CHAPTER III
LITERATURE REVIEW

3.1 Background Theory

The leaf consists of distinct parts with different properties and function so as to study the uptake of pesticides by leafs it is necessary to the study the physiology of leafs. Figure 3.1 shows the diagrammatic representation of various parts of leaf.

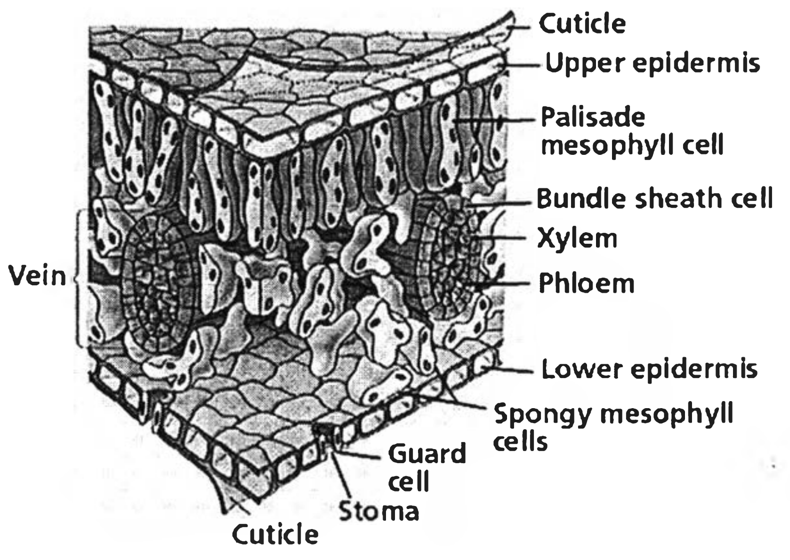

Figure 3.1 Diagrammatic representation of various parts of leaf.

The leaf is the primary photosynthetic organ of the plant. It consists of a flattened portion, called the blade that is attached to the plant by a structure called the petiole. Sometimes leaves are divided into two or more sections called leaflets. Leaves with a single undivided blade are called simple, those with two or more leaflets are called compound. The outer layer of the leaf is called cuticle and it serves several purposes. The main function is to be a barrier for penetration of water and gases into and out of plant as well as protecting the plant against diseases (Trapp *et al.*, 1995). The cuticle covers the largest part above ground surface of crop and weed plants and consequently, often plays an important role during the foliar uptake of agrochemicals. This extra cellular lipid membrane consists of biopolymer cutin and associated cuticular waxes (Baker, 1982). Cuticular waxes constitute the upper layer of leaf also referred to as epicuticular layer and provide the main barrier controlling the rate of transcuticular diffusion of active ingredients (Kirkwood, 1999). Waxes are semi crystalline solids and, therefore, solubility and mobility of organic solutes in cuticular waxes are fairly low (Burghardt *et al.*, 1998) The next layer between epicuticular waxes and plant compartment is cuticular layer, which primarily consist of long chain alcohols. The leaf also has tiny holes within the epidermis called stomata. Specialized cells, called guard cells surround the stomata and are shaped like two cupped hands. Changes within water pressure cause the stoma (singular of stomata) to open or close. If the guard cells are full of water, they swell up and bend away from each other, which opens the stoma. During dry times, the guard cells are close in this way the transport of gases and evaporation of water is controlled by stomata. For modeling purposes the epidermis and the underlying layers in the leaf are treated as one single compartment called plant compartment

A brief description of the different layers and properties with respect to the modeling of uptake of pesticides is as follows;

3.1.1 Epicuticular Wax

The epicuticular wax layer is the upper layer on the leaf. Its purpose is to prevent evaporation of water from the droplet. The fact that it prevents water from evaporating means that it is an effective barrier for water diffusing into the leaf. The pesticide formulations are aqueous solutions and the major resistance for uptake is found to be in the wax layer (Briggs *et al.*, 1994). Once the wax layer has been penetrated the diffusion into the plant is relatively fast. The wax layer contains some pores and cracks, which allow some diffusion, but it is very slow. The structure and thickness of the wax layer varies very much from plant to plant. For barley a typical wax thickness is approximately 0.2μm but it also depends on the age of the plant and the position on the leaf. Cuticular waxes are complex structures containing long chain hydrocarbons, alcohols, aldehydes, ketones, fatty and hydroxyl-fatty acids and esters.

The diffusion coefficient through the wax layer and the partition coefficient between the droplet and the wax are very important modeling parameters. The droplet consists mainly of water so the ratio of pesticide concentration in the cuticle and droplet is governed by cuticle/water partition coefficient, which is expressed as;

$$K_{wax/water} = \frac{c_{wax}}{c_{water}} \tag{3.1}$$

3.1.2 Cuticular Layer

The cuticular layer is situated between the epicuticular wax and the plant compartment. It is responsible for preventing gases to diffuse in and out of the plant. The cuticular layer is composed of cutin, which mainly consists of long chain alcohols.

The diffusion coefficient through the cuticluar layer and the partition coefficients are important parameters for modeling the transport of matter through the cuticular layer. The ratio of concentration in epicuticular wax closest to cuticular layer and cuticle itself is governed by wax/cuticle partitioning coefficient, which is expressed as;

$$K_{wax/cuticle} = \frac{c_{wax}}{c_{cuticle}} \tag{3.2}$$

3.1.3 Plant Compartment

The epidermis and the layers underneath it are treated as one single compartment in the modeling part. The plant compartment contains all the cells and constitutes the major part of the leaf. It contains a water rich phase and once the pesticide has crossed the cuticle/plant boundary it is rapidly distributed to the rest of the leaf. The plant compartment is assumed to contain lots of water therefore the ratio of the concentration in cuticle layer closest to the plant layer and plant itself is determined by the cuticle/water partition coefficient, which is expressed as;

$$K_{cuticle/water} = \frac{c_{cuticle}}{c_{water}} \tag{3.3}$$

3.2 Pesticide Solutions

Pesticide solution contains a lot of different compounds but the most important is active ingredients, this chemical compound which has desired biological effect on the plants The active ingredient is often referred to as the pesticide, the two words are used synonymously. Uptake of an aqueous solutions containing only active ingredient would be very slow because of the protective cuticular layer covering the leaves. In order to overcome this problem surfactants are added to the pesticide solution to improve uptake. They are also referred as adjuvants and have several different influences on the uptake process thereby giving better utilization of pesticides.

3.3 Pesticide Properties

The physical properties of the pesticide play an important role in the uptake rate of the compound. A very obvious factor is the size of the molecule; the larger the size is the slower will be the rate of diffusion. The molecular volume can be expressed in several ways; in connection with diffusion the McGowan Volume is often used. The McGowan Volume is not always easy to obtain from literature. In cases where it is not possible to get an accurate value an estimated value has been calculated using ProPred, a tool from ICAS.The solubility of the pesticide determines the concentration in the droplet when it is applied to the leaf. A higher solubility gives a greater driving for the diffusion process.

Another important factor is the lipophilicity of the pesticide. A more lipophilic compound usually has a higher solubility in the wax and can diffuse through this layer relatively fast. Unfortunately high lipophilicities have a disadvantage. The more the lipophillic the molecule is, the lower is its water solubility therefore the driving force for the diffusion is lower. Lipophilicity can be expressed by the octanol/water partition coefficient. Therefore higher the octanol/water partition coefficient higher will be the lipophillicity.

A perfect active ingredient or pesticide with high driving force for diffusion and high wax solubility is very difficult to find, therefore the surfactants are added to improve the uptake of the active ingredient.

3.4. Surfactant Properties

In the characterization of surfactants one of the parameters most often viewed at is the Hydrophile-Lipophile-Balance (HLB). The cuticular layer easily takes up the more lipophillic compound. Typical Surfactants are ethoxylated primary alcohols, which are proven to increase diffusion of the pesticide (Rodham, 2000). These surfactants have a hydrophilic ethylene oxide end which points to the water phase and a lipophillic alcohol end, which is towards the cuticle wax. In general it is not possible to establish a clear connection between the structure of the surfactant and its enhancement of pesticide uptake (Stock *et al.*, 1993). It is very dependent on the active ingredient and type of plant.factant Effects

One or more surfactants are usually added to pesticide solutions to achieve increased uptake of the active ingredient and thereby give better utilization of the pesticide. Surfactants have no biological activity their sole purpose is to promote uptake of the active ingredient. Surfactant can affect uptake in a variety of ways. Usually more surfactants are added to achieve several of the effects mentioned. The most important effects of surfactant on the uptake of active ingredient are given in the following.

a) Enhance diffusion of the active ingredient

A very important feature of the adjuvant is to enhance the diffusion of the active ingredient into the plant. This can happen by different mechanisms, which are not yet fully understood (Bell, 2003).

One theory is that some of the cuticular wax layer is dissolved by the surfactant. The cuticular layer consists of a water insoluble wax, which can be dissolved by a surfactant containing a lipophile group. The solution of wax can alter the structure of the cuticular wax in two ways. It can shorten the path, which the active ingredient needs to travel through the wax layer. The ratio between the length of the path the pesticide needs to travel through the layer and the thickness of the layer is defined as tortuosity factor. The tortuosity can be reduced by addition of wax-solubilizing surfactants; the diffusion path is straightened out. The other way the structure is altered is by increasing the free volume for diffusion. The cavities, which exist in the wax, are enlarged by the solution of wax and the pesticide molecules can easier move from one cavity to the next. This also improves diffusion coefficient.

The theory that surfactants improve diffusion of active ingredient is supported by the fact that transport of both pesticide and surfactant into the plant can be detected (Stock *et al.*, 1992). Another theory is that the surfactant increases the solubility of the pesticide in the solution. An improved pesticide concentration will increase the driving force for diffusion and thereby increase the uptake rate.

b) Induced swelling of the cubicle

Addition of surfactants can in some case causes induce swelling of the cuticle. Swelling can improve the free volume for diffusion and also reduce the tortuosity by reducing the diffusion path.

c) Increase spreading of the droplet

Surfactants can reduce surface tension and improve spreading of the droplet on the leaf, which means that the area covered by the droplet is increased. This usually gives an increased flux of matter into the leaf and therefore enhances the uptake rate.

d) Increase the number of droplet

The surfactant can have the ability to decrease the surface tension, which produces a greater number of droplets when the pesticide formulation is sprayed on the field. The greater the number of droplets doesn't itself increase the uptake rate but it improves the distribution of the pesticide solution so that more leaves will be exposed to the active ingredient.

e) Reduce Droplet Drift

The surfactant can increase the viscosity of the solution. This prevents the droplet from drifting away from the place where it has been deposited. The chance that it will fall off from the leaf and onto the ground where it has no effect will therefore be reduced.

f) Reduce droplet Evaporation

The surfactant can prevent the droplet from evaporating too fast. Slower evaporation enhances uptake because of the bigger area covered by the droplet. Furthermore a slower evaporation rate reduces the risk of pesticide recrystallisation. If the droplet evaporates too fast the pesticide concentration can exceed the saturation limit and crystals will form on the leaf. The active ingredient needs to be dissolved in order to be taken up by the plant.