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Dynamic Modelling of Pesticide Residues in Plants

Bimol Nath Roy, Abir Podder, S. M. Jahangir, M.A.A. Shoukat Choudhury*

Department of Chemical Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

E-mail: shoukat@che.buet.ac.bd

Abstract

With the continuous increment in the world population, the demand for food products has also increased noticeably. To meet this huge demand, a stable supply of food products is required to be maintained strictly. For this reason, different chemical substances such as fertilizers and pesticides are used to aid food production. But arbitrary uses of pesticides will certainly lead to various environmental and health hazards. Hence, uses of pesticides are to be strictly monitored. Models to predict the residual fate of chemicals in plants can be effectively used in pesticide design, human exposure, and environmental assessments. Often the emissions of pesticides are non- steady due to changing plant growth and transpiration. A first principle model (FPM) has been built correlating different mass transfer modes in plants. For the modelling purposes, a material balance approach was used to set up ordinary differential equations (ODEs) for four compartments of the plants, namely, root, stem, fruits/crops, and leaves. The four ODEs were then simultaneously solved in MATLAB to estimate concentrations of pesticides in plant compartments with respect to time. Chlorpyrifos (CP) and Endosulfan Sulfate (ESS) are chosen as pesticides and wheat is selected as the plant for experiment. Concentration profiles were obtained for each pesticide using different input scenarios such as spraying the pesticide in air and applying the pesticide into soil. The model results can be used to find the pre-harvest time before which pesticides should be applied and by the time of harvest the pesticide concentration will fall below the safe threshold limit.

Keywords: Prediction of residual fate, pesticides, first principle model, material balance approach, compartments of plants, concentration profile, application method.

1. Introduction

In the present scenario, the global population is estimated to grow by 70 million per annum, increasing the demand for food productivity by 70% (Popp et al., 2013). To do so, reliability in using chemical substances such as fertilizers, pesticides, etc. is increasing in most developing countries (Ecobichon, 2001). Pesticides are used to minimize yield loss in crop production by minimizing infestation of pests on the plants (Damalas, 2009). Proper measurement and fate or end-life analysis might be helpful to produce foods lowering the effects of pesticides. Many studies have been conducted regarding this issue, but few complete models to estimate the environmental fate have been developed. Also, the existing models are very complex to understand and use. Considering all the factors, an effective and simple approach was needed to be developed. The very early studies on the Life Cycle Analysis (LCA) of pesticides weren't based on any specific model or work of literature. Instead, several works were compiled and compared with the aspects of various models and addressed about the potential future directions for the study of the Life Cycle Impact Analysis (LCIA) of pesticides (Geisler, 2003). Moreover, Regional Mass Balance is a better option to anticipate different paths. For example, some pesticide particles will float away in the wind, some portions will deposit on the plant leaves, some will be absorbed by the soil (Charles, 2004). It has been observed from various studies that nearly 10% of the pesticides ascend into the air. This observation is modelled from a modular pattern named 'PestLCI' to estimate the emission of pesticides from field application to different environmental compartments. The model estimates the emission in the air, groundwater, and underground compartment (Birkved & Hauschild, 2006). A significant portion of the applied pesticide may fall on the soil and is absorbed by it and different physical and chemical processes take place which determine the fate of the pesticides (Fantke et al., 2013). To forecast the way that pesticides will be absorbed by plants in soil, a mathematical model was created. The model considers relationships between numerous characteristics like mobility, plant transpiration, root-soil transfer rate, plant growth, etc. The bioconcentration factor, root concentration factor, and transpiration stream concentration factor are some of the primary elements on which the models are built and to re-establish the model, several equations were developed (Hwang et al., 2017). For calculating dynamic residues, a chemical-specific residue model was created. The lack of other important parameters, such as those affecting pesticide desorption and leaching in soil, field topography, weather patterns, and the area where plant roots meet the soil, may cause variations between the concentrations predicted by models and those which are measured (Hwang et al., 2015). The main purpose of this study was to accumulate all the studies into a single compartment model which analyzed the time dependent behaviour of pesticides and that is based on the material balance and an engineering approach. Air, roots, leaves, soil, stem, fruits, and many other sections that are related to the transportation of pesticides can be considered as individual compartments and the relations can be pictured through the material balance approach. The results led to the development of a novel model idea for plant uptake models that approximate logistic growth and transpiration to expanding plant mass. With the unsteady state situation, or for constant input, the underlying system of differential equations was analytically solved (Rein et al., 2011).

2. Model Development

The mathematical model is based on the compartmental analysis of different parts of the plant. For any plant four major plant compartments are considered naming root, stem, leaves and fruits/grains and two input compartments are considered – Soil and Air. For each plant compartment, a differential equation can be formulated from the mass balance of pesticide. Two fundamental methods of mass transfer – advection and diffusion; can be considered in compartmental analysis along with dilution due to plant growth and metabolism (Trapp, 2010). Model structure with appropriate mass transfer modes are illustrated in figure 1.

General form of material balance equation for any system can be written as –

$$input - output + generation - consumption = accumulation$$

The input and output are respectively the amount that enters or leaves through the system boundary; amount of generation and consumption are the amount produced within the system or consumed within the system, respectively and accumulation refers to the amount buildup within the system. In this study, there is no pesticide generation within any compartment thus generation term can be excluded from the equation and dilution due to growth and metabolism is considered as the consumption. Thus, for a dynamic scenario this equation can be written as

$$accumulation\ rate = input\ rate - output\ rate - metabolism$$

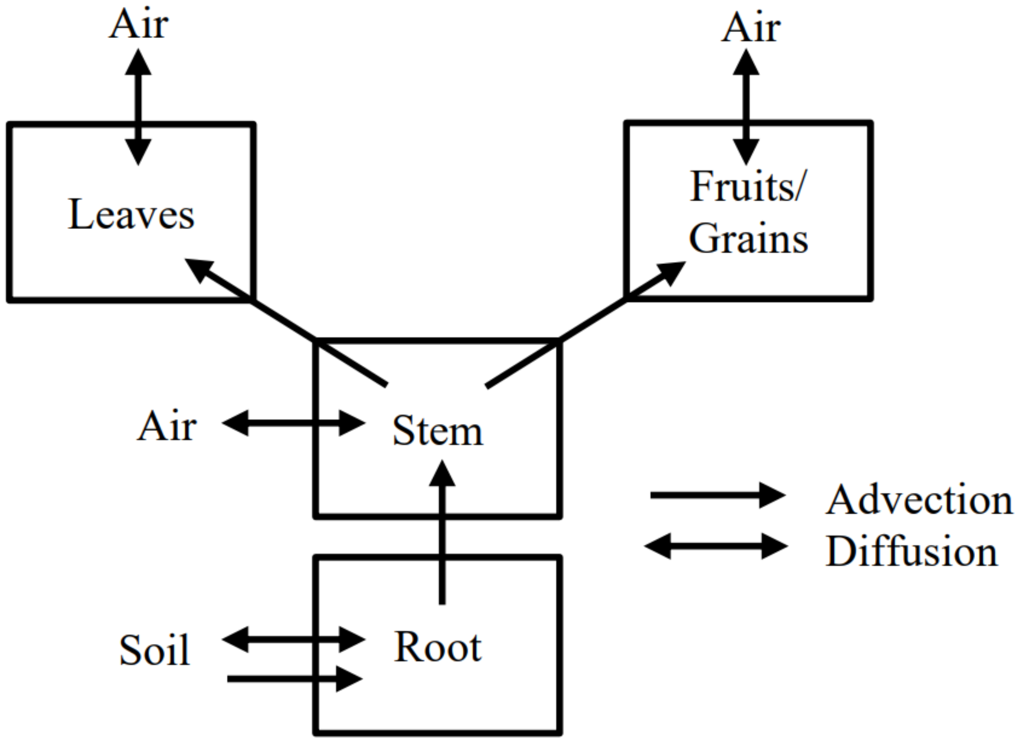

Figure 1: Model Structure

Differential equation set obtained by performing mass balance in each plant compartment is tabulated in table 1 (Rein et al., 2011).

Table 1: ODEs for change of concentrations of pesticides in different plant compartments

Root	$\frac{dC_R}{dt} = Q \times K_{WS} \times \frac{C_S}{M_R} - \frac{Q}{M_R \times K_{RW}} \times C_R + 1000A_R \times P_R \times \frac{K_{WS} \times C_S}{M_R} - 1000\frac{A_R \times P_R}{M_R \times K_{RW}} \times C_R - K_{R,deg} \times C_R$
Stem	$\frac{dC_{St}}{dt} = \frac{Q}{K_{RW} \times M_{St}} \times C_R - \frac{Q}{K_{StW} \times M_{St}} \times C_{St} + \frac{A_{St} \times P_{St}}{K_{AW} \times M_{St}} \times C_A \times (1 - f_p) + A_{St} \times v_{dep} \times C_A \times f_p - 1000\frac{A_{St} \times P_{St}}{K_{StW} \times M_{St}} \times C_{St} - K_{St,deg} \times C_{St}$
Leaf	$\frac{dC_L}{dt} = \frac{Q_L}{K_{StW} \times M_L} \times C_{St} + \frac{A_L \times P_L}{K_{AW} \times M_L} \times C_A \times (1 - f_p) + \frac{A_L \times v_{dep} \times C_A}{M_L} \times f_p - 1000\frac{A_L \times P_L}{K_{LW} \times M_L} \times C_L - K_{L,deg} \times C_L$
Fruit/ Grain	$\frac{dC_F}{dt} = \frac{Q_F}{K_{StW} \times M_F} \times C_{St} + \frac{A_F \times P_F}{K_{AW} \times M_F} \times C_A \times (1 - f_p) + \frac{A_F \times v_{dep} \times C_A}{M_F} \times f_p - 1000\frac{A_F \times P_F}{K_{FW} \times M_F} \times C_F - K_{F,deg} \times C_F$

Note: (1) C: concentration of pesticide in different compartments (mg/kg and mg/m3 for air); Q: transpiration (L/d); A: surface area (m2); P: permeability (m/d); KAB: partition coefficient between compartment A and compartment B (L/L or kg/L or L/kg) (Trapp, 2010); ki,deg: first order degradation rate constant for growth and metabolism in plant compartment i (/d); fp: fraction of particles and; vdep: deposition velocity of particles (m/d) (Klöpffer, 2000). (2) Subscripts used: W(water), A(air), S(soil), R(root), St(stem), L(leaf), F(fruit/grain).

Numerical values of different parameters are defined from literature and previous works on this field. The concentration of pesticide in soil and air are taken as the input and the concentration of pesticide in four compartments of plant is the output result of the model. Input concentration equations are tabulated in table 2.

Table 2: Input concentration equations for soil and air

Soil	$C_S = C_{S0} \times \left(1/2\right)^{t/T_S}$	(Hwang et al., 2017)
Air	$C_A = C_{A0} \times \left(1/2\right)^{t/T_A}$	(Das et al., 2020)

Note: Cj: concentration of pesticide after t days; Ci0: initial concentration of pesticide applied in soil/sprayed in air

Plant of mass is time dependent which defines the root mass, stem mass, leaf mass and fruit mass as time dependent variable in the previously mentioned differential equations. Many annual crops, such as wheat which is taken for this study shows a logistic growth curve (Richards, 1959). This means an exponential growth initially but slows down towards ripening and stops after a certain time. The mass change is described as follows (Rein et al., 2011) –

$$M(t) = \frac{M_{max}}{1 + \left(\frac{M_{max}}{M_0} - 1\right) \times e^{-kt}}$$

This expression is used for all the compartments in a plant with corresponding rate constant. Transpiration in plants is growth dependent and the relation between transpiration and plant growth are defined with transpiration coefficient TC(L/kg) (Larcher, 2003) and expressed as –

$$Q = T_C \times k \times M\left(1 - \frac{M}{M_{max}}\right)$$

Transpiration for leaves and fruits are calculated by averaging with the respective surface areas where phloem flux adds for fruits and subtracts for leaves (Trapp, 2010). Dynamic behaviour of input parameters, mass and transpiration of plants are incorporated in the previously derived four compartmental differential equations and then realized using MATLAB. Simultaneous ordinary differential equations (ODEs) for different compartments are solved using the built-in function ‘ode45’. To solve the equation set in MATLAB, at first time dependent growth of plant and transpirations are calculated. Parameters for implementing the model are divided into two categories: primary parameters – which are the literature value and not dependent on other parameters are defined and secondary parameters – which are calculated from the primary parameters afterward. Then the time dependent concentration of pesticide in soil and air are calculated. Now all the coefficients are ready to construct the differential equation set and finally the differential equation set is solved by specifying the initial conditions for discretized time range. The output matrix obtained by this technique consists of the time range and concentration of pesticide in different compartments against the time range. For visualization, the output concentration profile is plotted for different compartments against time.

3. Results and Discussion

The model was run for three different cases and in each case datasets of two different pesticides, CP and ESS, were used. In all of the cases, the time required for the pesticides to fall below the allowable threshold limit was observed.

Case 1 – Pesticides Sprayed into Air and Neglecting Concentration in Soil: In this scenario, pesticides were assumed to be sprayed into air and air to soil transfer is considered negligible. The pesticides were sprayed at a concentration of 10 mg/m3 on the 31st day and the concentration profile is represented in figure 2A and 2C. Initially the deposition of pesticides on the leaves is very rapid. Hence, the graph shows that the concentration decay is very sharp. After approximately 5 days for CP and 10 days for ESS the concentration in the air reaches nearly zero and till any further pesticide input, the concentration will remain the same.

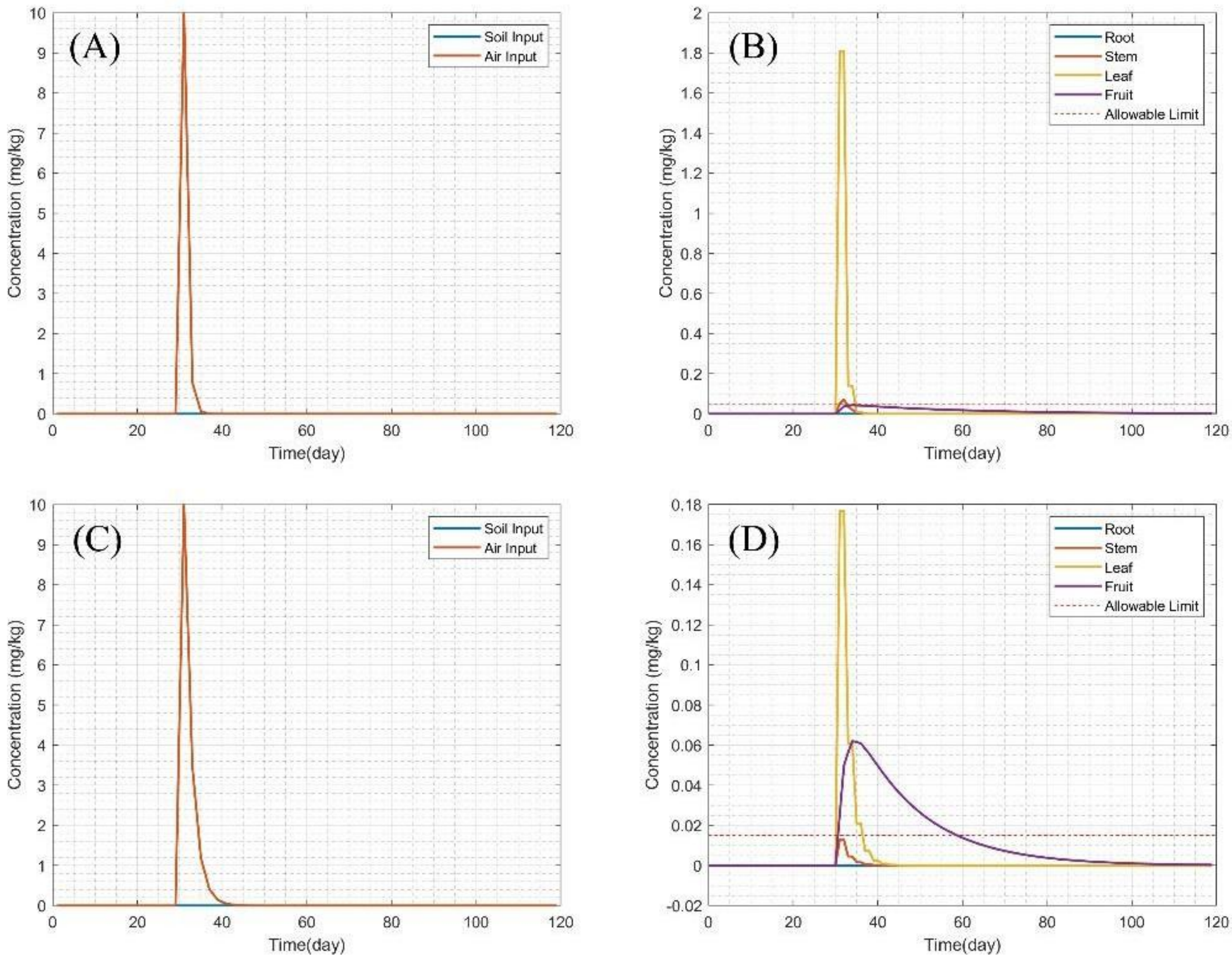

Figure 2: Case 1 results (A) CP input (B) CP outcome (C) ESS input and (D) ESS outcome

For both pesticides the concentration in the leaves is found to be very high. That is because the pesticide droplets directly deposit on the leaves and then enter the stem due to diffusion and absorption. But it can be clearly depicted from figure 2B and 2D that in 4 to 5 days for CP and 10 to 12 days for ESS, the concentration in leaves decreases and reaches nearly zero. Initially due to pesticide exposure, the concentration in the stem, fruit, and roots increases. The increment of ESS concentration in fruit is quite noticeable. But due to chemical decomposition and plant growth, the concentration decreases gradually. For CP and ESS, the safety limit for food consumption is 0.05 mg/kg and 0.015 mg/kg respectively (Das et al., 2020). During the harvesting time (120 days for wheat) the concentration is found to be much lower than the safety limits.

Case 2 - Pesticide Sprayed into Air and Considering Air to Soil Transfer: According to (Matoba et al., 1998) 93% concentration of the pesticide sprayed into air end up in floor concentration thus can be considered increasing soil concentration for this model. In this scenario, assumptions was made that pesticides are sprayed into the air directly and air to soil transfer is considered significant. Figure 3A and 3C are the input concentration profile found for CP and ESS respectively. The air input concentration profile is quite similar to that one of case 1. In addition, there is another curve that represents concentration in soil which had been found to be decreasing due to adsorption, transpiration and decomposition processes occurring in the soil.

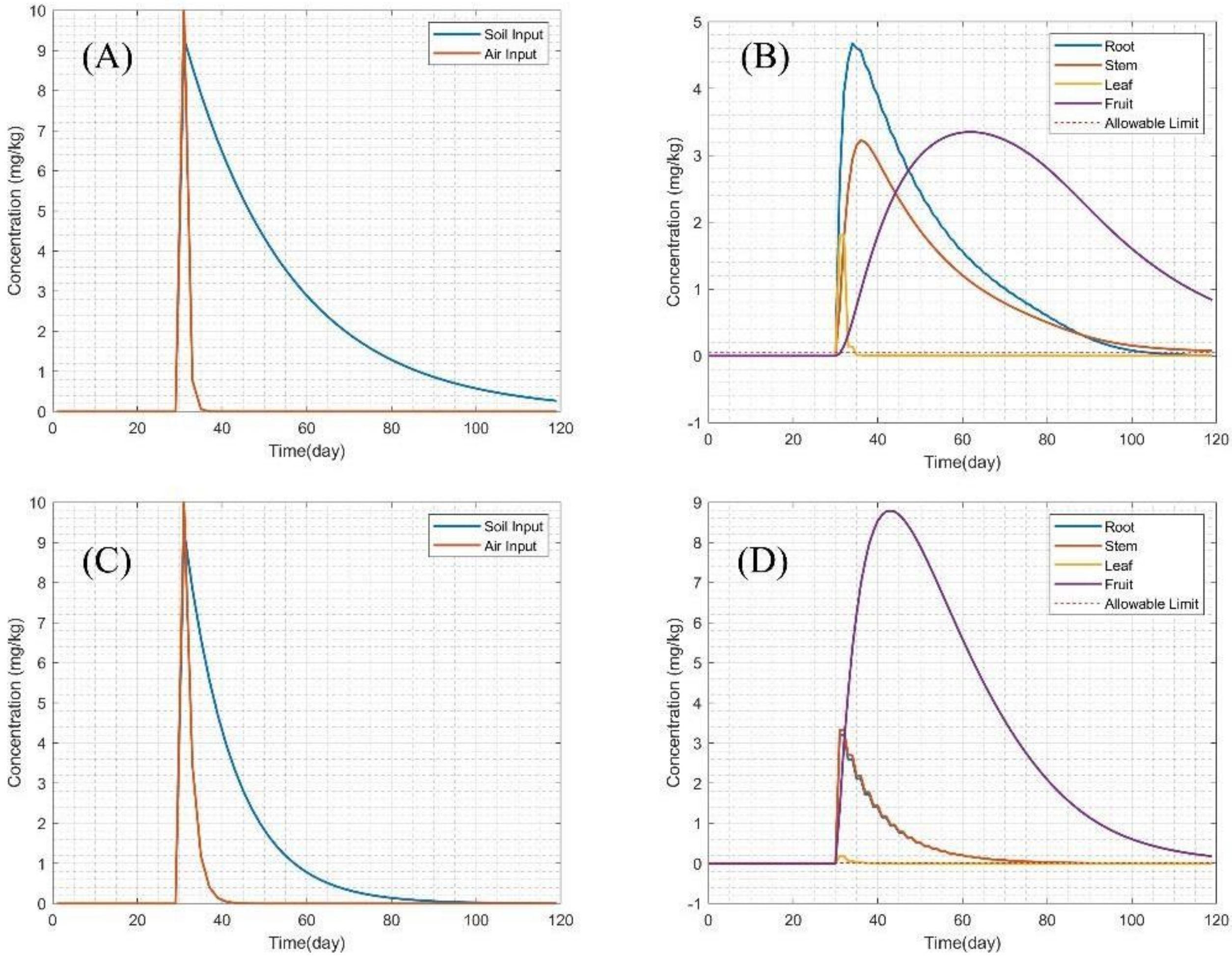

Figure 3: Case 2 results (A) CP input (B) CP outcome (C) ESS input and (D) ESS outcome

As a significant portion of the pesticides deposited on the soil, it is observed from figure 3B and 3D that the concentration in the roots is found to be very high at the beginning. But due to transpiration, pesticide enters the stem, and the concentration decreases gradually. Similar behavior can also be observed in the case of stems, fruits, and leaves. Plants' growth plays a vital role in decreasing concentration. But the concentration in the fruit exceeds the safety limit during the harvesting time. This is because of the dual mode entrance of pesticide in the plant, and it has yielded into higher concentration. For ESS the concentration is highest in the fruits whereas root has the highest concentration in case of CP.

Case 3: Pesticide Applied in Soil: In this case, pesticides are considered to be applied to the soil directly and soil to air transfer is considered negligible. Due to absorption, decomposition in soil and transpiration through the roots, concentration gradually decreases (Figure 4A and 4C).

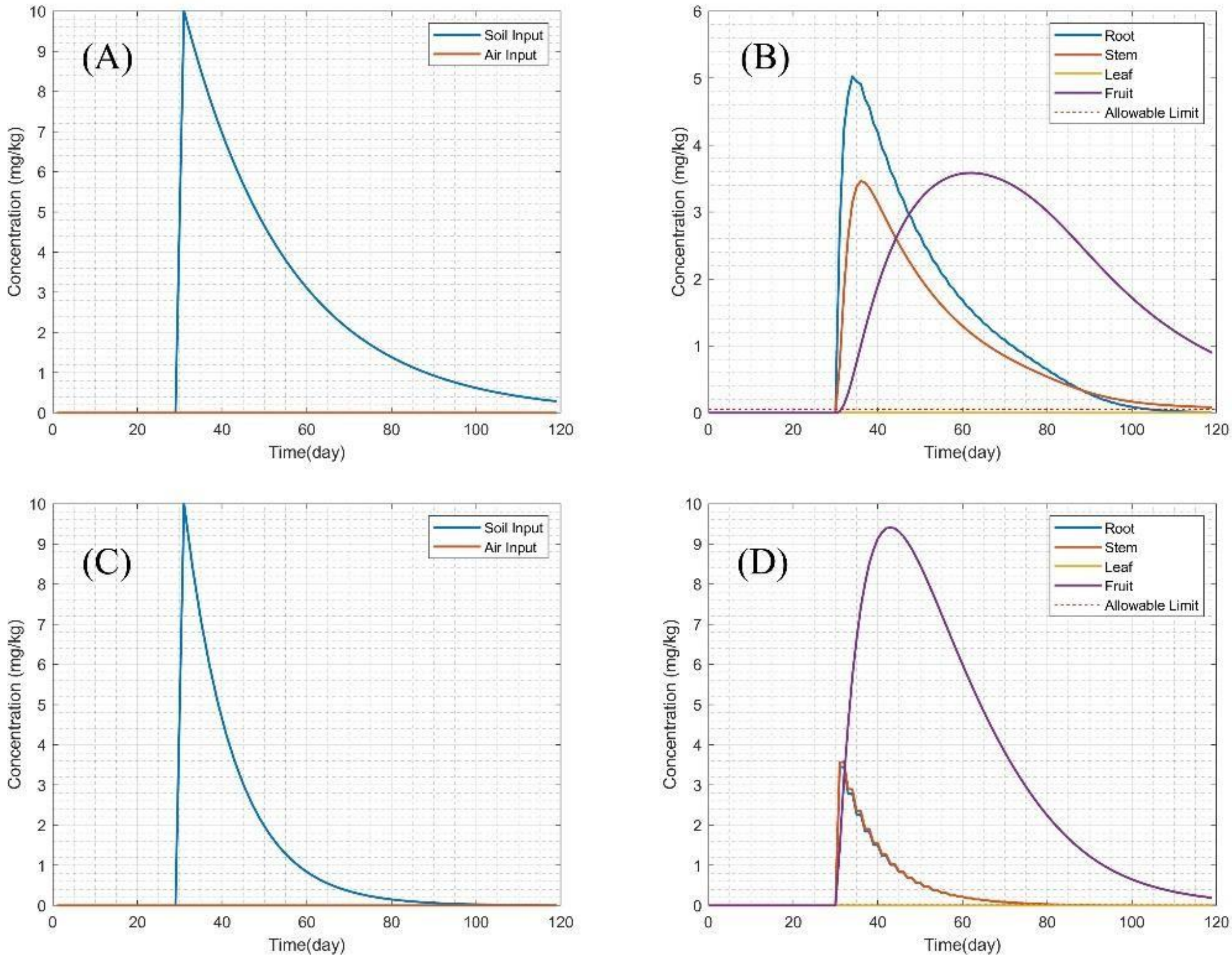

Figure 4: Case 3 results (A) CP input (B) CP outcome (C) ESS input and (D) ESS outcome

The output response for both pesticides was almost similar to that of case 2. But the only difference was regarding the leaf's concentration. The concentration of leaves depends on the deposition and absorption of pesticides on the outer surface of the leaves. As there was no input from the air, no pesticides could enter through the cuticles of the leaves. The very small concentration in it was the consequence of transpiration from the stem. The rest of the compartments demonstrate similar behavior as before. Here also in terms of ESS, the fruits have the highest concentration, but the root has the highest concentration in terms of CP.

A general result can be visualized that when the concentration of pesticide in soil is significant, pesticide concentration in fruit/grain is higher than the safe limits and never falls below the allowable limit before or during the harvesting time.

4. Conclusions

The model was developed following an engineering approach. The ODEs were obtained considering material balances that were occurring due to different mass transfer phenomena in different compartments in plant. The resulting pattern of the model analyzing the dynamic behaviour of pesticides used in agricultural products were portraited in the graphical analyses. The results obtained in the present study were found to be consistent with previously reported works by (Rein et al., 2011; Trapp, 2010). The concentration profiles were greatly affected by pesticide properties such as octanol- water partition co-efficient (KOC), air-water partition co-efficient (KAW) and half-life of pesticides in air (TA) and soil (TS). It was seen that initially the concentration in leaves was much higher when the pesticides were sprayed in air. On the contrary, when pesticides were applied in the soil, the concentrations in the fruits and roots were foundto be higher. From the responses, it can be concluded that the different concentration profiles were obtained due to the direct contact of the pesticides with certain compartments when applied. Thus, the application method of pesticides should be based on the plant type. Significant amount of pesticide in soil makes the concentration of pesticide in fruit/grain higher than the allowable limit. However, the concentration of pesticide should be applied can also be an interesting outcome of the model for which pesticide concentrations will fall below the threshold value before harvesting time.

On the downside, the major limitation of this study is that it was conducted based on purely theoretical knowledge. An experimental field trial must be conducted to observe the real-life scenarios. However, it should be considered that models are based on simplified theory where in real life situations more complex phenomena occur, thus deviations could occur in field trial.

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