Comparative Fugacity-based Multimedia Assessment of Acaricides: Methiocarb and Carbofuran

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Abstract. One of the main threats to the Sustainable Development Goals (SDGs) established by the United Nations is the widespread use of pesticides to meet the global food demand. Pesticide usage can be ensured more safely and effectively by having a better understanding of their environmental fate. Acaricides are a type of pesticides which aid in the management of ticks and mites that pose a risk to agriculture and animal health. Methiocarb and carbofuran, two carbamate acaricides, are evaluated in terms of their environmental fate using a fugacity-based multimedia approach, EQC Level III. The reactive characteristics and pertinent partitioning are evaluated as part of the assessment. Methiocarb and Carbofuran are projected to be present in minimal levels in the air and sediment (<1%), in case of equal emissions to soil, air, and water. Both the pesticides are predicted to be present predominantly in soil 76% with minor amounts in water 24%. Reaction has been found to be predominant method of removal from air, soil and water compartments for both Methiocarb and Carbofuran. Intermedia transport rates have been determined and both Methiocarb and Carbofuran show comparable air to soil and air to water transport rates. The total residence time of Carbofuran is predicted to be more than three times than that of Methiocarb in the standard EQC model environment.

Keywords: Fugacity, Methiocarb, Carbofuran.

1 Introduction

The potential for chemicals to contaminate multiple environmental compartments, including soil, water, and air, provides a compelling reason to carry out multimedia fate assessments of these substances to fully understand and mitigate their ecological and human health risks [1]. This becomes particularly important for toxic chemicals such as pesticides.

A greater understanding of the environmental fate of pesticides can help assure their use in a safer and more efficient manner [2]. Acaricides are a class of pesticide that are used to control ticks and mites which are harmful to livestock and crops [3]. Methiocarb (fig.1), (3,5-dimethyl-4-methylsulfanylphenyl) N-methylcarbamate and Carbofuran (fig.2), (2,2-dimethyl-3-oxo-1-benzofuran-7-yl) N-methylcarbamate are two carbamate acaricides that are widely used in agriculture. Methiocarb [4] also has

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application as a molluscicide and a bird repellent while carbofuran finds use as a nematicide as well. Methiocarb is poisonous to mammals on land. It is extremely hazardous to birds when consumed orally. Methiocarb is extremely harmful to aquatic invertebrates and extremely toxic to fish. Of all the insecticides that are often used on field crops, carbofuran has one of the highest acute toxicities to humans. For birds and other terrestrial vertebrates, Carbofuran is extremely poisonous [5].

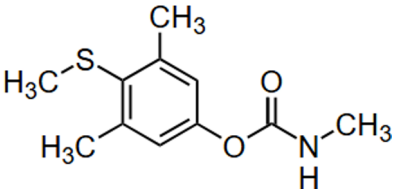

Fig. 1. Structure of Methiocarb

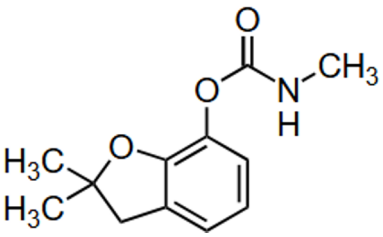

Fig 2. Structure of Carbofuran

Environmental fate models offer an understanding required for guiding a spill response and is simpler to utilize without requiring site-and spill-specific input data. Predominant exposure and fate pathways can be identified as well. Fugacity based environmental models pioneered by Mackay can numerically calculate the environmental fate of chemicals in an evaluative environment [6]. The environmental fate of two acaricides Methiocarb and Carbofuran have been calculated and analysed using EQC Level III environmental fate model [7].

2 Materials and Methods

A hypothetical environment of 100, 000 km2 has been considered consisting of land, water, air, and sediments, with 90% of the area covered by land and 10% water by Makay. The steady-state yet non-equilibrium conditions between environmental compartments are assumed by the Level III model. Details of mathematical formulations of Level III EQC model have been described in detail [6]. The input values required for the calculations have been taken from the University of Hertfordshire Pesticide Property database [8]. The output of the program has been critically analysed for the two acaricides. Additionally, for sensitivity analysis of the emission rates on the concentration of the chemicals in the different environmental compartments was carried out using Argo software as an Excel add-in [9]. One thousand iterations were carried out for each simulation and an uniform distribution of emission rate was assumed with 10% variation [10].

Table 1. Physiochemical Properties of Methiocarb and Carbofuran

S. No.	Property	Methiocarb	Carbofuran
1	Mol. Wt.	225.31	221.26
2	logK_{ow}	3.18	1.8
3	Solubility in water @20°C, gm/m^3	27	322
4	Vapour Pressure @20°C, Pascal	1.5E-5	8.0E-5
5.	Melting Point °C	118.5	153.1

Table 2. Half Life of Methiocarb and Carbofuran in deferent environmental compartments.

S. No	Phase	Methiocarb half-Life (h)	Carbofuran Half-Life (h)
1	Air	9.5	4.45
2	Water	38.4	146.4
3	Soil	70.56	307.2
4	Sediment	96	232.8

3 Result and Discussion

Understanding how physical-chemical factors affect the features environmental fate such partitioning, transport, conversion, and persistence is the main goal of this evaluative study. In these models, an emission rate of 1000 kg/h to the three environmental compartments air, water, and soil separately was considered, with no advection from nearby locations. Additionally, a scenario was also considered in which an equal emission rate (1000 kg/h) of both the chemical in all the three phases was studied [1]. These many situations were selected because it is widely acknowledged that chemical properties and discharge mode typically influence the characteristics of chemical fate in the environment.

Quantifiable vapor pressures, solubility in water, and octanol-water partition coefficients indicate that both the chemicals, Methiocarb and Carbofuran should partition to practically to all accessible environmental segments.

Both Methiocarb (K_{ow} of 103.18) and Carbofuran (K_{ow} of 101.8) are hydrophobic compounds. Mehthiocarb has low solubility in water (27 g/m3) while Carbofuran is fairly soluble in water (322 g/m^3). As both Methiocarb and Carbofuran have low vapour pressures (1.5x10-5 Pa, 8x10-5 Pa). Both the are expected partition to organic phases for instance soils and sediments with low partitioning in air phase. The calculated octanol-air partition coefficient for Methiocarb and Carbofuran is 2.94 x 10^{10} and 2.79 x10^9 respectively. The high value of K_{OA} [11] indicates that both Methiocarb and Carbofuran would preferentially partition to soil phase.

3.1 Half Life

Both the pesticides are degraded in less than one day in air. While Methiocarb degrades in a matter of few days in soil, water and sediment, carbofuran takes relatively longer, nearly a week in water and sediment and nearly two weeks in soil. The breakdown rate of Methiocarb in water is fast (1.6 days) so that its potential for long range transport through water is low. However, long-range transport potential in air is insignificant (half-life 0.32 days). Similarly, for carbofuran long range transport potential by air is tiny (half-life, 0.19 days) on the other hand through water carbofuran has a potential risk of long-range transport (half-life 6.10 days).

3.2 Mass Distribution and Removal Processes

Four Level III simulations' detailed results are provided in fig 3-6, for Methiocarb and fig. 7-10 for Carbofuran into the air, water, soil and equally into all three compartments. The key data on chemical fate and transport is provided by these mass balance diagrams.

Environmental Fate of Methiocarb. In the emission to air scenario (Figure 3) Methiocarb is very rapidly (836 kg/h) transferred to soil and to a less extent to water (92.9 kg/h). This results to 93.6 % and 5.45 % of the total Methiocarb to be predicted in the soil and water, respectively, while negligible quantities are predicted in the air compartment. Transfer to bottom sediments is negligible. Reaction from soil 835 kg/h, water (89.3 kg/h), and air compartments (62.3 kg/h) are the most important methods of removing Methiocarb from the environment.

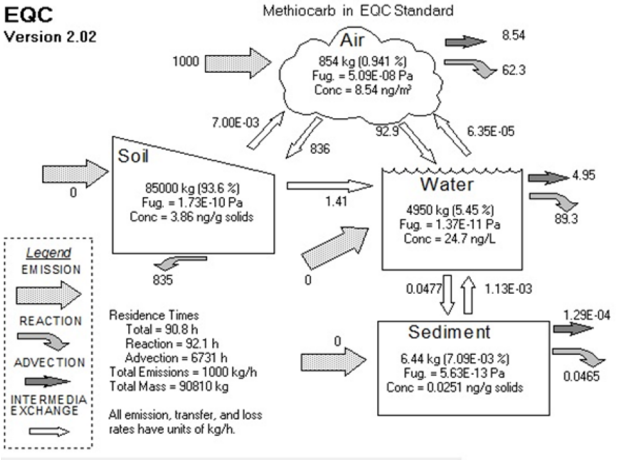

Fig. 3. Predicted Environmental Fate with Emission of 1000kg/h of Methiocarb in air compartment.

In the emission to water situation (Figure 4), 99.9% of the Methiocarb remains in water. Reaction (947 kg/h) and advection in water (52.5 kg/h) and are the two main removal processes for Methiocarb. Negligible amounts of the chemical (0.506 kg/h) are passed on the sediment media. Intermedia transport for Methiocarb is negligible in this case.

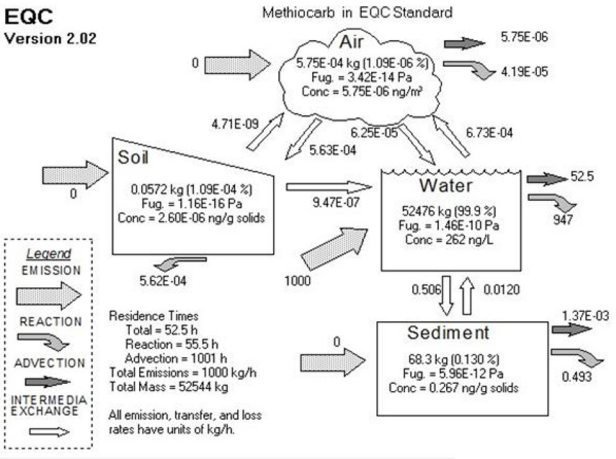

Fig. 4. Predicted Environmental Fate with Emission of 1000 kg/h of Methiocarb in water compartment.

In Figure 5, the scenario of emission to soil, 99.9% of the total Methiocarb entering the system is found in soil, with very small amounts found in the other compartments. 998 kg/h of soil reaction is the main removal processes for Methiocarb from the soil compartment. Intermedia transport results in a minor transfer of the chemical 1.68 kg/h to water from soil.

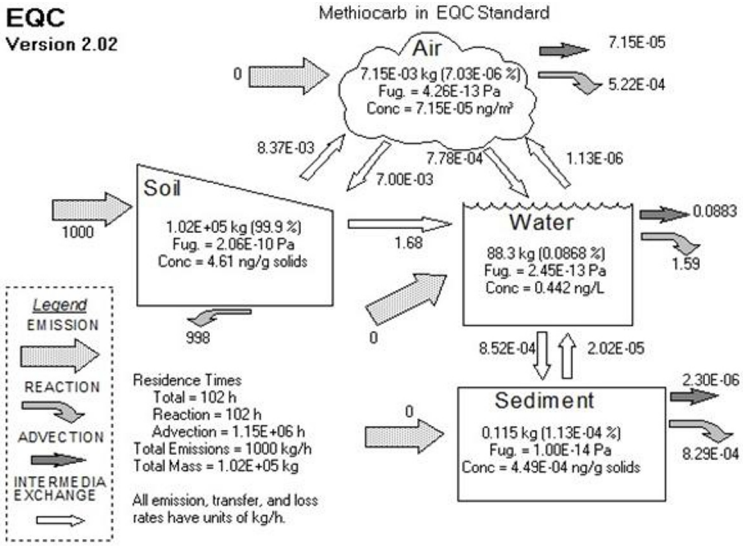

Fig. 5. Predicted Environmental Fate with Emission of 1000 kg/h of Methiocarb in soil compartment.

In Fig 6 equal emissions of 1000 kg/h to soil, air and water are simulated for Methiocarb. This results in 76.2 % of the chemical in soil and 23.5% in water. Reaction from soil and water are the two main removal process from the environment, followed by reaction from air. There is a clear transfer of 836 kg/h of the Methiocarb from air to soil and 92.9 kg/h from air to water (depleting the air compartment of Methiocarb) with minor transfer 0.555 kg/h to bottom sediments.

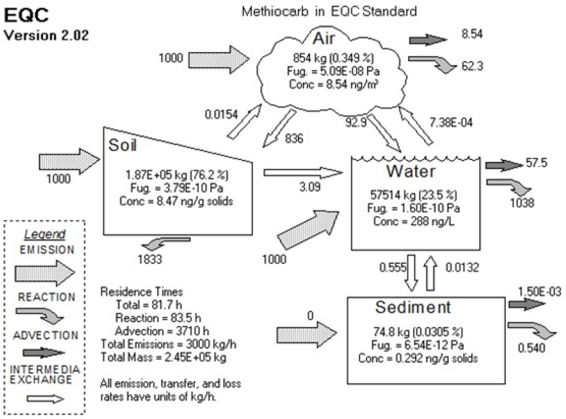

Fig. 6. Predicted Environmental Fate with Emission of 1000 kg/h of Methiocarb simultaneously in air, water and soil compartment.

Environmental Fate of Carbofuran. Four Level III simulations' detailed results are provided in fig 7-10, for Carbofuran into the air, water, soil and equally into all three compartments.

For carbofuran in the emission to air situation (fig.7), intermedia transference results in a net movement of 866 kg/h from air to soil, 96 kg/h from air to water resulting in 91.2% of the chemical remaining in soil and 8.8% in water. Reaction from soil (772 kg/h), water (156 kg/h) and air 36 kg/h are the main removal processes from the system. Advection from water removes 33 kg/h carbofuran from the EQC environment.

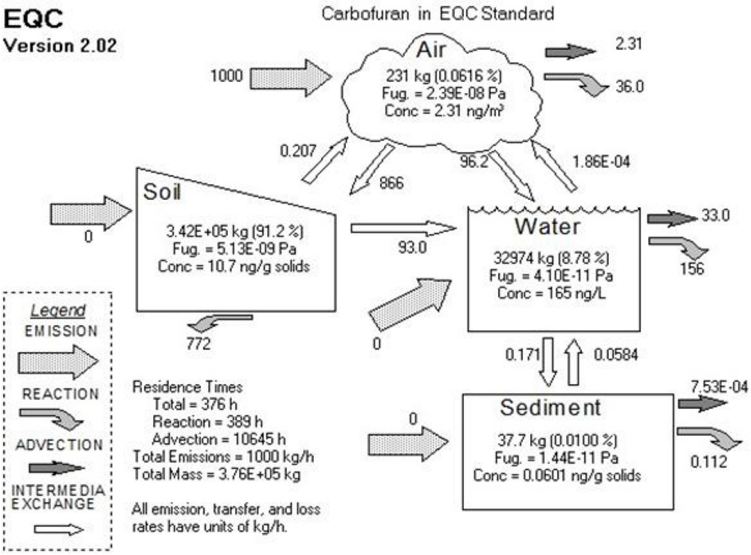

Fig. 7. Predicted Environmental Fate with Emission of 1000 kg/h of Carbofuran in air compartment.

In the emission to water scenario, (Fig. 8) 99.9% of the carbofuran is in water. Reaction (825 kg/h) and advection in water (174 kg/h) and are the two main elimination processes for Carbofuran. Intermedia transport for Carbofuran is negligible in this case resulting in the high distribution of Carbofuran in the water compartment.

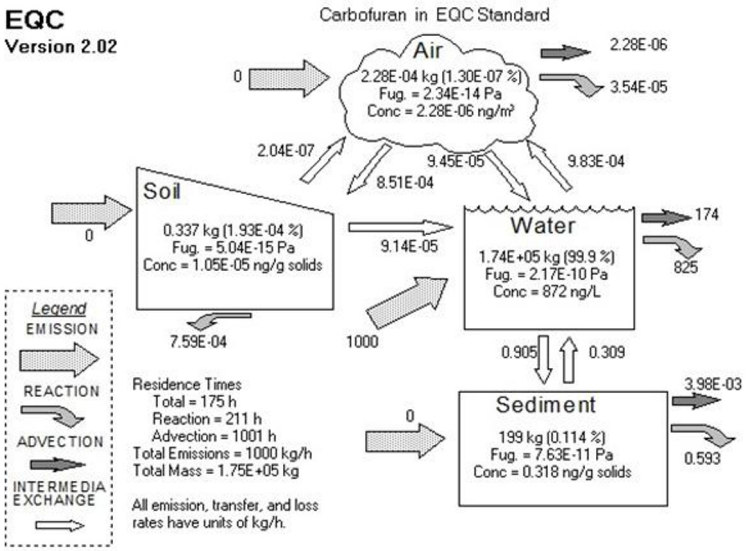

Fig. 8. Predicted Environmental Fate with Emission of 1000 kg/h of Carbofuran in water compartment.

In the scenario of emission to soil, (Fig. 9) 95.5% of the total Carbofuran entering the system is found in soil, with very small amounts found in the other compartments. 893 kg/h of soil reaction is the main removal processes for Carbofuran from the soil compartment. Intermedia transport results in a minor transfer of the chemical 107 kg/h to water.

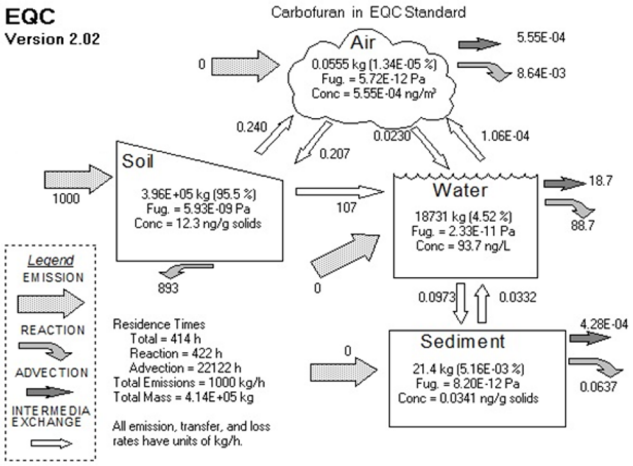

Fig. 9. Predicted Environmental Fate with Emission of 1000 kg/h of Carbofuran in soil compartment.

Equal emissions to soil, air and water are simulated for Carbofuran (Fig. 10). Reaction from soil (1665 kg/h) and water (1070 kg/h) are the two main removal process followed by advection from water (226 kg/h). There is a clear transfer of 866 kg/h of the Carbofuran from air compartment to soil together with 96.2 kg/h from air to water, 200 kg/h from soil to water. This results in 76.5 % of the chemical in soil and 23.4% in water.

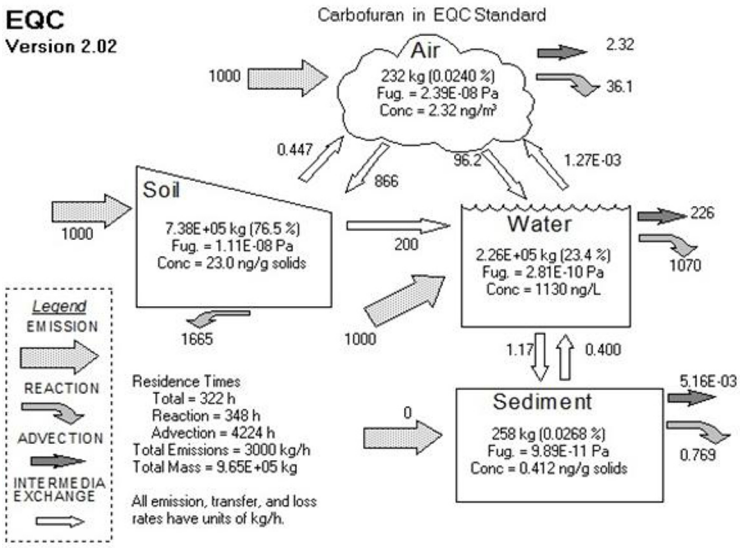

Fig. 10. Predicted Environmental Fate with Emission of 1000 kg/h of Carbofuran in simultaneously in air, water and soil compartment.

3.3 Predicted Concentrations.

The modelled fugacities, bulk concentrations and of Methiocarb are also depicted in Figures 3 - 5. In the scenario of release to air and water, individually, the maximum concentrations are expected in air (8.54 ng/m3) and water (262 ng/l). In the release to water and soil scenarios, separately, the maximum amounts are anticipated in sediments (0.267 ng/g solids) and soils (4.81 ng/g solids).
For carbofuran (Fig. 6-9), in the scenario of release to air and water, respectively, the highest concentrations are expected in air (2.31 ng/m3) and water (872 ng/l). In the emission to water and soil scenarios, correspondingly, the maximum amounts are anticipated in sediments (0.318 ng/g solids) and soils (12.3 ng/g solids. The outcomes can be utilized for risk assessment by contrasting relative multimedia concentrations, probable exposure pathways, and chemical fate in the environment [12].

3.4 Persistence and Residence Time.

For both the pesticides Methiocarb and Carbofuran, among the four possible scenarios predicted emission to water scenario, results in the shortest overall residence time (τ_0) 52.5 h and 175 h respectively. For emission to soil scenario results in the longest overall residence time (τ_0) among the four possible scenarios predicted for both Methiocarb and Carbofuran (102 h and 414 h respectively). The emission to soil scenario results in the highest reaction residence time (τ_R) for Methiocarb and Carbofuran (102 h and 422 h respectively). For emission to water scenario results in the lowest reaction residence time (τ_R) for Methiocarb and Carbofuran (55.5 h and 211 h respectively). For emission to soil the highest advection residence time (τ_A) for Methiocarb and for Carbofuran is ($1.15x10^5$ h and 22122 h respectively). For emission to water, the lowest advection residence time among the different scenarios, for both Methiocarb and Carbofuran is 1001 h.

A pseudo-first-order half-life for elimination of the pesticides from the environment can be predicted as ln2 (0.693) multiplied by the residence period [1]. The overall half-life (Table 3) for removal of Methiocarb from the environment by reaction is hence between 1.6 and 2.9 days and 6.1 and 11.9 days for carbofuran.

Table 3. Predicted Over all Half-Life of Methiocarb and Carbofuran in the EQC standard Environment

Emission Rate kg/h	Emission Compartment	Methiocarb (over all Half-life by reaction in days)	Carbofuran (over all Half-life by reaction in days)	Time for 99% Methiocarb Removal by reaction (days)	Time for 99% Carbofuran Removal from Environment by reaction (days)
1000	Air	2.6	11.2	17.3	114.9
1000	Water	1.6	6.1	10.6	70.4
1000	Soil	2.9	11.9	19.3	128.2
1000	All simultaneously	2.4	10.0	15.9	105.6

Time for elimination of 99% of Methiocarb from the environment by reaction is 7 times less than Carbofuran assuming first-order loss kinetics (Table 3). It has been suggested [12] that an examination of the distribution of carbofuran utilizing a steady state fugacity model type (level I, II, or III fugacity model) in the air, water, rice plants, and soil should be carried out after 41.6 days.

3.5 Sensitivity Analysis

Sensitivity analysis indicates that both Methiocarb and Carbofuran distributions are most sensitive to emission compartment (Table 4). Concentrations in air, water and soil compartment are most sensitive to emissions in air, water and soil correspondingly, while concentrations in the sediment compartment are most sensitive to emission in water. In addition, concentrations in soil compartment are sensitive to emissions to air compartment also, due to high rate of intermedia transfer from air to soil fig 6 and fig 10.

The air to water and air to soil, intermedia transfer rate was found to be sensitive to emissions to air compartment, while the water to air, water to sediment, sediment to water intermedia transfer rates were found to be sensitive to emission in water compartment for both the acaricides (Table 5). Soil to water and soil to air intermedia transfer rates were found to be sensitive to emission to both air and soil compartments.

The advective loss processes from air, water and sediment compartments were found to be sensitive to emissions to air and water only (Table 6 and Table 7). For advection from sediment compartment is sensitive to emission in water. The reactive loss process from the air and water compartments were also found to be sensitive to emissions to the respective compartments, while the loss from sediment compartment being sensitive to emissions in water. However, reactive loss process from soil compartment is sensitive to emissions to both air and water compartment.

Table 4. Sensitivity of Conc. of Methiocarb and Carbofuran to Emission to different Environmental Compartments.

Fungicide	Conc. in phase	% Sensitivity (Emission to air)	% Sensitivity (Emission to water)	% Sensitivity (Emission to soil)
Methiocarb	bulk air	9.99	<1	<1
	bulk water	<1	9.12	<1
	soil solids	4.55	<1	5.44
	sed. Solids	<1	9.12	<1
Carbofuran	bulk air	9.99	<1	<1
	bulk water	1.46	7.71	<1
	soil solids	4.63	<1	5.36
	sed. Solids	1.46	7.71	<1

Table 5. Sensitivity of Intermedia Phase Transfer Process to Emission Rates of Methiocarb and Carbofuran

Acaricide	Intermedia Phase Transfer Process	% Sensitivity (Emission to air)	% Sensitivity (Emission to water)	% Sensitivity (Emission to soil)
Methiocarb	Air to Water	9.99	<1	<1
	Air to Soil	9.99	<1	<1
	Water to Air	<1	9.12	<1
	Water to Sediment	<1	9.12	<1
	Soil to Air	4.55	<1	5.44
	Soil to Water	4.55	<1	5.44
	Sediment to Water	<1	9.12	<1
Carbofuran	Air to Water	9.99	<1	<1
	Air to Soil	9.99	<1	<1
	Water to Air	1.45	7.71	<1
	Water to Sediment	1.45	7.71	<1
	Soil to Air	4.63	<1	5.36
	Soil to Water	4.63	<1	5.36
	Sediment to Water	1.45	7.71	<1

Table 6. Advection and Reaction Loss Rates for Methiocarb

Loss Process	Compartment	% Sensitivity (Emission to air)	% Sensitivity (Emission to water)	% Sensitivity (Emission to soil)
Advection Process	Air	9.99	<1	<1
	Water	<1	9.12	<1
	Soil	NA	NA	NA
	Sediment	<1	9.12	<1
Reactive Process	Air	9.99	<1	<1
	Water	<1	9.12	<1
	Solids	4.55	<1	5.45
	Sediment	<1	9.12	1

Table 7. Advection and Reaction Loss Rates for Carbofuran

Loss Process	Compartment	% Sensitivity (Emission to air)	% Sensitivity (Emission to water)	% Sensitivity (Emission to soil)
Advection Process	Air	5.49	<1	<1
	Water	<1	7.71	<1
	Soil	NA	NA	NA
	Sediment	<1	7.71	<1
Reactive Process	Air	5.49	<1	<1
	Water	<1	7.71	<1
	Solids	2.55	<1	5.36
	Sediment	<1	7.71	<1

4 Conclusion

The study found that for emission to air compartment both Methiocarb ad Carbofuran distributes to predominantly to soil and less amounts in water. For emission to water and soil compartments both the chemicals predominantly distribute to the compartment emitted. For simultaneous emission to air, water and soil compartments distribution is mainly to soil compartment. Calculations also indicate that Methiocarb will be removed by reaction seven times quickly than Carbofuran. The study of sensitivity analysis finds that the distributions, advective and reactive loss processes of carbofuran and methiocarb are the most susceptible to emission compartments.

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