Persistence of carbaryl pesticide in environment using system dynamics model

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Abstract. Carbaryl, one of the carbamate insecticides are used extensively for pest control in agriculture. The chemical is highly valued for its rapid action and relatively short environmental persistence. Because of its widespread and intensive use, residues of carbaryl have the potential to contaminate the environment. This study aims to formulate a system dynamics model to simulate a degradation process of carbaryl. Since carbaryl was not readily volatilizing, this study only estimates the concentration and degradation of carbaryl in soil and water. The result revealed that carbaryl degraded rapidly, with a half-life of 7 days in soil and two days in water. The model was validated with a laboratory experiment using solid phase extraction reversed-phase high-performance liquid chromatography to determine carbaryl concentration. 12.82 % percentage error compared to the experimental value indicated that the developed model's prediction was acceptable. The model can be used to estimate the presence of carbaryl pesticide in soil and water. Findings from this study can be used to assess the fate and the impact of carbaryl pesticide in the environment.

1. Introduction

Widespread application of pesticides in agriculture contributes significantly to toxic materials in the soil, water and air. Carbaryl, I-nepthyl N-methyl carbamate is one of the most effective broad-spectrum insecticides used throughout the world on about 125 crops to control about 565 different species of pests [1]. Carbaryl has gained wide acceptance because of its low mammalian toxicity, less persistent nature and has been used as a substitute for some organochlorine pesticides [2]. Although carbaryl does not persist in the environment and the compound does not accumulate in mammals, there may still be short term cumulative effects on the reproduction of aquatic organisms like a freshwater snail (Lymnaea acuminate) [3], zebrafish (Danion rerio) [4] also plankton and fish [5]. Therefore, its application near water bodies must be careful before its use.

Pesticides reach water bodies by spray drift, aerial spraying, or runoff from agricultural land [6]. It dissipates by hydrolysis, photolysis, and microbial degradation, depending on its chemical structure, water characteristics and bioavailability [7]. Carbaryl is moderately soluble in water, and its solubility increases with increasing temperature and amount of organic solvents. It has been found in surface waters, groundwater [8], agriculture soil and urban environments of 14 U.S. states at several concentrations (0.001 - 33.5 μg/L) [9]. Carbaryl is also found in water and soil in Southern Malawi [10].
Modeling the presence of contaminant can be a useful tool for assessing the fate and also the impact of it in the environment, and may be used to determine the concentration and degradation rate that provide the information for how long the contaminant could be practically eliminated from the system, for which System Dynamics Model can play an important role. Models become important when estimating chemical fate in the environment because, in most cases, this cannot be measured directly [11]. Several carbaryl residue models in the environment have already been described [5, 6, 12–14]. Those models generally assumed simple first-order kinetics, which may not accurately predict carbaryl residue in soil and water. This study's objective was to formulate a model based on system dynamics to simulate a degradation process of carbaryl in soil and water. The carbaryl presence in the air was being ignored since carbaryl was not readily volatilizing [9]. Furthermore, the model was validated with a laboratory experiment using solid phase extraction reversed-phase high-performance liquid chromatography (RP-HPLC) to determine carbaryl concentration.

2. Methodology

2.1. Data collection
The data were obtained from previous studies, published data and literature information with similarities in physical properties of soil and water like pH, temperature, and soil moisture. Carbaryl residue and biodegradation data were also used to estimate carbaryl's persistence using the system dynamics model (table 1).

2.2. Model analysis
A model for describing carbaryl pesticide persistence was developed in the system dynamics software using Vensim PLE (Ventana System, Inc.) based on several assumptions and equations below. Six assumptions were considered to formulate the model:
(i) The system is closed, and mass conservation is assumed.
(ii) Microbes were considered homogeneously distributed in the system.
(iii) Carbaryl input and carbaryl release were calculated using equation (1) and equation (2), respectively
\[ C_i = sr \cdot \left( \frac{V_0 \times C_0}{V_i} \right) \] (1)
\[ C_r = k_r \cdot C_i \] (2)
where \( C_i \) is the concentration of carbaryl input (ppm), \( sr \) is spraying rate, \( V_0 \) is initial volume as a result of area \( \times \) carbaryl dosage (L), \( V_i \) is volume input with dilution factor (L), \( C_0 \) is the initial concentration of carbaryl in the product (ppm), \( C_r \) is a concentration of carbaryl release from a plant (ppm), and \( k_r \) is release rate of carbaryl from a plant (d\(^{-1}\)).
(iv) Microbial growth or biomass was modeled following Verhulst logistic equation (3) [15] and assumed constant once asymptotic growth was reached.
\[ \frac{dB_M}{dt} = BM_0 + k_1 \cdot BM \cdot \left( 1 - \frac{BM}{BM_{\text{max}}} \right) \] (3)
where \( BM \) is the concentration of microbial biomass in the system (CFU g\(^{-1}\)), \( BM_0 \) is the initial concentration of biomass inoculated, \( BM_{\text{max}} \) is the maximum concentration of biomass reached, and \( k_1 \) is a constant parameter from logistic function (d\(^{-1}\)).
(v) Carbaryl concentration in soil (\( C_s \)) was a result of carbaryl release (first term), desorption from soil to water (second term) and biodegradation in soil (third term) as shown in equation (4) [16]:
\[ \frac{dC_s}{dt} = C_r - C_{\text{wmax}} \cdot \frac{n \cdot \left( k_w b \cdot t \right)^{n-1}}{e^{(k_w b \cdot t)^n}} - \frac{\mu_{\text{max}} \cdot C_s \cdot BM}{K_s + C_s} \cdot \frac{BM}{Y_s} \] (4)
where \( C_r \) corresponds to a concentration of carbaryl release (ppm), \( C_{\text{wmax}} \) is the maximum concentration of carbaryl in water (ppm), \( k_w b \) and \( n \) are kinetic parameters from Weibull adjustment.
[17], $\mu_{\text{max}}$ is the maximum specific growth rate in soil (d\(^{-1}\)), $K_s$ is the saturation or half-rate constant of bacteria colonizing in soil, and $\gamma_s$ is the growth yield coefficient of bacteria colonizing in soil (CFU g\(^{-1}\)), and Biomass (BM) was included as equation (3).

(vi) Carbaryl concentration in water ($C_w$) will increase due to desorption from the soil and decrease due to biodegradation in water, as in equation (5) [16]:

$$\frac{dC_w}{dt} = C_{w\text{max}}\frac{m(k_{wb}t)^{n-1}}{e^{(k_{wb}t)^n}} - C_w e^{-kt}$$  \hspace{1cm} (5)

where $k$ is the biodegradation rate in water (d\(^{-1}\)). $C_{w\text{max}}$ is not a constant parameter since, in soil and water, it is continuously changing due to biodegradation. Therefore, $C_{w\text{max}}$ was calculated as a function of soil ($C_s$) and water ($C_w$) concentration, using the distribution coefficient between soil and water of the desorption process, which expressed as equation (6):

$$k_d = \frac{C_s}{C_w}$$  \hspace{1cm} (6)

2.3. Model validation
The model was validated with a laboratory experiment using solid phase extraction reversed-phase high-performance liquid chromatography to determine carbaryl concentration conducted in a previous study [18]. MAPE (Mean Absolute Percentage Error) test, as in equation (7), was used to validate carbaryl concentration obtained from model simulation compared to experimental results. MAPE is calculated using the absolute error in each period divided by the observed values evident for that period [19]. Then, averaging those fixed percentages:

$$MAPE = \frac{1}{n} \sum \frac{|X_d - X_m|}{X_d} \times 100\%$$  \hspace{1cm} (7)

where $n$ is period, $X_d$ is the actual value, and $X_m$ is simulated/predicted value. The model results were good if the MAPE percentage error of less than 10% was acceptable if less than 20%.

3. Results and discussion
3.1. Model formulation and estimation of parameters
A persistence of carbaryl pesticide in the environment was developed and formulated in Vensim PLE software (figure 1). The complete system dynamics model shows how flows connect these state variables.
Figure 1. The formulation of VENSIM model for carbaryl persistence in the environment.

The model parameter required to formulate the model is specified in table 1. This table includes the numerical values, estimation methods and references from which they were obtained. The carbaryl input process, carbaryl release, biodegradation in soil, microbial growth, desorption flow, and biodegradation in water were calculated using equation (1, 2, 3, 4 and 5) respectively.

Table 1. Values, methods and references of a parameter used in the model.

| Process                        | Parameter               | Value                  | Method/Reference |
|--------------------------------|-------------------------|------------------------|------------------|
| Carbaryl input                 | Spraying rate           | Once every four days   | Farmer interview |
|                                | Area                     | 1 m²                   | Sampling area    |
|                                | Dilution factor          | 20 %                   | Farmer interview |
|                                | Carbaryl concentration   | 43 % w/t               | [20]             |
|                                | Dosage                   | 1 quart per acre       | [20]             |
| Carbaryl release               | Release rate             | 9 %                    | [21]             |
| Microbial growth               |                          |                        |                  |
|                                | $k_i$                    | 0.1386 d⁻¹             | [22]             |
|                                | $BM_{max}$               | $153 \times 10^3$ CFU/g| [22]             |
|                                | $BM_o$                   | $50.15 \times 10^3$ CFU/g| [22]             |
| Biodegradation in soil         | $K_s$                    | 3.22 µ/g               | Estimated from [23] |
|                                | $\mu_{max}$              | 0.0693 d⁻¹             | [23]             |
|                                | $Y_i$                    | $2.2 \times 10^6$ CFU/g| [23]             |
| Desorption flow                | $k_d$                    | 5.18                   | [24]             |
|                                | $k_{wb}$                 | 0.0908 d⁻¹             | Estimated from [24] |
|                                | $n$                      | 4.00                   | Estimated from [24] |
| Biodegradation in water        | Biodegradation rate ($k$)| 0.3465 d⁻¹             | [13]             |

Plant uptake represents the value of carbaryl input minus carbaryl release to the soil. It was only about 91 % of carbaryl pesticide absorbed by plants [21]. The carbaryl input concentration was dependent on spraying rate, crop area, dilution factor, carbaryl initial concentration in product and dosage. Every crop has a different dosage of carbaryl. In this study, tomatoes and chilis were planted in the area. Carbaryl pesticide was sprayed one quart per acre once every four days for the optimum dosage of pest control. Despite virtually eliminating pest, carbaryl accumulates in soil and water because it tends to adsorb onto soil and due to its properties of low water solubility and limited biodegradation [25].
3.2. Model prediction of carbaryl degradation in soil and water

Figure 2 shows the decrease of the total concentration of carbaryl in soil, using 0 to 14 days as model boundaries. It has been reported that the degradation of carbamate insecticides in soil was occurred for maximal in two weeks [26]. The results revealed that for the application of carbaryl in table 1, the complete elimination could be practically achieved after seven days. The other reports showed that the half-life of carbaryl in the soil varies from 5 days to 14 days, depending on temperature, pH, soil moisture, soil type and initial concentration [22,23,26,27]. Higher application rates will lead to higher persistence. Carbaryl is expected to sorb more readily on soils with high organic matter content than on sandy soils [24].

In this study, the model for the biodegradation process in soil was carried out by azotobacters that utilized carbaryl as carbon and energy sources with main product of carbaryl hydrolysis is an a-naphthol [22]. The population of azotobacters had significantly increased in the first five to seven days, then the population decreased. This was indicated that azotobacter shows promising results in degrading carbaryl in soil. Reports show that other bacteria such as Pseudomonas sp., Rhizobium sp., Rhodococcus sp., Micrococcus spp., Bacillus sp., Morganella sp., Aeromonas sp. and Corynebacterium sp. also degraded carbaryl effectively [23,27,28,29,30,31].

Carbaryl reaches surface and groundwater as a result of runoff, desorption and leaching. It has been mentioned that carbaryl has a harmful effect to aquatic organisms. The biological effects of carbaryl in an aquatic environment depend on several factors, including the concentration of the pesticide in water and the length of time the organism of interest is exposed. As well as in soil, carbaryl can be removed from the water through biodegradation. Aquatic organisms can biodegrade some pesticides because it acts as a source of carbon and nitrogen [5]. The degradation of carbaryl concentration in water is presented in figure 3 with six days using model boundaries [6].
The model predicted that carbaryl in water would be eliminated two days after entering the water body. Literature data on its half-life in aquatic environments varied from 1.3 days in a fish aquarium [32], 1.7 and 2 days in river water [13,33] to 5.8 days in mountain streams [34]. It was reported that the degradation of carbaryl in water depends on the concentration of dissolved oxygen that varies with seasons and locality [14]. Besides, the presence of exogenous organic nutrients could significantly shorten the half-life because it would encourage the rapid development of biodegradation [12]. This study shows that the persistence of carbaryl in water would be transient because of the short half-life.

The concentration of carbaryl in drinking water and groundwater was varied in each country; 0.1 μg/L in Europe [35], 700 μg/L in USA, 5 μg/L in Australia and 90 μg/L in Canada. From model prediction, the concentration of carbaryl in water still meets the regulations only for USA and Canada standards with the value of 12 μg/L in the second days after carbaryl entering the water body. With the result that, water treatment is required in order to use it as a drinking water.

3.3. Model validation
Model validation was conducted using the MAPE test that has been expressed in equation (7). MAPE test can be useful for evaluating the accuracy of a prediction and indicates how much error in predicting compared with the real value.

The carbaryl concentration in soil has been determined previously using solid-phase extraction and reversed-phase high-performance liquid chromatography with UV detection [18]. Carbaryl was detected in two soil samples (Pengalengan and Lembang) with a value of 0.3350 and 0.2958 ppm, respectively. Those soil samples were taken on the third day after spraying.

Refer to carbaryl concentration from the model prediction in figure 2, the value of carbaryl concentration on day 3 is 0.2739 ppm. The percentage error of experimental value and model prediction using the MAPE test is 12.82%. It is acceptable (< 20%) that indicates that the model can estimate the presence of carbaryl at the given conditions pesticide in soil and water.

4. Conclusion
The persistence of carbaryl pesticide in the environment has been predicted using the system dynamics model. The half-life of carbaryl in soil was seven days after application and two days after entering the water body. With a 12.82 % percentage error compared to the experimental value, it can be concluded that the prediction of the developed model was acceptable, and the model can be used to estimate the presence of carbaryl pesticide in soil and water.

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