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Rainfall Runoff Characteristics and Risk Assessment of Agro-chemicals Used in Golf Links

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Abstract

A rainfall runoff model described in this paper which is based on Basin- wide Ecological Model(BAWEM) calculates the fate of agro-chemicals in a watershed located of golf links. The rainfall runoff coefficients of agro-chemicals,which are the dominant parameters to predict the movement of agro-chemicals from soil and turfgrass to downstream water, are estimated.

Also, the model is used to estimate the level of health risks the residents around golf links are exposed to. The fidelity of rainfall runoff model of agro-chemicals was validated by the observed data obtained during rainy period. The calculated results from this model were found to be in the same order of that of the observed. The rainfall runoff coefficients of four agro-chemicals used in golf links were 5.4×10^{-3}, 1.9×10^{-3}, 3.0×10^{-4} and 4.4×10^{-3} for flutolanil, isoprothiolane, chlorpyrifos and simazine, respectively. The health risk level to the residents around golf links is evaluated to be rather low: the ratio of estimated dose through drinking water to the 10% of ADI(Acceptable Daily Intake) value or VSD for 10^{-6} life time risk varied in the range of 0.005~0.04 and 0.003~0.11, respectively, for both the annual mean and maximum monthly mean cases.

Keywords : Rainfall runoff; fate; health risk; agro-chemicals; golf links

1. Introduction

Few past practices of health risk assessment of agro-chemicals in golf links have sufficient validation process. There are rare cases(for example, Morioka and Tokai, 1989) of research with emphasis on the rainfall runoff characteristics of agro-chemicals used in golf links and subsequent quantitative risk assessment concept. Residents taking drinking water in downstream are exposed to health risk in any day. The level of health risk during the rainy season becomes higher than in dry weather.

In this paper, the authors identify runoff characteristics of some agro-chemicals in rainfall event by means of systematic monitoring. The characteristics of rainfall runoff of agro-chemicals coming from golf links into downstream is generally judged by using the following processes of chemicals fate: 1) transfer processes such as soil-to-air volatilization or adsorption on particles and turfgrass, 2) transportation processes such as land surface wash-off and other hydrological processes and 3) transformation process of biochemical degradation.

A simple first-order reaction model is introduced. Runoff model once introduced is verified by practice of simulation using continuosly observed data obtained during a storm period in spring and summer. The model is used to calculate the fate of agro-chemicals used in golf links in water of the retention pond close to golf links and in water of river downstrem through the year.

The health risks on residents around golf links are quantified by relating ADI(10% of ADI) and VSD(Virtually Safe Dose) to the dose from drinking water for chronic and carcinogenic effects, respectively.

2. Description of Rainfall Runoff Model

Any rainfall runoff model aims to predict the concentration of agro- chemicals in water of small pond close to golf links and water in river downstream. The runoff model for these agro-chemicals is structured based on a number of simplified assumptions as follows:

1) Soil compartment with constant ratio of air and water, uniform bulk density and constant organic carbon fraction,

2) soil compartment with linear and equilibrium adsorption isotherm,

3) soil compartment with linear and equilibrium liquid-vapor partition(Henry's Law),

4) soil depth(2cm) with uniform concentration of agro-chemicals,

5) soil compartment with equilibrium distribution of agro-chemicals among air, water and solid phase in soil,

6) Leaching into lower soil layer is regarded as negligible,

7) Rainfall runoff loss of agro-chemicals is regarded as losses from interstitial water,

8) Pond water is completely mixed.

2.1 Mass Balance

In a homogeneous porous medium, the mass balance equation for agro- chemicals in the soil is formulated as

$$Rs-(Rsw+Rsa+Rss)=0 \tag{1}$$

where R denotes the mass(g) of agro-chemicals in soil and the subscripts, sw, sa, and ss stand for soil compartment, water, air and solid phase in soil compartment, respectively.

The mass balance equation for each agro-chemical with first order decay and runoff loss in rainfall period may be written as

$$\frac{dRs}{dt+f\cdot i\cdot Rs}w+K\cdot Rs=0 \tag{2}$$

where f is rainfall runoff coefficient of an indicative chemical(1/mm), i is rainfall intensity(mm/hr) and K is the other overall loss rate composed of soil-water-air transfer and degradation in soil.

2.2 Concentration

The concentration of the agro-chemical in water of the pond close to golf links is predicted using Basin-wide Ecological Model(BAWEM) as

$$Vw\cdot\frac{dCw}{dt} = f\cdot i\cdot Rsw-\frac{vst}{Hw}\cdot Rssd- Cw\cdot Q-kdw\cdot Rw-kwa\cdot Rw \tag{3}$$

where the capital letters, C, V, H and Q are the concentration(g/m³) of agro-chemicals, volume(m³), depth(m) of water and effluent flowrate(m³/sec) from the pond, respectively. Furthermore, the subscripts w and ssd denote water and suspended solid in the pond and air, accordingly. Moreover, symbol kdw, kwa and vst denote the degradation rate constant in

Table 1 Physico-chemical properties of selected agro-chemicals *

ISO	Flutolanil	Isoprothiolane	Chlorpyrifos	Simazine
CAS No.	66332-96-5	50512-35-1	2921-88-2	122-34-9
Mole. formula	$C_{17}H_{16}NO_2F_3$	$C_{12}H_{18}O_4S_2$	$C_9H_{11}C_{13}NO_3PS$	$C_7H_{12}N_6Cl$
MW(g)	323.3	290.4	350.57	201.7
Henry' const.	2.494×10^{-5}	4.67×10^{-5}	1.8×10^{-4}	1.36×10^{-6}
Solubility(ppm)	9.6	48	2.0	5.0
Vapor pre.(atm)	1.78×10^{-8}	1.86×10^{-7}	2.47×10^{-8}	8.09×10^{-10}
logPow	3.7	2.81	3.92	3.6
Koc	1259	525	2144	1801
Kds(/d)	2.8×10^{-3}	2.06×10^{-3}	6.81×10^{-6}	4.62×10^{-3}
kdw(/d)	3.0×10^{-3}	1.30×10^{-2}	3.42×10^{-7}	3.92×10^{-3}
kwa(/d)	0.21	0.42	1.44	9.32×10^{-5}
ksa(/d)	5.6×10^{-3}	2.66×10^{-2}	9.53×10^{-3}	5.53×10^{-7}

* Estimated through the analysis of some reported results.

water, water-to-air interphase transfer rate constant and settling velocity of suspended solid(SS).

3. Rainfall Runoff Simulation

Judging from the results of some researches(Morioka and Tokai, 1989; Tsuji *et al.*, 1991) showing a high level of concentration during rainly season, a considerable amount of the applied agro-chemicals are assumed to be directly transported by surface runoff during the rainy period.

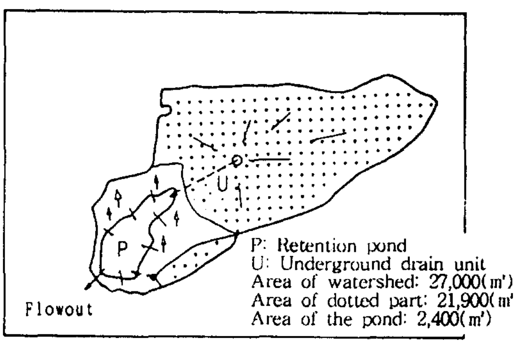

Fig. 1. Map of the small watershed in golf links for rainfall runoff survey.

Among the many agro-chemicals used in golf links, flutolanil and isoprothiolane(fungicides), chlorpyrifos(pesticides) and simazine(herbicides) were selected as indicative materials because of their wide application and frequent detection in river water. Tabel 1 show the physico-chemical properties of those indicative agro-chemicals.

3.1 Rainfall Runoff Coefficient of Agro-chemicals

An intended field survey was performed in small watershed of a golf links(as in Fig. 1) at two rainfall events, besides in dry weather once per month. The dotted area is concerned for the determination of rainfall runoff coefficients. Runoff water with agro-chemicals is drained through drain unit located in downstream of the retention pond. The first runoff event after the application of agro-chemicals in spring or summer was observed on each drain unit with the intervals of 15 minutes~2 hours.

Rainfall runoff coefficient is defined in the manner of the instantaneous or the cummulative. One is derived from regression analysis of cummulative rainfall intensity with respect to the overall runoff rate(F_1) of agro-chemicals at rainy period, and the other is from same process of the hourly rainfall intensity with responding runoff rate(F_2) of agro-chemicals at rainly period as;

$$F_1 = \Sigma \frac{R_l}{R_0} = f_1 \cdot \Sigma i \quad (4)$$

$$F_2 = \frac{R_l}{R_{sw}} = f_2 \cdot i \quad (5)$$

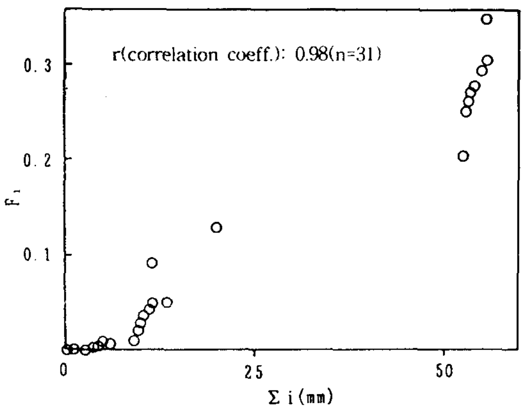

Fig. 2. The correlation between cummulative rainfall intensity(Σi) with the overall runoff rate(F_1) for flutolanil at two rainy events.

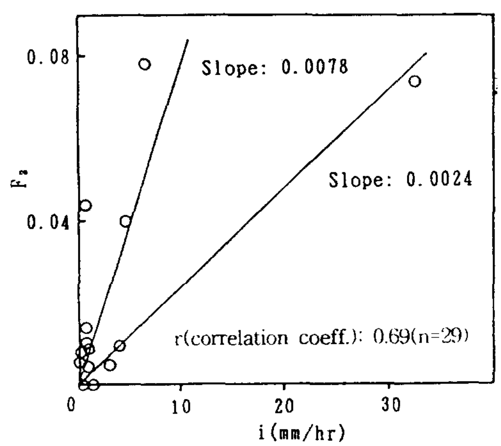

Fig. 3. The correlation between hourly rainfall intensity(i) with responding runoff rate(F_2) for flutolanil at two rainfall events.

where R_l is rainfall runoff(g) of agro-chemicals from soil (R_l=$f \cdot i \cdot Rsw$), R_0 is remaining mass(g) of agro-chemicals in the interstitial water in soil before rain, and f_1 and f_2 are rainfall runoff coefficients determined from regression line of a example for flutolanil as shown in Fig. 2 and Fig. 3.

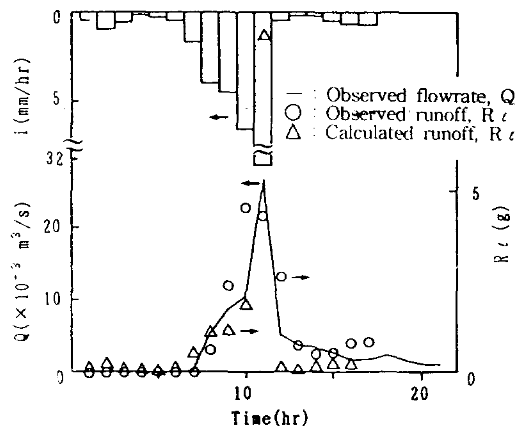

Fig. 4. The observed and caluculated rainfall runoff(R_l) of flutolanil in the small watershed in a golf links at rainy period in July 1989.

The rainfall runoff coefficient(f_1) of each chemicals were 5.4×10^{-3}, 1.9×10^{-3}, 3.0×10^{-4} and 4.4×10^{-3}, respectively, and they were in the range of the values of f_2, those are 2.4×10^{-3} ~ 7.8×10^{-3}, 0.8×10^{-3} ~ 2.5×10^{-3}, 1.4×10^{-4} ~ 4.4×10^{-4} and 1.4×10^{-3} ~ 7.2×10^{-3} for flutolanil, isoprothiolane, chlorpyrifos and simazine, accordingly. The concentrations of agro-chemicals in runoff water are calculated with suffcient fidelity by using above mentioned value. Fig. 4 shows the predictability of these estimated coefficients when compared to observed data. Then suitable value of f_1 is determined for calculation throughout the year.

Table 2. Observed and calculated concentrations of agro-chemicals in the pond water before and after rain.

(unit : ppb)

		Flutolanil		Isoprothiolane		Chlorpyrifos		Simazine	
		Obser.*	Simul.	Obser.*	Simul.	Obser.*	Simul.	Obser.*	Simul.
'89 Mar.	Before	<0.5	0.5	<0.5	0.5	<0.5	0.5	5.3	5.3
	After	0.6~23	13.3	<0.5~17	8.2	<0.5	0.5	3.6~41	7.6
'89 July	Before	3.2~58(37)	37	2.3~38(26)	26	<0.5~0.7	0.5	0.7~28(5)	5.0
	After	19~81(77)	38.4	14~39(38)	26.0	<0.6~3(2.5)	1.5	3.2~29(26)	13.8

*The upper, the middle, and the lower layers at 3 or 4 points in the pond.
( ): for the middle layer at the center point.

3.2 Rainfall Runoff Simulation of Agro-chemicals

Rainfall runoff of agro-chemicals are drained into the retention pond, mixed and then flowed out to downstream. The concentration of agro-chemicals in the pond water is a function of mass flux from upper watershed, amount of chemicals settled onto sediment, outflow mass flux into the downstream, and other parameters(Equation (3)). Table 2 shows the results of observed and calculated concentrations of agro-chemicals in the pond water before or after rainfall events. The calculated concentrations of agro-chemicals show a good agreement with the observed data in the range of same order at both events.

The authors evaluated the predictability of rainfall runoff model of agro-chemicals using monthly observed data for one year starting from October 1988 to September 1989 in same watershed. Fig. 5 shows the observed and calculated concentration of selected agro-chemicals in the pond water throughout the year. High concentration was observed for two chemicals namely, flutolanil and isoprothiolane, which have higher water solubility than others, from spring to summer season.

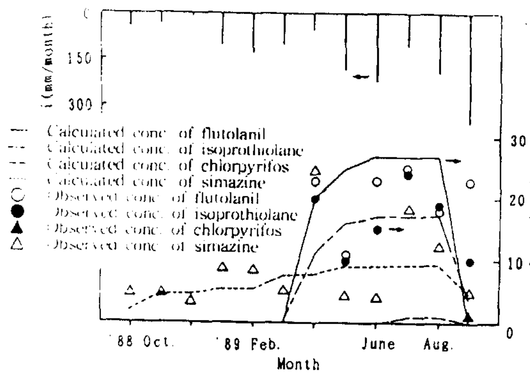

Fig. 5. The observed and calculated concentrations of indicative agro-chemicals in the pond water.

3.3 Fate of Agro-chemicals and Exposure

It is a significant step in risk assesment processes to identify faithfully the fate, exposure route and exposure level of agro-chemicals. Longer the persistence of agro-chemicals in the environment implies higher degree of possible human exposure to them. Assumptions and scenarios to estimate exposure route and exposure level are provided as follows:

1) Residents around golf links are to take drinking water contaminated from agro-chemicals used in glof links,

2) The amount of elimination of agro-chemicals in water by the purification processes of water supply is regarded as negligible,

Table 3. Calculated and Observed Concentrations of Agro-chemicals in River Water (unit : ppb)

	Station 1			Station 2			Station 3		
	Annual range	Annual mean	Month. max.	Annual range	Annual mean	Month. max.	Annual range	Annual mean	Month. max.
Fluto-	0.24~0.29	0.26	0.29	1.39~1.70	1.55	1.70	0.97~1.22	1.09	1.22
lanil	<0.5	<0.5	<0.5	<0.5~0.8	<0.5	0.8	<0.5~1.1	<0.5	1.1
Isopro-	0.16~0.20	0.17	0.20	0.88~1.11	0.99	1.11	0.72~0.94	0.82	0.94
thiolane	<0.5	<0.5	<0.5	<0.5~1.4	<0.5	1.4	<0.5~1.1	<0.5	1.1
Chlor-	0.03~0.04	0.03	0.04	0.02~0.03	0.03	0.03	0.03~0.05	0.04	0.05
pyrifos	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sima-	0.83~1.20	0.99	1.20	0.42~0.72	0.56	0.72	0.31~0.61	0.49	0.61
zine	<0.5~1.4	<0.5	1.4	<0.5~0.7	<0.5	0.7	<0.5~0.6	<0.5	0.6

* Lower part shows the observed results.

3) All golf links have own retention pond, and all agro-chemicals used in golf links are drained into the retention ponds,

4) Two scenarios are applied to predict the concentration of agro-chemicals in river water namely; annual mean case and maximum case of monthly mean concentrations(the worst case).

The authors evaluate the fate of agro-chemicals by using rainfall runoff model of chemicals in river water in a watershed having some golf links. Station 1 and 2 in Fig. 6 are two water intake points for supplying drinking water

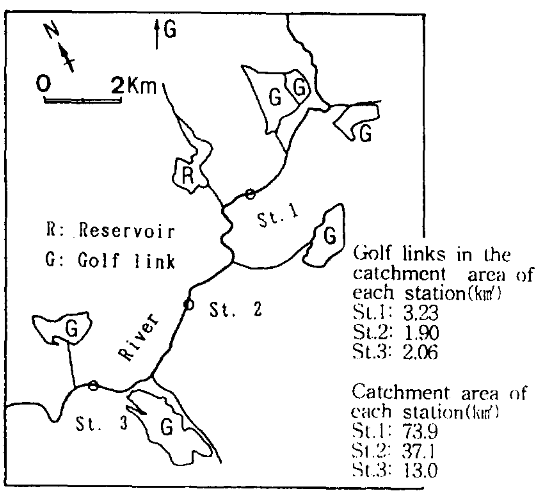

Fig. 6. Map of the studied watershed having some golf links for the concentration of agro-chemicals in the river water.

The application amount of indicative chemicals mostly influencing the results was estimated from actual monthly reported data coming from regulatory office. The results of simulated and observed concentrations of agro-chemicals in river water are shown in Table 3.

Calculated concentrations of each chemicals in all cases are in the range of same order of observed level. The annual maximum levels of monthly mean concentrations of each chemical for both observed or calculated are slightly higher than their annual mean levels.

4. Health Risk Assessment

Toxicological effects are categorized grouped into lethal/chronic and reversible/irreversible effects. Carcinogenicity indicates one important type of irreversible effects to be evaluated in terms of TD_{50} and VSD(Virtually Safe Dose), The reversible effects are evaluated in terms of NOAEL(Non Observed Adverse Effect Level), LD_{50} and ADI(Acceptable Daily Intake).

Exposure to residents around glof links are quantified and evaluated by relating the dose via the drinking water to ADI for chronic

Table 4 Toxicological parameters of each chemicals.

	Flutolanil	Chlorpyrifos	Simazine
NOAEL(mg/kg/d)	8.7	0.03	7
ADI(mg/kg/d) *1	0.087	0.0003	0.07
10% of ADI(mg/kg/d)	0.0087	0.00003	0.007
LC_{50}(mg/ℓ)	Not Available	0.003 *2	6.6 *2
Mutagenicity	Not Available	Not Available	Not Available
TD_{50}(mg/kg/d)	Not Available	203 *3	260 *3
VSD for 10^{-6} risk(mg/kg/d)	Not Available	2.93×10^{-4}	3.75×10^{-4}

*1 : NOAEL, reported by small number of researchers, is devided by uncertainty factor 100.
*2 : Verschuern, 1983. * 3 : Gold *et. al.*, 1984.

effects and by comparing the dose with VSD for carcinogenic effects based on TD_{50}. The acceptable dose through drinking water is specified to be 10% of acceptable daily intake. In the process of dose-response analysis with the non-threshold concept, formular explaining the results of animal tests is extrapolated into the level for low dose to human. One-hit model is used to quantify the carcinogenic probability of dose-response relationship, as follows:

$$P(D) = 1 - \exp(-\lambda \cdot D) \qquad (6)$$

where $P(D)$ is the probability of human cancer developing from dose D of each chemical, and λ is the constant which would be determined from known carcinogenicity data such as TD_{50}. The probable dose through polluted drinking water is estimated by multiplying the concentration of agro- chemicals in the drinking water with its volume to be consumed(2ℓ/d). Toxicological indices of eachchemical are shown in Table 4.

The estimated probable doses of these chemicals are compared with the values of 10% of ADI and VSD for 10^{-6} risk. Table 5 shows the results of risk estimation for the two probable scenarios: the risks caused by drinking polluted water of annual mean and maximum of monthly mean concentrations originated from agro-chemicals used in golf links. The ratios of estimated dose to the 10% of ADI value varied in the range of 0.005~0.04 for both cases of the annual mean and maximum level of monthly mean concentrations. The risk levels and the ratios of dose to the VSD were in the range of 0.003~0.11 through the year.

Table 5 Estimated risk levels of three agro-chemicals.

		Flutolanil	Chlorpyrifos	Simazine
Annual mean conc. (ppb)	a)	1.55	0.03	0.99
Monthly max. conc. (ppb)	b)	1.70	0.04	1.20
Ratio to 10% of ADI	a)	0.006	0.03	0.005
	b)	0.007	0.04	0.006
Ratio to VSD for 10^{-6}	a)	-	0.003	0.09
life time cancer	b)	-	0.005	0.11

5. CONCLUSIONS

Rainfall runoff model based on Basin-wide Ecological Model(BAWEM) was developed to predict fate of agro-chemicals in rainfall runoff used in golf links, and used in order to evaluate the risk to residents lived around there.

The dominant parameter to calculate the rainfall runoff of agro-chemicals was the rainfall runoff coefficient of each chemical, that was found to be in wide range relevant to water solubility. The authors estimated the rainfall runoff coefficients of agro-chemicals, and then verified their respective value with the observed data at two rainfall events. The coefficients were 5.4×10^{-3}, 1.9×10^{-3}, 3.0×10^{-4}, and 4.4×10^{-3} for flutolanil, isoprothiolane, chlorpyrifos and simazine for unit precipitation, respectively.

Furthermore, the authors recognized that the concentrations of agro- chemicals in water of the retention pond close to glof links and in river water near the drinking water supply at rainy period were higher than at dry weather through the year. In the sense of annual mean, the concentrations of agro-chemicals in the river water were in the range of 0.26~1.6, 0.17~0.99, 0.03~0.04 and 0.49~0.99 for flutolanil, isoprothiolane, chlorpyrifos and simazine, respectively.

The risk level of residents exposed to these agro-chemicals were estimated by using the ratio of probable dose to 10% of ADI for chronic effects and VSD for carcinogenic effects. Estimated risks in terms of the ratios of dose to 10% of ADI ranged in the value of 0.005~0.04 for both cases of annual mean and maximum. On the other hand, the values of the ratios of dose to VSD for 10^{-6} for life time risk were around 0.11 for the maximum level of monthly mean concentrations in river water.

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골프장에 산포되는 농약의 강우유출특성과 risk assessment

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본 연구에서는, 골프장에서 사용되는 농약의 강우유출특성과 인체의 건강에 대한 risk assessment를 행하였다.

골프장에 살포되는 농약의 강우시의 강우유출특성을 모델화하여, 지표농약의 강우유출특성을 구하였다. 이 유출계수를 이용하여 하류 하천에서의 농약의 농도를 예측하여, 인체의 건강에 대한 risk를 평가하였다.

농약의 강우유출특성을 파악하기 위하여 농약이 유입되는 조정연못의 유역을 선정하여 강우시의 농약의 강우유출특성을 조사하였다. 지표농약으로 선정한 농약의 유출계수(1/mm)는, Flutolanil가 0.0054, Isoprothiolane이 0.0019, Chlorpyrifos가 0.0003, Simazine이 0.0044 였다. 이 유출계수를 지역수계의 특성을 고려하여 설정한 지역수계모델에 대입하여 조정연못에서의 농약의 년간 농도변화를 예측하여 관측치와 비교하여 모델의 재현능력을 확인하였다.

또, 이 지역수계모델을 이용하여 하류 하천에서의 농약의 농도를 예측하여 농약에 오염된 하천수를 이용하는 하류주민에 대한 건강 risk의 평가를 행하였다. 폭로경로로서는 음료수로서의 섭취만을 고려하였으며, risk의 평가지표로서는 10% ADI(Acceptable Daily Intake) 와 VSD(Virtually Safe Dose)를 이용하였다. 인체의 건강에 대한 risk는 발암 risk로서 Simazine의 경우 10^{-7}~10^{-9}로 비교적 낮은 risk수준인 것으로 판단되었다.