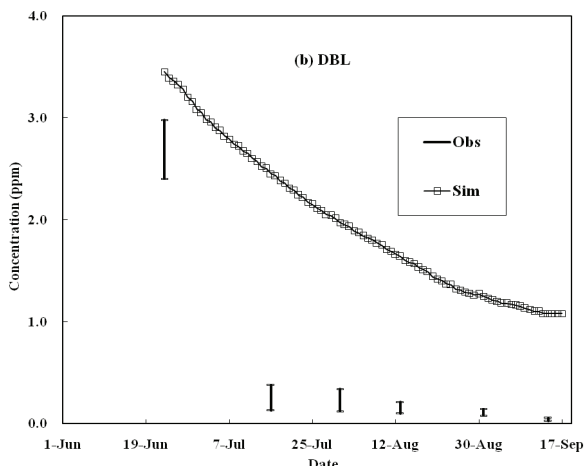


Fig 8. Observed and simulated pesticide residue in soil for Endosulfan during validation period

Fig. 9 shows the observed and simulated pesticide residue in soil for Cypermethrin. The Cypermethrin concentration in soil residue for STD and DBL ranged 0.257-0.09 and 0.32-0.13 ppm, respectively. The simulated concentrations of Cypermethrin in soil residue for STD and DBL ranged 0.68-0.29 and 1.12-0.49 ppm, respectively.

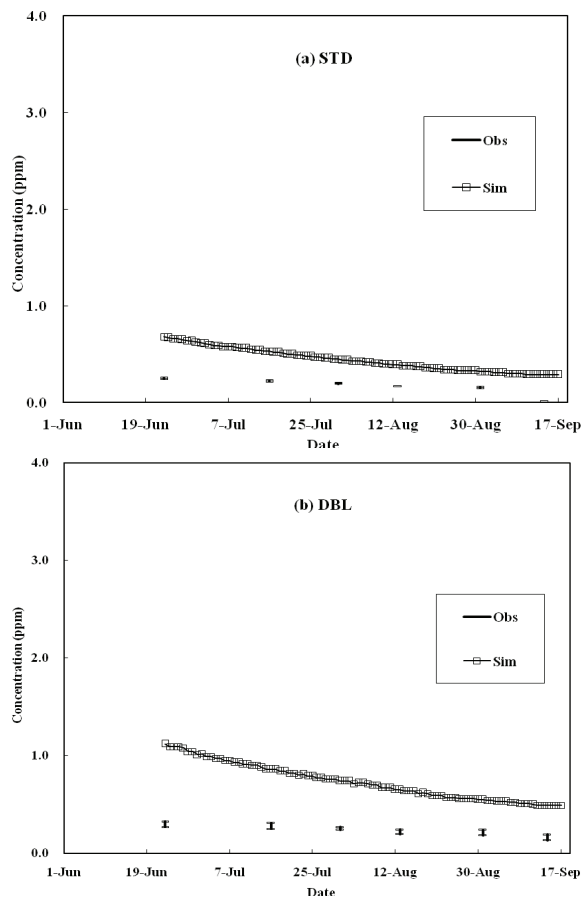


Fig 9. Observed and simulated pesticide residue in soil for Cypermethrin during validation period

Fig. 10 shows the observed and simulated pesticide residue in soil for Fenvalerate. The Fenvalerate concentration in soil residue for STD and DBL ranged 0.098-0 and 0.594-0.037 ppm, respectively. The simulated concentrations of Fenvalerate in soil residue for STD and DBL ranged 0.18-0.036 and 0.49 0-0.098 ppm, respectively.

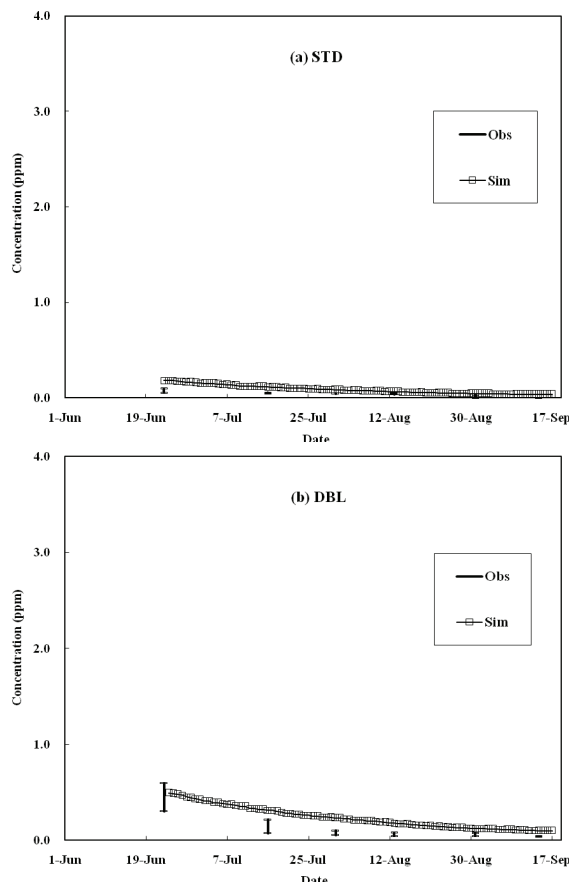


Fig 10. Observed and simulated pesticide residue in soil for Fenvalerate during validation period

Overall, the observed and simulated results were showed similar trend in 2008 and 2009. GLEAMS fairly simulated effect of the application rate on Alachlor and Endosulfan residues in soil. On the other hand, Cypermethrin and Fenvalerate were emulsion, and application rates of these pesticides were lower than those of Alachlor and Endosulfan. So, Cypermethrin and Fenvalerate residues were not much affected by application rate and GLEAMS reflected the observed trend.

Statistical evaluation for validation period

Table 6. provides the statistical evaluation results by SPSS (ver. 12.0) for validation period (2009). In standard application rate conditions, the statistics of R² and

p-value were 0.76 and <0.001 for Alachlor, 0.72 and <0.001 for Cypermethrin, 0.37 and <0.05 for Endosulfan and 0.56 and <0.001 for Fenvalerate, respectively. In double application rate conditions, the statistics of R^2

and p-value were 0.78 and <0.001 for Alachlor, 0.88 and <0.001 for Cypermethrin, 0.57 and <0.001 for Endosulfan and 0.76 and <0.001 for Fenvalerate, respectively.

Table 6. Evaluation of observed and simulated pesticide residue in soil for validation period (2009)

	Alachlor		Cypermethrin		Endosulfan		Fenvalerate	
	STD	DBL	STD	DBL	STD	DBL	STD	DBL
R^2	0.76	0.78	0.72	0.88	0.37	0.57	0.56	0.76
p-value ($\alpha=0.05$)	<0.001	<0.001	<0.001	<0.001	<0.05	<0.001	<0.001	<0.001

Statistical calculations demonstrated pesticide residue in soil by GLEAMS had higher R^2 and p-values closer to 1 except Endosulfan. Therefore, statistically, simulated results for pesticide residue of Alachlor, Cypermethrin and Fenvalerate in soil were better than those of Endosulfan.

CONCLUSION

The GLEAMS model was calibrated and validated for soil pesticide residue. The calibration was performed using experimental data from conventional pesticide application rate. The major calibrated parameters in GLEAMS pesticide submodel were K_{oc} and WSHFRC. The K_{oc} (organic carbon distribution coefficient) parameter affected most the pesticide residue in soil except Fenvalerate. The concentrations of Alachlor were highly sensitive to K_{oc} value, while the concentrations of Fenvalerate did not affected by K_{oc} value. The WSHFRC (Washoff fraction) parameter represents fraction of pesticide on the foliage available for washoff by rainfall influenced strongly to Fenvalerate concentration in soil residue. Validation results revealed that GLEAMS simulated soil residue fairly for Alachlor, Cypermethrin and Fenvalerate except Endosulfan. However, GLEAMS successfully simulated the effect of application rate on soil residue for four pesticides studied. The results suggested that GLEAMS model would be a useful tool for the prediction of pesticide residue concentration in soil.

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