CHAPTER IV
PESTICIDE UPTAKE MODEL

4.1 Model Description

A generalized model that can reproduce and explain the behavior of the pesticide uptake into the plant has been developed using Computer Aided modeling software called ICAS-MoT (Sales-Cruz and Gani, 2003) and is included in the framework. The model is based on Fick's laws of diffusion and employs predictive constitutive models for some of the important parameters and properties. Figure 4.1 shows the diagrammatic representation of scenario modeled.

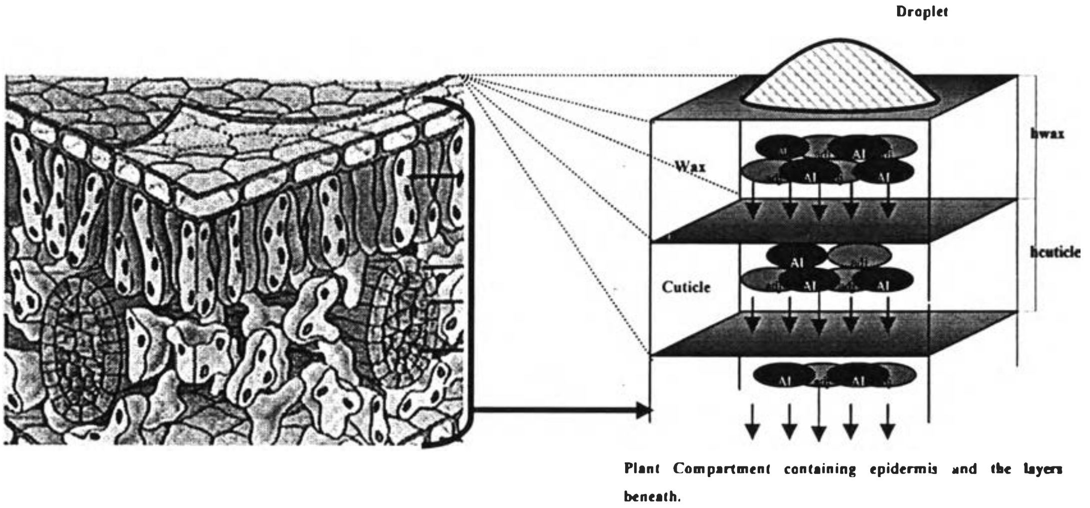

Figure 4.1. Diagrammatic representation of scenario modeled.

The model, which is developed, describes the uptake of pesticide and adjuvants into the leaf as a function of time. In order to model the whole scenario the leaf is divided into three compartments; wax, cuticle and plant compartment which have distinct diffusion coefficients and partition coefficients for both pesticide and surfactant. The droplet that consist of both active ingredient and adjuvant consist of uniformly distributed liquid phase, i.e.the concentration of Active ingredient and adjuvant are same all over the droplet. It acts as donor for both active ingredient and adjuvant. The active ingredient and adjuvant are assumed to be deposited on the leaf both as solid particles as well as dissolved molecules. Equilibrium conditions are assumed at the beginning of the simulation. This means that the concentration of dissolved active ingredient and adjuvant in the droplet is equal to the respective saturation concentration. The concentration in the wax, cuticle and plant are zero at this point. The dissolved active ingredient and adjuvant will penetrate the droplet/wax and wax/cuticle interface and than diffuse into the plant. This leaves the droplet concentration unchanged but reduces the mass of undissolved solids. It is assumed that the dissolution of solids is rapid process compared to diffusion into the plant. The rate of crystal dissolution is therefore not considered. The scenario described above is only applicable as long as we have solid phase remaining in contact with the droplet. When the last solid phase has disappeared the concentration of active ingredient and adjuvant in the droplet will decrease and the model equation will change. Now the reservoir of crystalline phase has been depleted and the only active ingredient and adjuvant left in the droplet is dissolved matter.

The model involves the two-decribed scenarios for active ingredient and adjuvant and the switch between them is made when the mass of solid active ingredient and adjuvant becomes zero.

The wax and cuticle layer were split into 15 equally sized sub compartments with a uniformly distributed liquid phase, i.e the concentrations of active ingredient and adjuvant is same all over the droplet. The division into separate layers is necessary to be able to solve the equations numerically with better accuracy. The equations are partial differential equations. The plant compartment acts as a big sink where the active ingredient and adjuvant is collected. In reality the number of droplets on the wax and cuticle surfaces influences the concentration in the plant because each droplet contributes to the total amount of matter in the plant compartment, since the plant compartment is relative large compared to the volume of droplet so the error introduced by, neglecting the number of droplets is very small. The assumptions made while developing the multi layer model are as follows;

- Active ingredient and surfactant are treated as two distinct compounds with independent concentrations. They don't interfere with each other in any way except through the diffusion coefficient of active ingredient, which is dependent on the concentration of surfactant.
- The saturation concentration of both active ingredient and surfactant is constant with respect to time.

- The partition between boundaries (droplet/wax, wax/cuticle and cuticle/plant) is instantaneous.
- Only dissolved matter diffuse into the leaf, solid matter doesn't penetrate the boundaries.
- The vapor pressure of active ingredient and surfactant are assumed to be zero.
- Crystal dissolution is rapid process compared to diffusion. This means that the droplet concentration is equal to saturation concentration as long as the solid phase exists.
- Diffusion only happens in one dimension that is perpendicular to the interface boundary; it is neglected in other directions.
- There is no concentration difference in the droplet; the dissolved matter is distributed uniformly.
- The influence of gravitational force is neglected.

4.1.1 Droplet Evaporation Model

The evaporation of droplet is very important factor, which might have a very large effect on the uptake of pesticide once the formulation had been sprayed over the leaf so it is essential to take it into account while the uptake model is developed. As we know that if the humidity is very low the evaporation rate will be very high, especially if the temperature is high. This could result in a situation where all the water has vaporized before the pesticide has been taken up by the plant. This would leave crystalline pesticide on the leaf, which cannot be taken up by the plant. The model scenario for evaporation of droplet can be seen in figure 4.2.

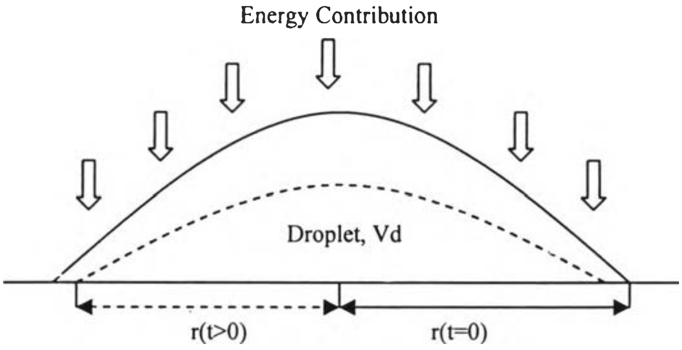

Figure 4.2 Model scenario for evaporation of droplet.

The model describes the evaporation of a water droplet as a function of time. The model takes into account that the droplet volume and area both can decrease and/or increase. Droplet evaporation is usually a quite rapid process; the final droplet volume is often reached within minutes. Normally the droplet doesn't vaporize completely but reaches a final volume, which could typically be 5-10% of the original volume (Bell, 2003). The final volume depends primarily on the composition of the formulation used.

Often it is seen that the droplet actually spreads out on the leaf after it has been applied. It is also seen that the droplet area decreases as evaporation is taking place. The droplet volume will normally decrease because of evaporation but it is also possible that it increases. This could happen in the evening or at the night when dew starts to set on the leaf. The model accounts for those phenomena through the surface and volume factors which are described in model derivation.

It is assumed that the energy contribution to then droplet is proportional to the surface area, which is covered by the droplet. There is no restriction on where the supplied energy can come from; it could be solar radiation and /or heat transfer from the surroundings. In this model there is no energy supply parameter. Instead the starting and final area and volume must be set parameters. The final time where the area and volume have reached their final values must be known. An assumption is made that the conditions for the energy contribution do not change during the simulation time. There are no restrictions on what shape the droplet can have, any ratio between volume and surface is possible. This model doesn't predicts final area or volume but how the volume and surface area is changing with time when their final values are known. The assumptions is made that the droplet only consists of water, all other compounds are neglected. The physical properties of the water are constant, i.e independent of temperature and the presence of other substance. It is also assumed that all energy provide is used to vaporize water. This implies that the temperature of the system is constant and its not changing even though energy is supplied to the droplet.

It is assumed that droplet area is changing linearly with time. This assumption is completely arbitrary. The droplet surface as a function of time can be written as;

$$S(t) = S_0 + k.t \tag{4.1}$$

At final time t_f, the area has reached its final value;

$$S_f = S_0 + k.t_f \tag{4.2}$$

The surface factor, sf, is defined as;

$$s_f = S_f / S_0 \tag{4.3}$$

From equation (4.2) the constant k can be isolated and substituted in equation (4.1). Together with the equation (4.3), it gives us;

$$S(t) = S_0\left(1 + \left(s_f - 1\right).\frac{t}{t_f}\right) \tag{4.4}$$

Enthalpy Balance:

An Enthalpy balance of the system could be written as;

$$H_{in} + H_{prod} = H_{out} + H_{acc} \tag{4.5}$$

Where;

H_{in} is the Enthalpy supplied to the droplet.

H_{prod} is equal to the negative value of the enthalpy used for evaporation.

H_{out} is set to zero because heat transfer to the surroundings is neglected.

H_{acc} is zero because the temperature of droplet is constant.

With respect to time each of above four terms can be written as,

$$\frac{dH_{in}}{dt} = P = P_{specific}.S(t) \tag{4.6}$$

$P_{specific}$ denotes the enthalpy supplied to the droplet per unit area. The unit in SI system will be $W/m^2 = J^{s-1}m^{-2}$, This value is assumed to be constant and it is calculated out from the supplied parameters.

$$\frac{dH_{prod}}{dt} = -\frac{dH(Evaporation)}{dt} = \frac{d(mJ)}{dt} = -L.\frac{dm}{dt} = -L.\rho.\frac{dV}{dt} \tag{4.7}$$

m is the mass of droplet and L is specific enthalpy of vaporization which is assumed to be constant. The mass of droplet can be written as density of droplet multiplied by volume ($m=\rho.V$), where it is assumed at the density of droplet is also constant.

The two terms on RHS of equation (4.5) are zero and therefore the total enthalpy balance in units of energy per time becomes;

$$P_{specific}.S(t) - L.\rho.\frac{dV}{dt} = 0 \tag{4.8}$$

This can be written as;

$$\frac{-L.\rho}{P_{specific}}.\frac{dV}{dt} = S(t) \tag{4.9}$$

The surface area as a function of time is given by equation (4.4) so integration of the above equation gives:

$$\int_{V=V_0}^{V} \frac{-L.\rho}{P_{specific}}.dV = \int_{t=0}^{t} S_0\left(1+\left(s_f-1\right).\frac{t}{t_f}\right).dt \Leftrightarrow \tag{4.10}$$

$$\frac{-L.\rho}{P_{specific}}.\left(V-V_0\right) = S_0\left(t+.\frac{\left(s_f-1\right)}{2t_f}.t^2\right) \tag{4.11}$$

At final time, t_f we have $V=V_f$

$$\frac{-L.\rho}{P_{specific}}.\left(V_f - V_0\right) = S_0\left(t + .\frac{\left(s_f - 1\right)}{2t_f}.t^2\right) \Leftrightarrow \tag{4.12}$$

$$\frac{-L.\rho}{P_{specific}} = \left(\frac{S_0.t_f}{2\left(V_f - V_0\right)}.\left(s_f + 1\right)\right) \tag{4.13}$$

The LHS of equation (4.13) is substituted in equation (4.11) to obtain the following equation;

$$\frac{S_0.t_f}{2\left(V_f - V_0\right)}.\left(s_f + 1\right).\left(V - V_0\right) = S_0\left(t + .\frac{\left(s_f - 1\right)}{2t_f}.t^2\right) \tag{4.14}$$

The volume factor v_f is defined in similar way as surface factor s_f;

$$v_f = \frac{V_f}{V_0} \tag{4.15}$$

It is simple the ratio between final volume and initial volume and in substituted in equation (4.14) to give,

$$\frac{S_0.t_f}{2.V_0\left(v_f - 1\right)}.\left(s_f + 1\right).\left(V - V_0\right) = S_0\left(t + .\frac{\left(s_f - 1\right)}{2t_f}.t^2\right) \tag{4.16}$$

The final expression for the volume of droplet as a function of time is the following,

$$V_d = V_0 - \left\{\frac{2V_0\left(1 - v_f\right)}{t_f\left(1 + s_f\right)}\left(1 + \frac{\left(s_f - 1\right)}{2t_f}.t\right).t\right\} \tag{4.17}$$

4.1.1.1 Representation in MoT

The volume is a polynomial function of time so differentiating it with respect to time will leave the time as an explicit variable. It is therefore necessary to calculate the time as a dependent variable. This is done by equation:

dt=1

The Surface area of droplet is calculated as,

S=S0*(1+(sf-1)*t/tf)*post (tf-t)+S0*sf*(1-post(tf-t))

The equation has two parts the first part contains equation (5.7) and is only active when t<tf, here the post command is evaluated to one. The second part is active when t>tf and gives constant surface area.

Similarly droplet volume is calculated using equation (5.20) and is divided into two parts to handle time greater and smaller than tf.

Vd=(V0-(2*V0/tf)*((1-vf)/(1+sf))*(1+t*(sf-1)/(2*tf))*t)*post(tf-t)+vf*V0*(1-post(tf-t))

4.1.1.2 Estimation of Evaporation Rate

In this evaporation model the necessary inputs are: initial volume (V0), initial surface area (S0), volume factor (vf), surface factor (sf) and final time (tf).

Under typical circumstances it will take a droplet around 10 minutes to evaporate to its final volume. This means that tf must be set to 1/6th of an hour(0.166 hr).If the droplet volume is reduced to 10% of its original volume the volume factor is set to 0.1.If the final surface area is twice as large as the initial one the surface factor is set to 2.0.An example of result using these values is shown below in figure (4.3).

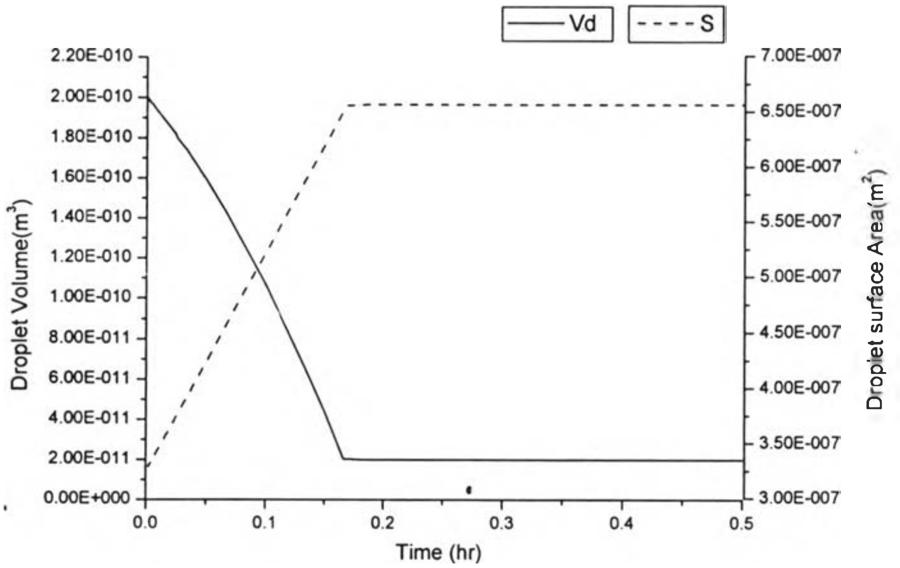

Figure 4.3 Droplet Volume (Vd) and Surface area (S) vs. time for evaporation of water

4.1.2 Mass Balances

a) Active Ingredient in Droplet: Solubility Model

The work done in the past was not able to account for the solubilisation of the pesticide into the water droplet by the adjuvant because that is going to change the concentration gradient between the droplet and the top wax layer of the leaves and hence the rate of uptake will be altered (Baur *et al.*, 1997a & 1997b). Solubility of pesticide in the water droplet, the leaf wax, the cutin and the underlying part should also be dependent on the concentration of the adjuvant in each layer (Hess, 2000) however it is not known at this point how critical each layer would be. The solubility of the pesticide in the water droplet can be estimated from its solubility in water, its solubility in pure adjuvants and their compositional ratio. Therefore the solubility of the pesticide in the pure adjuvant is added as a parameter in the model. The solubility of some pesticide in the C13 adjuvants has been estimated in the literature and has been extracted. Figure 4.4 shows the scenario of droplet at times t1 and t2 containing active ingredient and adjuvant. The mass balance was made for active ingredient within droplet at times t1 and t2.and it was assumed that the droplet volume is not changing with time and the concentration of Active Ingredient at time t1 is more than at time t2.

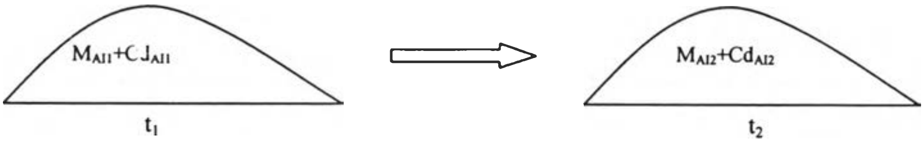

Figure 4.4 Scenario of droplet at times t1 and t2.

$$M_{AI1} + (Cd_{AI1}.V_d) = M_{AI2} + (Cd_{AI2}.V_d) + D_{wax}.S.\left.\frac{dC_{AI}}{dx}\right|_{x=0}.\Delta t \qquad (4.18)$$

$$M_{AI1} + (Cd_{AI1}.V_d) = M_{AI2} + (Cd_{AI2}.V_d) + D_{wax}.S.\left(\frac{C_1 - C_0}{h_{wax}}\right).\Delta t \qquad (4.19)$$

$$M_{AI2} - M_{AI1} = - D_{wax}.S.\left(\frac{C_1 - C_0}{h_{wax}}\right).\Delta t + V_d\left(Cd_{AI1} - Cd_{AI2}\right) \qquad (4.20)$$

$$\frac{M_{AI2} - M_{AI1}}{\Delta t} = -D_{wax}.S.\left(\frac{C_1 - C_0}{h_{wax}}\right) + \frac{Vd.(Cd_{AI1} - Cd_{AI2})}{\Delta t} \tag{4.21}$$

Taking $Lim_{\Delta t \to 0}$

$$\frac{dM_{AI}}{dt} = \frac{-D_{wax}.S.(C_1 - C_0)}{h_{wax}} + Vd.\frac{dCd_{AI}}{dt} \tag{4.22}$$

Where;

M_{AI} is moles of solid component of active ingredient (AI) at any time (*moles*).

D_{wax} is the diffusivity of AI in wax (m^2/s).

S is the surface area of droplet (m^2).

h_{wax} is the thickness of each layer in wax(m)

C_1, C_0 are the concentrations of AI in zeroth and 1st wax layer (*moles/* m^3).

V_d is the volume of droplet (m^3).

Cd_{AI} is the concentration of AI in droplet at any time (*moles/* m^3).

It is assumed that the solubility of the active ingredient will depend on the volume fraction of adjuvant and water present in the droplet therefore correlation given in equation (4.23) was proposed in order to calculate the solubility.

$$S_{droplet} = S_{water} * vfr_{water} + S_{adj} * vfr_{adj} \tag{4.23}$$

$S_{droplet}$ is the solubility of AI in water droplet (g/l).

S_{water} is the solubility of AI in water (g/l).

S_{adj} is the solubility of AI in adjuvant (g/l).

vfr_{adj} is the volume fraction of adjuvant in droplet.

$vfr_{water} = 1 - vfr_{adj}$,is the volume fraction of water in droplet.

Therefore,

$$vfr_{adj} = \frac{Volume\ of\ adjuvant\ in\ Droplet}{Total\ Volume\ of\ Droplet} \tag{4.24}$$

$$vfr_{adj} = \frac{(Cdadj.Vd + Madj).MWadj}{\rho_{adj}.Vd} \tag{4.25}$$

$$vfr_{water} = 1 - \frac{(Cdadj.Vd + Madj).MWadj}{\rho_{adj}.Vd} \tag{4.26}$$

$$S_{droplet} = S_{water}\,(1 - \frac{(Cdadj.Vd + Madj).MWadj}{\rho_{adj}.Vd}) + S_{adj}\,(\frac{(Cdadj.Vd + Madj).MWadj}{\rho_{adj}.Vd}) \tag{4.27}$$

$$S_{droplet} = S_{water} + \frac{(S_{adj} - S_{water}).MWadj}{\rho_{adj}.Vd}.(Cdadj.Vd + Madj) \tag{4.28}$$

$$\frac{dS_{droplet}}{dt} = \left(\frac{(S_{adj} - S_{water}).MWadj}{\rho_{adj}.Vd}\right).\left(Vd.\frac{dCdadj}{dt} + \frac{dMadj}{dt}\right) \tag{4.29}$$

We know that,

$$CdAI = \left(\frac{1000}{MWAI}\right).S_{droplet} \quad \text{, Taking differential} \tag{4.30}$$

$$\frac{dCdAI}{dt} = \frac{1000}{MWAI}.\frac{dS_{droplet}}{dt} \tag{4.31}$$

Therefore substituting the equation (4.29) into equation (4.31) we get equation (4.32)

$$\frac{dCd_{AI}}{dt} = 1000 * \left(\frac{MW_{adj}}{MW_{AI}}\right) * \left(\frac{(S_{adj} - S_{water})}{\rho_{adj} * Vd}\right) * \left(Vd * \frac{dCd_{adj}}{dt} + \frac{dM_{adj}}{dt}\right) \tag{4.32}$$

Equation (4.32) and equation (4.22) where used in the MoT model in order to take into account the solubilisation of the pesticide into the water droplet by the adjuvant.

b) Active Ingredient in Wax and Cuticle: Multilayer Model

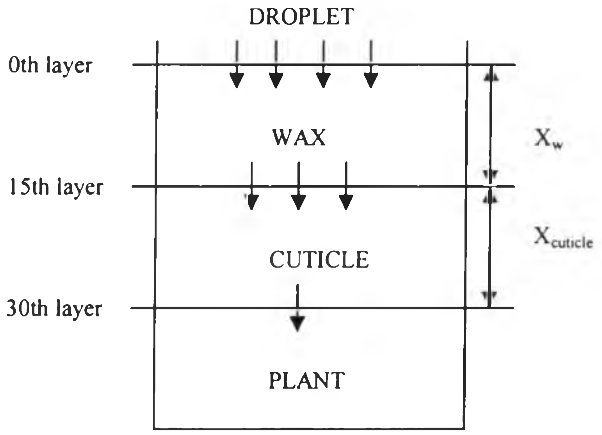

Figure 4.5 Scenario for Multilayer Model.

The concentration of active ingredient in the zeroth layer of wax is calculated using the partition coefficient between the wax and the droplet, K_{wdAI}. Equation (4.33) is used in the model to calculate $C_{adj,0}$.

$$C_{adj,0} = K_{wdAI}.Cd_{AI} \tag{4.33}$$

Figure (4.5) above shows the number of layers in which each compartment has been discretisized and therefore mass balances were made on each layers of wax as well as cuticle.

i) Mass balance for Layers 1 through 14.

A general mass balance is made to calculate concentration of active ingredient in each layers, the diffusion in and out of each layers is described by Fick's Law of diffusion, which is as follows,

$$J = -D.\frac{dC}{dx} \tag{4.34}$$

Where,

$$J = flux\left(\frac{moles}{m^2.s}\right)$$

$$D = Diffusivity\left(\frac{m^2}{s}\right)$$

$$\frac{dC}{dx} = Concentration - Gradient\left(\frac{moles/m^3}{m}\right)$$

$D_{AI,wax}$ is used as diffusion coefficient for active ingredient in wax layers and the expression for it is given in section (2.2.5).

The mole balance for n layer of wax is given as,

$$\text{In-Out=Accumulated} \tag{4.35}$$

$$In = -D_{AI,wax}.S.\left.\frac{dC_{AI}}{dx}\right|_{x=n} \tag{4.36}$$

$$Out = -D_{AI,wax}.S.\left.\frac{dC_{AI}}{dx}\right|_{x=n+1} \tag{4.37}$$

$$Accumulated = \frac{dN_n}{dt} = S.h_{wax}.\frac{dC_{AI,n}}{dt} \tag{4.38}$$

Where, S is the surface area of droplet, h_{wax} is the thickness of each wax layers, N_n is number of moles of active ingredient and $C_{AI,n}$ is concentration of active ingredient in nth layer of wax.

Substituting the equations (4.36), (4.37) and (4.38) in equation (4.35) gives the following,

$$-D_{AI,wax}.S.\left.\frac{dC_{AI}}{dx}\right|_{x=n} - \left(-D_{AI,wax}.S.\left.\frac{dC_{AI}}{dx}\right|_{x=n+1}\right) = S.h_{wax}.\frac{dC_{AI,n}}{dt} \tag{4.39}$$

The two concentration gradient terms are rewritten as:

$$\left.\frac{dC_{AI}}{dx}\right|_{x=n} \square \frac{C_{AI,n} - C_{AI,n-1}}{h_{wax}} \tag{4.40}$$

$$\left.\frac{dC_{AI}}{dx}\right|_{x=n+1} \square \frac{C_{AI,n+1} - C_{AI,n}}{h_{wax}} \tag{4.41}$$

Equation (4.39) can be written as,

$$-D_{AI,wax}.S\left(\frac{C_{AI,n} - C_{AI,n-1} - \left(C_{AI,n+1} - C_{AI,n}\right)}{h_{wax}}\right) = S.h_{wax}.\frac{dC_{AI,n}}{dt} \tag{4.42}$$

Therefore the final equation becomes,

$$\frac{dC_{AI,n}}{dt} = \frac{D_{AI,wax}}{h_{wax}^{\ 2}}\left(C_{AI,n+1} - 2C_{AI,n} + C_{AI,n-1}\right) \text{ Where n=1 to 14} \tag{4.43}$$

In equation (4.43) the value of n is taken from 1 to 14 to obtain differential equation for each layer in wax. All the equations obtained below have been put into the model to get concentration of active ingredient in each layer.

ii) Mass balance for 15th layer.

The mass balance in 15th layer can be written as,

$$\text{In-Out=Accumulated} \tag{4.44}$$

Where,

$$In = -D_{AI,wax}.S.\left.\frac{dC_{AI}}{dx}\right|_{x=15} \tag{4.45}$$

$$Out = -D_{AI,wax}.S.\left.\frac{dC_{AI}}{dx}\right|_{x=16} \tag{4.46}$$

$$Accumulated = \frac{dN_{15}}{dt} = S.h_{wax}.\frac{dC_{AI,15}}{dt} \tag{4.47}$$

The two concentration gradient terms are rewritten as:

$$\left.\frac{dC_{AI}}{dx}\right|_{x=15} \square \frac{C_{AI,15}-C_{AI,14}}{h_{wax}} \tag{4.48}$$

$$\left.\frac{dC_{AI}}{dx}\right|_{x=16} \square \frac{K_{wc,AI}.C_{AI,16}-C_{AI,15}}{h_{wax}} \tag{4.49}$$

In equation (4.49) $C_{AI,16}$ is multiplied with cuticle/wax partition coefficient ($K_{wc,AI}$) because the 16th layer is in the cuticle and the driving force for diffusion is the concentration difference that would be observed if both layers were in the wax. Therefore, The final equation for 15th layer becomes,

$$\frac{dC_{AI,15}}{dt} = \frac{D_{AI,wax}.B}{h^2_{wax}}.(K_{wc,AI}.C_{AI,16} - 2.C_{AI,15} + C_{AI,14}) \tag{4.50}$$

iii) Mass balance for 16th layer.

The 16th layer represents the starting layer of the cuticle. In equation (4.44) the out term of 15th layer is similar to the in term in 16th layer. The diffusion coefficient in the out term is of Cuticle because 16th layer is situated in cuticle. The approximation for diffusion gradient will be:

$$\left.\frac{dC_{AI}}{dx}\right|_{x=16} \square \frac{K_{wc,AI}.C_{AI,16}-C_{AI,15}}{h_{wax}} \tag{4.51}$$

$$\left.\frac{dC_{AI}}{dx}\right|_{x=17} \square \frac{C_{AI,17}-C_{AI,16}}{h_{cut}} \tag{4.52}$$

Therefore,

$$In = -D_{AI,wax}.S\left(\frac{K_{wc,AI}.C_{AI,16} - C_{AI,15}}{h_{wax}}\right) \quad (4.53)$$

$$Out = -D_{AI,cut}.S\left(\frac{C_{AI,17} - C_{AI,16}}{h_{cut}}\right) \quad (4.54)$$

$$Accumulated = \frac{dN_{16}}{dt} = S.h_{cut}.\frac{dC_{AI,16}}{dt} \quad (4.55)$$

The final equation for 16th layer becomes,

$$\frac{dC_{AI,16}}{dt} = \left(\frac{D_{AI,cut}}{h_{cut}^{2}}\left(C_{AI,17} - C_{AI,16}\right)\right) - \left(\frac{D_{AI,wax}}{h_{cut}.h_{wax}}\left(K_{wc,AI}.C_{AI,16} - C_{AI,15}\right)\right) \quad (4.56)$$

iv) Mass balance for layers 17 through 30.

The equation for layers 17 to 30 have same structure as for layers 1 to 14.A generalized equation (4.46) is used except for difference that now these layers are in cuticle section therefore the diffusion coefficient and the thickness of each layer will be taken in cuticle.

Equation (4.46) can be generalized for cuticle section in equation (4.57),

$$\frac{dC_{AI,n}}{dt} = \frac{D_{AI,cut}}{h_{cut}^{2}}\left(C_{AI,n+1} - 2C_{AI,n} + C_{AI,n-1}\right) \quad (4.57)$$

In equation (4.57) the value of n is taken from 17 to 30 to obtain equation for each layer in cuticle. All the equations obtained were put into the model to get concentration of active ingredient in each layer.

c) Active ingredient in Plant

The concentration of active ingredient in the plant is calculated using the partition coefficient between the cuticle and the plant, K_{cpAI}. Equation (4.58) is used in the model to calculate Cp_{AI}.

$$Cp_{AI} = K_{cpAI}.C_{AI,30} \quad (4.58)$$

d) Adjuvant in Droplet

A mass balance for the number of dissolved moles of adjuvant in the droplet can be written as,

$$\text{Accumulated}=\text{In}-\text{Out} \tag{4.59}$$

Accumulated is the increase in number of dissolved moles in droplet, this is equal to the product of droplet concentration and droplet volume of adjuvant. The In term is the negative of increased in solid matter in droplet and the Out term is the number of moles which have diffused out of droplet. With respect to time, equation (4.59) can be written as,

$$\frac{d\left(C_{d,adj}.V_d\right)}{dt}=-\frac{dM_{adj}}{dt}+D_{adj,wax}.S\left.\frac{dC_{adj}}{dx}\right|_{x=0} \tag{4.60}$$

The diffusion gradient term on RHS of equation (4.60) is approximated as,

$$\left.\frac{dC_{adj}}{dx}\right|_{x=0}=\frac{C_{adj,1}-C_{adj,0}}{h_{wax}} \tag{4.61}$$

Where $C_{adj,1}, C_{adj,0}$ are concentration of adjuvant in zeroth and first layer of wax and h_{wax} is thickness of each layer in wax.

In first scenario the droplet concentration is constant in equation (4.60) is therefore written as;

$$C_{d,adj}\frac{dV_d}{dt}=-\frac{dM_{adj}}{dt}+\left(\frac{C_{adj,1}-C_{adj,0}}{h_{wax}}\right)\Leftrightarrow\frac{dM_{adj}}{dt}=D_{adj,wax}.S.\left(\frac{C_{adj,1}-C_{adj,0}}{h_{wax}}\right)-C_{d,adj}\frac{dV_d}{dt} \tag{4.62}$$

The droplet volume differentiated with respect to time can be derived in this way,

$$\frac{dV_d}{dt}=\frac{d\left\{V_0-\frac{2V_0}{t_f}.\frac{(1-vf)}{(1+s_f)}\left(1+\frac{(s_f-1)}{2t_f}.t\right).t\right\}}{dt} \tag{4.63}$$

Therefore, $$\frac{dV_d}{dt}=-\frac{2V_0}{t_f}.\frac{(1-vf)}{(1+s_f)}\left[\left(1+\frac{(s_f-1)}{2t_f}.t\right)+\left(\frac{(s_f-1)}{2t_f}\right).t\right] \tag{4.64}$$

$$\frac{dV_d}{dt}=-\frac{2V_0}{t_f}.\frac{(1-vf)}{(1+s_f)}\left(1+\frac{(s_f-1)}{t_f}.t\right) \tag{4.65}$$

Substituting the equation (4.65) in equation (4.62) we obtain,

$$\frac{dM_{adj}}{dt} = D_{adj,wax}.S.\left(\frac{C_{adj,1} - C_{adj,0}}{h_{wax}}\right) + C_{d,adj}.\frac{2V_0}{t_f}.\frac{(1 - vf)}{(1 + s_f)}\left(1 + \frac{(s_f - 1)}{t_f}.t\right) \tag{4.66}$$

Equation (4.66) is valid for time smaller than final time of evaporation. In MoT the above equation is multiplied by post (t-tf).

In second scenario the solid adjuvant is constant so equation (4.60) can be rewritten as,

$$\frac{dC_{d,adj}}{dt} = \frac{D_{adj,wax}.S}{V_d}\left.\frac{dC_{adj}}{dx}\right|_{x=0} - \frac{C_{d,adj}}{V_d}.\frac{dV_d}{dt} \tag{4.67}$$

or

$$\frac{dC_{d,adj}}{dt} = \left(\frac{D_{adj,wax}.S}{V_d}.\left(\frac{C_{adj,1} - C_{adj,0}}{h_{wax}}\right)\right) + \frac{C_{d,adj}}{V_d}.\frac{2V_0}{t_f}.\frac{(1 - vf)}{(1 + s_f)}\left(1 + \frac{(s_f - 1)}{t_f}.t\right) \tag{4.68}$$

e) Adjuvant in Wax/Cuticle layers

The concentration of adjuvant in the zeroth layer of wax is calculated using the partition coefficient between the wax and the droplet. Equation (4.69) is used in the model to calculate $C_{adj,0}$.

$$C_{adj,0} = K_{wdadj}.Cd_{adj} \tag{4.69}$$

i) Mass balance for Layers 1 through 14.

A general mass balance is made to calculate concentration of adjuvant in each layers. The mass balances is similar to one made for active ingredient, the diffusion in and out of each layers is described by Fick's Law of diffusion, which is as follows,

$$J = -D.\frac{dC}{dx} \tag{4.70}$$

Where,

$J = flux\left(\frac{moles}{m^2.s}\right)$

$D = Diffusivity\left(\frac{m^2}{s}\right)$

$\frac{dC}{dx} = Concentration - Gradient\left(\frac{moles/m^3}{m}\right)$

$D_{adj,wax}$ is used as diffusion coefficient for adjuvant in wax layers.

The mole balance for n^th^ layer of wax is given as,

$$\text{In-Out=Accumulated} \tag{4.71}$$

$$In = -D_{adj,wax}.S.\left.\frac{dC_{adj}}{dx}\right|_{x=n} \tag{4.72}$$

$$Out = -D_{adj,wax}.S.\left.\frac{dC_{adj}}{dx}\right|_{x=n+1} \tag{4.73}$$

$$Accumulated = \frac{dN_n}{dt} = S.h_{wax}.\frac{dC_{adj,n}}{dt} \tag{4.74}$$

Where, S is the Surface area of droplet, h_{wax} is the thickness, N_n is number of moles and $C_{adj,n}$ is concentration of adjuvant in nth layer of wax.

Substituting the equations (4.72), (4.73) and (4.74) in equation (4.71) gives the following,

$$-D_{adj,wax}.S.\left.\frac{dC_{adj}}{dx}\right|_{x=n} - \left(-D_{adj,wax}.S.\left.\frac{dC_{adj}}{dx}\right|_{x=n+1}\right) = S.h_{wax}.\frac{dC_{adj,n}}{dt} \tag{4.75}$$

The two concentration gradient terms are rewritten as:

$$\left.\frac{dC_{adj}}{dx}\right|_{x=n} \square \frac{C_{adj,n} - C_{adj,n-1}}{h_{wax}} \tag{4.76}$$

$$\left.\frac{dC_{adj}}{dx}\right|_{x=n+1} \square \frac{C_{adj,n+1} - C_{adj,n}}{h_{wax}} \tag{4.77}$$

Equation (4.77) can be written as,

$$-D_{adj,wax}.S\left(\frac{C_{adj,n} - C_{adj,n-1} - \left(C_{adj,n+1} - C_{adj,n}\right)}{h_{wax}}\right) = S.h_{wax}.\frac{dC_{adj,n}}{dt} \tag{4.78}$$

Therefore the final equation becomes,

$$\frac{dC_{adj,n}}{dt} = \frac{D_{adj,wax}}{h_{wax}^{2}}\left(C_{adj,n+1} - 2C_{adj,n} + C_{adj,n-1}\right) \tag{4.79}$$

In equation (4.79) the value of n is taken from 1 to 14 to obtain equation for each layer in wax. All the equations obtained below have been put into the model to get concentration of adjuvant in each layer.

ii) Mass balance for 15th layer.

The mass balance in 15th layer can be written as,

$$\text{In-Out=Accumulated} \tag{4.80}$$

Where,

$$In = -D_{adj,wax}.S.\left.\frac{dC_{adj}}{dx}\right|_{x=15} \tag{4.81}$$

$$Out = -D_{adj,wax}.S.\left.\frac{dC_{adj}}{dx}\right|_{x=16} \tag{4.82}$$

$$Accumulated = \frac{dN_{15}}{dt} = S.h_{wax}.\frac{dC_{adj,15}}{dt} \tag{4.83}$$

The two concentration gradient terms are rewritten as:

$$\left.\frac{dC_{adj}}{dx}\right|_{x=15} \square \frac{C_{adj,15} - C_{adj,14}}{h_{wax}} \tag{4.84}$$

$$\left.\frac{dC_{adj}}{dx}\right|_{x=16} \square \frac{K_{wc,adj}.C_{adj,16} - C_{adj,15}}{h_{wax}} \tag{4.85}$$

In equation (4.85) $C_{adj,16}$ is multiplied with cuticle/wax partition coefficient ($K_{wc,adj}$) because the 16th layer is in the cuticle and the driving force for diffusion is the concentration difference that would be observed if both layers were in the wax.

iii) Mass balance for 16th layer.

The 16th layer represents the starting layer of the cuticle. In equation (4.80) the out term of 15th layer is similar to the in term in 16th layer. The diffusion coefficient in the out term is of Cuticle because 16th layer is situated in cuticle. The approximation for diffusion gradient will be:

$$\left.\frac{dC_{adj}}{dx}\right|_{x=16} \square \frac{K_{wc,adj}.C_{adj,16} - C_{adj,15}}{h_{wax}} \tag{4.86}$$

$$\left.\frac{dC_{adj}}{dx}\right|_{x=17} \square \frac{C_{adj,17} - C_{adj,16}}{h_{cut}} \tag{4.87}$$

Therefore,

$$In = -D_{adj,wax}.S\left(\frac{K_{wc,adj}.C_{adj,16} - C_{adj,15}}{h_{wax}}\right) \tag{4.88}$$

$$Out = -D_{adj,cut}.S\left(\frac{C_{adj,17} - C_{adj,16}}{h_{cut}}\right) \tag{4.89}$$

$$Accumulated = \frac{dN_{16}}{dt} = S.h_{cut}.\frac{dC_{adj,16}}{dt} \tag{4.90}$$

The final equation for 16th layer becomes,

$$\frac{dC_{adj,16}}{dt}=\left(\frac{D_{adj,cut}}{h_{cut}^{2}}\left(C_{adj,17}-C_{adj,16}\right)\right)-\left(\frac{D_{adj,wax}}{h_{cut}.h_{wax}}\left(K_{wc,adj}.C'_{adj,16}-C_{adj,15}\right)\right) \qquad (4.91)$$

iv) Mass balance for layers 17 through 30.

The equation for layers 17 to 30 have same structure as for layers 1 to 14.A generalized equation (4.91) is used except for difference that now these layers are in cuticle section therefore the diffusion coefficient and the thickness of each layer will be taken in cuticle.

Equation (4.91) can be generalized for cuticle section in the following equation.

$$\frac{dC_{adj,n}}{dt}=\frac{D_{adj,cut}}{h_{cut}^{2}}\left(C_{adj,n+1}-2C_{adj,n}+C_{adj,n-1}\right) \qquad (4.92)$$

In equation (4.92) the value of n is taken from 17 to 30 to obtain equation for each layer in cuticle. All the equations obtained were put into the model to get concentration of adjuvant in each layer similar to one done for active ingredient.

f) Active ingredient in Plant

The concentration of adjuvant in the plant is calculated using the partition coefficient between the cuticle and the plant, K_{cpAI}. Equation (4.93) is used in the model to calculate Cp_{adj}.

$$Cp_{adj}=K_{cpadj}.C_{adj,30} \qquad (4.93)$$

The main equations of the model are presented in figure 4.6 together with a schematic representation of the scenario modeled.

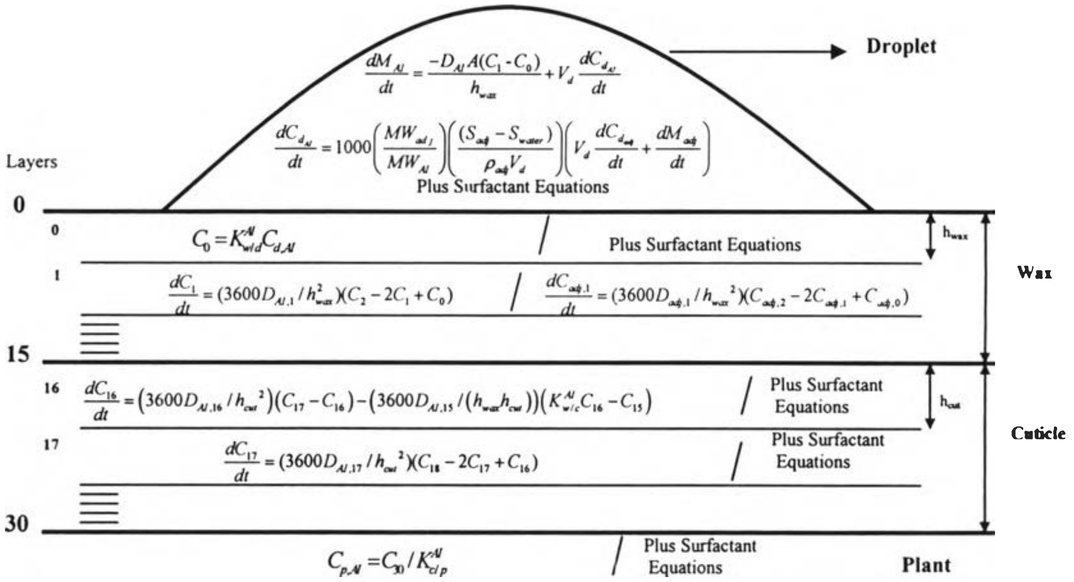

Figure 4.6 Pesticide uptake: scenario modeled and equations.

4.1.3 Uptake Definition

The total uptake ($Uptake_{AI,total}$) is defined as the total number of moles which is taken up by the cuticle and the plant. It is the number of moles, which are not located in the droplet. The cuticle uptake ($Uptake_{AI,cuticle}$) is defined as the number of moles located in the cuticle and the plant uptake is similarly defined as the number of moles located in the plant compartment.

These three definitions can be expressed for both active ingredient and adjuvant through the following equations, which were used in MoT model for predicting the uptake behavior of both active ingredient and adjuvant.

i) Active Ingredient

$$Uptake_{AI,total} = M_{AI,total} - M_{AI} - Cd_{AI}.V_d \tag{4.94}$$

$$Uptake_{AI,cuticle} = M_{AI,total} - M_{AI} - Cd_{AI}.V_d - Cp_{AI}.V_p \tag{4.95}$$

$$Uptake_{AI,plant} = Cp_{AI}.V_p \tag{4.96}$$

The relative uptake of active ingredient is defined as the ratio of the total uptake to the total active ingredient spread initially over the leaf.

$$\mathrm{Re}\,lUptake = \frac{Uptake_{AI,total}}{M_{AI,total}} \quad (4.97)$$

ii) Adjuvant

$$Uptake_{adj,total} = M_{adj,total} - M_{adj} - Cd_{adj}.V_d \quad (4.98)$$

$$Uptake_{adj,cuticle} = M_{adj,total} - M_{adj} - Cd_{adj}.V_d - Cp_{adj}.V_p \quad (4.99)$$

$$Uptake_{adj,plant} = Cp_{adj}.V_p \quad (4.100)$$

The relative uptake of adjuvant is similarly defined as the ratio of the total uptake to the total adjuvant spread initially over the leaf.

$$\mathrm{Re}\,lUptake = \frac{Uptake_{adj,total}}{M_{adj,total}} \quad (5.103)$$