Estimating input data for computations on the volatilisation of pesticides from plant canopies and competing processes

Estimating input data for computations on the volatilisation of pesticides from plant canopies and competing processes

M. Leistra

ABSTRACT

Volatilisation of pesticides from the crop can be an important emission pathway to the environment. A computation module was developed for making estimates on this emission. However, various input data for this module are not measured directly in registration procedures, so they have to be estimated from theory or from a diversity of experimental data. Vapour pressure is the most important property in volatilisation, which needs a critical evaluation in case of conflicting data. Diffusion coefficients for transport in a laminar boundary layer are estimated from theory. Penetration of pesticides into the leaves is highly affected by substances in the formulation and by environmental conditions. Pesticide deposit is often vulnerable to washoff by rainfall. Often, no directly measured rates are available for photochemical transformation on plant surfaces, so these have to be estimated from a variety of experimental results. In critical cases, comprehensive experiments with micro-agro-ecosystems and/or in the field are needed.

Keywords: deposit, diffusion, emission, environment, formulation, penetration, photochemical degradation, plant leaves, uptake, vapour pressure, washoff

Contents

Preface

Volatilisation of pesticides sprayed on plants can be an important emission pathway, dependent on their vapour pressure. In pesticide registration procedures and environmental quality policy, tools are needed for the fast estimation of the rate and extent of this emission. For this purpose, a volatilisation module has been developed for the PEARL model which describes pesticide behaviour in soil-plant systems. The volatilisation module asks for input data, but only some of them are measured directly in the framework of the registration procedures.

Besides volatilisation, various competing processes have to described because they have a large impact on the rate and extent of volatilisation. An extensive literature study was carried out to see how estimates of input data can be made. This report deals with a critical evaluation of directly-available input data and with the estimation of not-directly-available input data from theory or from divergent types of experiment. An application of the suggested procedure to input data for a specific pesticide is described in an Appendix. The input data for the advanced computation of volatilisation on the basis of atmospheric resistances are described elsewhere.

This study has been carried out in the framework of Theme A-5 "Emission to the air" of Research Program 416 "Pesticides in the Environment" funded the Netherlands Ministry of Agriculture, Nature and Food Quality.

Samenvatting

Vervluchtiging van bestrijdingsmiddelen vanaf planten is één van de omvangrijkste emissieroutes naar het milieu. In het kader van registratieprocedures en van meer algemeen milieubeleid moeten de snelheid en omvang van deze emissie worden geschat. Hiertoe is een vervluchtigingsmodule ontwikkeld voor het rekenmodel PEARL dat het gedrag van bestrijdingsmiddelen in bodem-plant systemen beschrijft. Processen die concurreren met vervluchtiging kunnen veel invloed hebben, zodat de snelheden daarvan ook moeten worden geschat. Enkele invoergegevens voor de vervluchtigingsmodule zijn te vinden in literatuur en/of dossier en deze dienen kritisch te worden geëvalueerd, met name bij tegenstrijdigheden. Diverse andere invoergegevens zijn niet direct beschikbaar en dienen daarom te worden geschat op basis van theorie of van uiteenlopende experimentele gegevens.

De snelheid van vervluchtiging is evenredig met de (resterende) hoeveelheid bestrijdingsmiddel op het plantendek, als gevolg van dosering en afname. Gebruikelijke formuleringen hebben weinig invloed op de vervluchtigingssnelheid op zich; speciale formulering zijn nodig om de vervluchtiging af te remmen. Over de invloed van de vochttoestand van de afzetting (deposit) op de vervluchtiging is nog weinig bekend. Er zijn aanwijzingen voor verschillende klassen in beschikbaarheid van de afzetting in de gewaslaag voor vervluchtiging.

De vervluchtiging zelf wordt vooral bepaald door de dampdruk van het bestrijdingsmiddel. De opgaven hiervoor kunnen tegenstrijdig zijn, zodat de kwaliteit kritisch beoordeeld moet worden. Dampdruk en vervluchtiging nemen sterk toe bij stijgende temperatuur.

Schattingsmethoden zijn beschikbaar voor de diffusiecoëfficiënten van bestrijdingsmiddelen in lucht, bijv. in een laminaire grenslaag. Geleidelijk komen waarden beschikbaar voor de equivalente dikte van deze grenslaag; veelal liggen ze voor planten rond 0,5 mm. Kwantitatieve relaties voor het effect van windsnelheid en turbulentie op deze grenslaag zijn nog niet bekend.

Penetratie van bestrijdingsmiddelen in de bladeren is veelal een belangrijk proces dat concurreert met vervluchtiging. Kwantitatieve relaties tussen penetratie en fysisch-chemische eigenschappen van een verbinding zijn niet beschikbaar en mogelijk zelfs niet bruikbaar. Stoffen in de formulering kunnen grote invloed hebben op de penetratie. De vochttoestand van de afzetting heeft vermoedelijk grote invloed op de penetratie (water als transportmedium), maar er is geen kwantitatieve relatie gelegd. Een classificatie van de penetratiesnelheid op basis van uiteenlopende (experimentele) gegevens wordt voorgesteld.

Regenval kan een aanzienlijk deel van het bestrijdingsmiddel in het deposit op de bladeren afwassen, waardoor de beschikbaarheid voor vervluchtiging sterk afneemt. Het afwassen verloopt evenredig met de hoeveelheid neerslag. De relatie tussen het

afwassen en de oplosbaarheid van de verbinding in water is zeer gebrekkig; andere factoren lijken een grote rol te spelen. Speciale formuleringen zijn nodig om het afwassen te verminderen. Naarmate de afzetting langer op de bladeren aanwezig is lijkt de afwasbaarheid af te nemen, maar kwantitatieve relaties zijn niet beschikbaar. Een voorstel wordt gedaan voor de classificatie van de afwasbaarheid van het deposit, gebaseerd op algemene literatuurgegevens.

Voor de fotochemische omzetting van een bestrijdingsmiddel op plantoppervlakken zijn veelal geen directe metingen beschikbaar. Voorgesteld wordt een schattng van deze omzetting te maken uit een diversiteit aan onderzoekgegevens, zoals absorptiespectrum voor licht, fotolyse in water en fototransformatie op uiteen-lopende oppervlakken.

Indien er te veel onzekerheid is over de vervluchtiging van een bestrijdingsmiddel dan zijn aanvullende studies nodig. Onderzoek met radioactief-gemerkte verbindingen in micro-agro-ecosystemen met planten leveren kwantitatieve informatie, ook over de concurrerende processen. Controle-experimenten in het veld kunnen nodig zijn, zodat ook de veldmethoden verder moeten worden ontwikkeld.

Summary

Volatilisation of pesticides from plants is one of the most important emission pathways to the environment. In the framework of registration procedures and of more general environmental policy, the rate and extent of this emission has to be estimated. For this purpose a volatilisation module has been developed for the computation model PEARL wich describes the behaviour of pesticides in soil-plant systems. Processes competing with volatilisation can have much effect, so their rates have to be estimated also. Some input data for the volatilisation module can be found in the literature and/or in registration dossiers and these should be evaluated critically, especially in case of conflicting data. Various other input data are not directly available; therefore these have to be estimated on the basis of theory or divergent experimental data.

The rate of volatilisation is taken to be proportional to the amount of the pesticide on the plant canopy as the result of application and decrease. Usual formulations have little effect on the rate of volatilisation as such; special formulations are needed to reduce volatilisation. Little information is available on the effect of moisture condition of the deposit on the rate of volatilisation. There are indications for different classes of availability of the deposit for volatilisation from the crop canopy.

Volatilisation itself is mainly determined by the vapour pressure of the pesticide. The data may be contradictory, so quality has to be evaluated critically. Vapour pressure and volatilisation increase strongly with rising temperature.

Estimation methods are available for the coefficients of diffusion of pesticides in the air, e.g. in a laminar boundary layer. Gradually, more values become available for the equivalent thickness of this layer; most of the values for plants are around 0.5 mm. Quantitative relationships for the effects of wind speed and turbulence on this boundary layer are not available.

Penetration of pesticides into the leaves is often an important process competing with volatilisation. Quantitative relationships between penetration and physico-chemical properties of a compound are not available and possibly even not usable. Substances in the formulation can have a large effect on penetration. Presumably, the moisture condition of the deposit has a large effect on the penetration (water as transport medium), but there is no quantitative relationship. A classification of penetration rate on the basis of a diversity of (experimental) data is proposed.

Rainfall can wash a substantial part of the pesticide deposit from the leaves, resulting in a large decrease in availability for volatilisation. Washoff proceeds in proportion to the amount of rainfall. The relationship between washoff and water solubility is very poor; other factors seem to play a large role. Special formulations are needed to reduce washoff. As the deposit is present in the leaves for a longer time, washoff

tends to decrease, but quantitative relationships are not available. A proposal is made for a classification of the washability of the deposit, based on general literature data.

Usualy no direct data are available for the photochemical transformation of a pesticide on plant surfaces by sunlight. It is supposed to make an estimate on the basis of a diversity of research data, like the absorption spectrum for sunlight, photolysis in water and phototransformation on divergent surfaces.

In cases in which there is too much uncertainty on volatilisation of a pesticide, supplementary studies are needed. Research with radioactively labelled substance in micro-agro-ecosystems delivers much information, also on the competing processes. Check experiments in the field can be needed, so field methods also have to developed further.

1   Introduction

Volatilisation of pesticides from plant surfaces is one of the main pathways of their emission to the environment. People in the surroundings of treated fields can be exposed to the pesticide vapours. Further, the pesticides can be transported in the air and subsequently deposited (wet, dry) in residential areas, drinking water catchments, nature conservation areas, recreational areas, etc. Reviews on this research area have been presented by van den Berg et al. (1999) and Bedos et al. (2002).

The volatilisation of pesticides from plant surfaces can be studied experimentally in the laboratory, in micro-agro-ecosystems (e.g. in wind tunnels with plants) and in the field. Besides it is desirable to model this process for making computations, to obtain a tool for explanation of results and for translation to other conditions. Ultimately, a certain degree of prediction of the rate and extent of pesticide volatilisation from plants is needed in the framework of registration procedures.

Model development in this research area seems to be in an early stage, as was noted also by van den Berg et al. (1999) and Bedos et al. (2002). The available experimental results should be utilised to make a start with model development. This start must also indicate how future experiments should be designed to enhance their usefulness for model development.

Only recently, a module for pesticide volatilisation from plant canopies, together with the competing processes, has been incorporated in models on pesticide behaviour in soil-plant systems. In the first version of the PEARL model (Leistra et al., 2001), the pesticide processes in the plant canopy were described in a simplified way. Volatilisation was described as a first-order process, for which a rate coefficient can be introduced. The competing processes of penetration into the plant and (photochemical) transformation on the plant surface were described also as first-order processes. Of course, pesticide wash-off from the leaves was set dependent on the rainfall. It was desirable to describe pesticide volatilisation in a more mechanistic way, accounting for the factors influencing this process. The development of such an improved module is described by van den Berg & Leistra (2004).

There is a need for both, simplified and more advanced computations for pesticide behaviour in plant canopies. Simplified computations are needed for cases in which there is limited understanding of the processes and when input data are scarce or highly uncertain. Some pesticide-behaviour models concentrate on the processes in soil; they have limited possibilities to include crop canopy processes. A more advanced module is needed for utilising more detailed input information and for model development.

Some input data for volatilisation modules can be measured directly, e.g. the vapour pressure of the pesticide. In these cases it is important to consider the reliability of the data, especially if conflicting data are reported. Estimation methods (especially

those with a sound theoretical basis) to test the reliability of measured data are useful. For various other processes, often no directly measured input data are available. Then the input has to be derived from different kinds of experiment or from estimation methods. This report describes how the input data for computations on pesticide behaviour in plant canopies can be collected, checked and estimated. Research needs to improve the measurement and estimation of input data are indicated.

2 General characterisation of pesticide volatilisation

The rate of pesticide volatilisation from plants mainly depends on its vapour pressure, but it is also influenced by the rate of the competing processes. If the effect of competing processes is small, a large fraction of the dosage will volatilise, possibly within a few days (e.g. lindane). Volatilisation of low to moderately volatile and persistent pesticides (like some other chlorinated hydrocarbon insecticides) continues for several weeks (at a decreasing rate). When the competing processes play a major part for a pesticide, only a fraction of the dosage will volatilise. Then the rate of volatilisation may decrease to very low values within a few days.

2.1 Older more persistent pesticides

The older research on the volatilisation of pesticides from plants was mainly carried out with persistent chlorinated hydrocarbon insecticides. The volatilisation of these compounds continued for a long time (e.g. a month) and a large fraction of the dosage volatilised (Bentson, 1990). This indicates that the competing processes (penetration, wash-off, phototransformation) were of minor importance for these compounds.

Taylor et al. (1977) studied the volatilisation of dieldrin and heptachlor sprayed on short pasture in summer. There was a marked diurnal fluctuation in flux density, with a peak around noon and very low fluxes at night. After the comparatively high volatilisation of the insecticides on the first day, the emission slowed down in time but continued for at least 23 days.

The course of volatilisation in time from grass in the field for heptachlor and dieldrin was also described by Taylor (1978). Competing processes like plant penetration and phototransformation played a minor part for these pesticides. The decrease of volatilisation rate in time was explained for the greater part from the decrease in evaporating deposit surface in time: thinner parts of the deposit became depleted first.

The course of pesticide volatilisation in time under field conditions is illustrated also by the work of Harper et al. (1983) for toxaphene and DDT sprayed on a field with cotton plants. The highest fluxes were obtained for the middle of the day, when solar radiation, temperature and wind speed were highest. Although pesticide concentrations above the canopy were substantial at nighttime, the transport to the atmosphere was much slower than at daytime.

The volatilisation of lindane (vapour pressure 4.4 mPa at 24 0C; Tomlin, 2003) from four crops was measured by Gottschild et al. (1995). The amounts volatilised in the first day after application corresponded to 76 to 94% of the dose. So crop species had little effect on the rate of volatilisation of lindane. The extent of volatilisation of

lindane from plants was almost equal to the decrease of the residue on the plants. So the effect of competing processes on the volatilisation of lindane was small.

2.2   Newer less persistent pesticides

The rate of volatilisation of modern pesticides is usually highest just after spraying the canopy. Already on the first day, there may be a distinct decrease in volatilisation rate of the more modern pesticides. This is the result of processes competing with volatilisation, such as penetration into the plants, wash-off by rainfall and phototransformation on the plant surface.

The rate of volatilisation of the herbicide pendimethalin from grass (under movable glass chambers in the field) was highest on the middle of the day, when solar radiation and temperature were highest (Cooper et al., 1990). Overnight, vapour loss of the herbicide was only small.

The volatilisation of fenpropimorph from dwarf beans in a wind tunnel placed on a lysimeter was studied by Stork et al. (1998b) and Ophoff et al. (1999). Under the simulated field conditions, the volatilisation showed a distinct diurnal rithm, with the highest values at daytime.

3 Deposit on the plant surfaces

3.1 General description

The distribution of a pesticide deposit on the plant surfaces is dependent on application factors like formulation, spray volume and droplet-size spectrum. The initially wet deposit dries at a rate dependent on the environmental conditions. The deposit can be in different states, such as solid, (viscous) liquid, saturated solution, unsaturated solution, mixture, covered, etc. The distribution of the deposit over the plant surface is important as it may be expected to influence the rate of volatilisation. Aspects of this distribution are: distribution in the canopy, surface fraction of the leaves covered, thickness of the deposit, etc.

3.2 Factors and relationships

3.2.1 Dosage and coverage

The rate of volatilisation of fenitrothion from glass plates decreased in proportion to the decrease in its mass on the plates (Hashimoto, 1989). In a series of measurements for parathion-methyl, the rate of volatilisation from plants in a climate chamber was proportional to the dose (Kubiak, 1999).

The deposit of practical dosages of pesticides on the plants may be considered to form a pattern of patches with variable thickness. Then the volatilisation leads to a decrease of the volatilisaton surface in time (Hartley & Graham-Bryce, 1980). It seems realistic to assume that the volatilisation rate decreases in proportion to the decrease in pesticide deposit. Willis & McDowell (1987) also assumed that the coverage of foliage deposit decreases as the amount of compound on the leaves decreases. The rate of volatilisation of pendimethalin from grass decreased in time, in proportion to the decrease of dislodgeable residue (1 min with methanol) on the grass (Cooper et al., 1990).

Observations on the distribution pattern of the deposit on plant leaves are often not available. Because of the lack of information, a standard distribution pattern may be assumed. This assumption can be adjusted if relevant information is available.

3.2.2 Distribution and decrease in the canopy

The fungicide chlorothalonil was sprayed on potato crop canopies by field sprayer (high volume) and by helicopter sprayer (low volume), after which the distribution of deposit with depth in the canopy was studied (Bruhn & Fry, 1982a). The measurements of the deposition on leaf disks showed a substantial decrease of deposit with increasing depth in the canopy. Further, the distribution of deposit in

each canopy layer was rather heterogeneous (skew distribution with many low values), especially in the deeper canopy layers. The deposition in the top layers of a well-developed canopy was comparable for the two application methods, but downward penetration into the canopy was less for the (low volume) helicopter application.

An experiment on spray deposition in various layers of a field crop canopy was also carried out by Porskamp et al. (2003). They sprayed the coloring agent brilliant sulfoflavine (BSF) on a potato crop using a field sprayer. The deposition measured on strips of chromatographic paper attached to the leaves was: 51.4% (upper layer), 14.1% (middle layer) and 8.9% (lowest layer) of the dosage. The deposition on the upper side of the leaves was much higher than that on the lower side.

Chlorothalonil was sprayed on a potato crop by field sprayer (high volume), after which leaf disks were collected at different times to measure the decrease of the residue (Bruhn & Fry, 1982b). The half-lives of chlorothalonil in the four layers (from top to bottom) of the canopy were 3.6, 5.4, 10.3 and 21.3 days, respectively. This difference is explained by the higher exposure of the deposit in the upper layers to the weather conditions. There were indications of redistribution of the fungicide from the upper layers to the deeper layers in the canopy in the course of time.

In some volatilisation experiments, an initial period with comparatively fast volatilisation of the pesticide was followed by a second period with comparatively slow volatilisation (Leistra & Wolters, 2004). It was found to be impossible to describe the course of the volatilisation in time by assuming a single deposit class. Two deposit classes were distinguished: a well exposed and a poorly exposed class. The deposit in the latter class can be enclosed by plant parts (e.g. in leaf axils), it can land on plant parts at the lee side of the air flow, or it is deposited deeper in the canopy. To trace the effect of two deposit classes on the course of volatilisation, the fraction of poorly exposed deposit was set at, for example, 0.20 times the dosage. In addition, the rate of decrease processes for the poorly exposed deposit was set at, for example, 0.20 times the rate of the corresponding process for the well exposed deposit.

3.2.3   Formulation and admixtures

In various experiments, the effect of the formulation on the volatilisation of a pesticide from plants etc. has been studied. In other cases, the volatilisation of a pesticide from a mixture of pesticides has been studied. Appendix 1 gives a brief survey of the results of such studies. The conclusion is that the influence of common formulations like emulsifiable concentrates (EC) and wettable powders (WP) on the volatilisation of a pesticide is small. Special formulations (e.g. slow release) seem to be needed to reduce pesticide volatilisation. However, a requirement for practical use of such a special formulation is that it does not detract from pesticide effectiveness.

With respect to mixtures of pesticides (non-formulated), there seems to be little mutual interaction in the rate of volatilisation (Appendix 1). Possible exceptions are mixtures of compounds with highly different physico-chemical properties.

The deposit is a complex mixture of the pesticide with solvents (water, organic), surfactants, adjuvants, stabilisers, etc. (Bentson, 1990). The composition of the deposit changes in time, e.g. by evaporation of the solvents. The condition of the deposit often changes from a more fluid state to a more solid state (amorphous or even crystalline).

3.2.4   Condition of the deposit

McCall et al. (1986b) distinguished the amounts of atrazine in solid form and in solution on the plant surface. They considered only the solution form of the herbicide to be available for penetration into the leaves. Transfer from the solid to the solution was assumed to occur at a limited rate. The relative rates of volatilisation from each of such states are not known.

Addition of crop oil concentrate to the spray liquid increased the penetration of atrazine into plant leaves (McCall et al., 1986b). They explained this from the higher fraction of the atrazine in the deposit being in fluid form. The effect of such an additive and of the resulting state of the herbicide on the rate of volatilisation is not known. Such an oily additive could act as a keeper. In general, some of the pesticide in the deposit may be entrapped by low-volatile formulation constituents.

3.3   Quantities and equations

The dosage of pesticide applied to the field $A_{f,i}$ is expressed in kg m^{-2}. A certain fraction I_p (-) of this dosage is intercepted by the plants:

$$A_{p,i} = I_p\, A_{f,i} \qquad\qquad \text{(Eq. 1)}$$

where $A_{p,i}$ is the initial areic mass of pesticide on the plants (kg m^{-2}). Note that this quantity is expressed on the basis of field surface area. The interception will be dependent on factors like soil cover by the crop and on the way of spraying (e.g. overall or directed to plant rows).

The pesticide is assumed to be deposited on the leaves in spots of variable thickness. The thinner the deposit at a certain place, the sooner that place will be depleted by volatilisation. The concept is that the volatilising surface decreases in proportion to the decrease in mass of pesticide in the deposit. So the factor f_{mass} (-) for the mass of pesticide present on the leaf surfaces is:

$$f_{mass} = \frac{A_p}{A_{p,ref}} \qquad\qquad (Eq.\ 2)$$

where

A_p = the areic mass of pesticide on the plants (kg m^{-2});

$A_{p,ref}$ = the reference areic mass of pesticide on the plants (1.0 10^{-4} kg m^{-2}) (= 1 kg/ha).

The equation for the conservation of mass of pesticide in the deposit on the plant surface reads:

$$\frac{dA_p}{dt} = -J_{vol,act} - R_{pen} - R_w - R_{ph} \qquad\qquad (Eq.\ 3)$$

where

t   = time (d);

$J_{vol,act}$ = actual rate of volatilisation (kg m^{-2} d^{-1});

R_{pen} = rate of penetration into the plants (kg m^{-2} d^{-1});

R_w = rate of wash-off by rainfall (kg m^{-2} d^{-1});

R_{ph} = rate of phototransformation on the plant surface (kg m^{-2} d^{-1}).

The equations used for describing each of the processes are given in the following chapters.

3.4 Research needs

It is desirable to have observations on the distribution of the pesticide deposits on the plant surface: macroscopic, light-microscopic, electron-microscopic, etc. Further, the state of the deposit can be expected to be relevant: wet (with solution present), (viscous) liquid, amorphous solid, crystalline solid, etc.

The rate of some processes at the leaf surface may be expected to depend on the moisture condition of the deposit. Especially, penetration into the plants from a moist deposit may occur at a much higher rate than from a dry deposit. Quantitative observations on this condition seem to be scarce. Drying of the deposit could be slowed down due to constituents in the deposit, e.g. with hygroscopic properties, or due to fine pores. Then water plays it part in the deposit for a longer time than would follow from superficial observation.

Solubility of the pesticide in water can only be expected to play a role in its volatilisation when the deposit is moist or wet. It should be noted that constituents in the formulation may be expected to affect pesticide solubility in the aqueous phase on the leaves. Information on the effect of moisture condition of the deposit on pesticide volatilisation is needed.

The tendency of non-charged pesticides to adsorb to non-polar organic substances (e.g. of cuticle on leaf surface) is often represented by the octanol/water partitioning coefficient K_{ow}. It is not known to which extent this adsorption reduces volatilisation of a pesticide.

The formation of a poorly exposed fraction of deposit could be the result of entrapment between plant parts (e.g. in leaf axils), deposition on the lee side of plant parts, deposition deeper in the canopy, etc. The mechanisms, factors and rates for the poorly exposed deposit demand for further study.

It is essential that the different states of the pesticide on the leaves are distinguished better in the experiments: dislodgeable deposit, adsorbed residue, superficially penetrated residue (e.g. in wax layer) and more deeply penetrated residue. This kind of measurements on the state of availability is very scarce in experiments.

In further model development, different layers in the plant canopy could be distinguished. Pesticide deposit in each of these layers may be expected to decrease from top to bottom layer of the canopy. The resistance to volatilisation may be expected to increase going from the upper to the bottom layer of the canopy. Wash-off could be highest on top of the canopy with the more uniform water distribution there. Because of the shading effect, phototransformation may decrease when going down into the canopy. These considerations illustrate that more detailed modelling requires additional input data to be measured or estimated.

4　Transfer to the vapour phase

4.1　The importance of vapour pressure

In some studies, attempts were made to correlate the rate and extent of volatilisation of the pesticides from surfaces (e.g. plants, glass) to their physico-chemical properties or to combinations of these properties. The rate of volatilisation of eight pesticides (seven of them organophosphates) from glass plates in a chamber (at 30 ^{0}C) was measured in the first few hours after application (Hashimoto, 1989). There was a good correlation between volatilisation rate and vapour pressure of the pesticide.

The rates of volatilisation of 14 pesticides from rice leaves and glass beads were measured by Watanabe (1993) in a purge-and-trap system (25 ^{0}C). There was a good correlation between the rate of volatilisation and the vapour pressure of the pesticides. Vapour pressure seemed to be the main factor in volatilisation. The volatilisation rate from rice leaves tended to be higher than that from glass beads in a tube.

Data on the rate of volatilisation of organic chemicals from plants and inert surfaces measured in divergent experiments (lab, field) in the first few hours after spraying were collected by Woodrow et al. (1997). They found a good correlation of volatilisation with vapour pressure. Unfortunately, their procedure is not described clearly and the work seems to contain contradictions.

Publications on well-defined experiments dealing with pesticide volatilisation from plants were studied to develop an estimation method for the extent of this emission (Smit et al., 1998). The cumulative percentage of the dosage volatilised after 7 days was estimated by interpolation or extrapolation of the course of volatilisation in time. The relationship between extent of volatilisation and vapour pressure was found to have the highest correlation coefficient. The extent of pesticide volatilisation from plants ranged from less than 5% of the dose at vapour pressures < 0.1 mPa (20 ^{0}C) to almost 100% at vapour pressures > 10 mPa (20 ^{0}C). Relationships including the partitioning of the pesticide to water and organic materials showed a worse correlation or no correlation at all.

The limitations in the use of empirical relationships between volatilisation and vapour pressure for predictive purposes should be kept in mind. When volatilisation was measured from deposit on inert surfaces, e.g. in the lab, competing process may have played a minor part. The data from prolonged experiments partly deal with outdated persistent chlorinated hydrocarbon insecticides, with little influence of the competing processes on volatilisation. The wide scatter in the relationship indicates that other processes and factors affect volatilisation. More modern pesticides may show substantial penetration into the plants and may be less persistent than the older (outdated) pesticides. Further research is aimed at modelling pesticide volatilisation in

a more mechanistic and accurate way, accounting for the effect of the competing processes on the plant surfaces.

4.2   Values for the vapour pressure

Pesticide molecules in the deposit can escape into the air by molecular movement, which is dependent on temperature. This escape is counteracted by the molecular interaction forces in the deposit, which may vary from weak (volatile liquids) to very strong (low-volatile crystalline solids). One question is whether vapour pressure at the deposit surface can be considered to be always saturated or whether the rate of transfer into the vapour state can be limiting.

The vapour pressure of a pesticide can, in principle, be obtained from various types of sources:
- handbooks like the Pesticide Manual (Tomlin, 2003), mostly based on company data;
- summary of the dossier in the framework of the registration procedure, e.g. National Summary or EU Monograph, mostly based on company data;
- publication of method and result in a scientific journal (quite rare);
- estimate obtained with a calculation method, like those described by Dearden (2003).

A critical attitude with respect to the values reported for the vapour pressure of pesticides is needed. Sometimes even different values are reported or cited for the vapour pressure of a pesticide. It should be checked whether the method of determination of the vapour pressure has been adequate, in view of the guideline of the OECD (1995). Citations of vapour pressures without reference to the original sources are questionable. Calculation methods for estimating vapour pressures are useful as a check when reported values are highly uncertain or when conflicting data were reported.

The problem of deriving the most reliable vapour pressure for a pesticide is illustrated for parathion-methyl in Appendix 2. The ratios between the vapour pressures for the strongly related compounds fenitrothion, parathion-methyl and parathion(-ethyl) were highly non-logical. The vapour pressure of 1.13 mPa at 20 ^{0}C was derived as being the most reliable value for parathion-methyl. When the value is taken from the Pesticide Manual (Tomlin, 2003), a large error is made.

Physical properties like vapour pressure usually hold for pure liquids or solids. Attention should be paid to the change in the parameters for the mixtures with other substances (e.g. from the formulation) which commonly occur in practice.

4.3   Effect of temperature on vapour pressure

The reference temperature for all temperature-dependent quantities is taken to be 293 K (20 ^{0}C). The most reliable value in the literature for the saturated vapour pressure of the pesticide at reference temperature is selected for the computations. Vapour pressure at the deposit surface on the leaves is assumed to be saturated, and is dependent on the temperature. The saturated vapour pressure of the pesticide at the prevailing temperature is calculated by the following form of the Clausius-Clapeyron equation (Tinsley, 1979; Grain, 1982):

$$P_{act} = P_{ref} \exp\left[\left(\frac{-H_v}{R} \right) \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]$$ (Eq. 4)

with:

P_{act}	=	actual saturated vapour pressure of the pesticide (Pa)
P_{ref}	=	reference saturated vapour pressure of the pesticide (Pa)
H_v	=	molar enthalpy of volatilisation (J mol^{-1})
R	=	molar gas constant (8.314 J mol^{-1} K^{-1})
T	=	temperature (K)
T_{ref}	=	reference temperature (K)

Some values reported recently for the molar enthalpy of vaporisation H_v of pesticides are given in Table 1. If no specific value for a compound is reported, the molar enthalpy of vaporisation is taken to be 95 000 J mol^{-1}, which is the average of the values reported for many pesticides (Smit et al., 1997).

Table 1. Some values reported for the molar enthalpy of vaporisation, H$_v$, of pesticides, with the way in which they were obtained.

Pesticide or group	Molar enthalpy of vaporisation (J mol^{-1})	Details	Reference
Parathion (-ethyl)	101 000		Spencer et al. (1979)
Parathion-methyl	109 000	Below melting point	Spencer et al. (1979)
Many pesticides	95 000	Average of many reported values	Smit et al. (1997)
fenpropimorph	98 400		Stork et al. (1998b)
terbutylazine	92 600		Stork et al. (1998a)

The saturated vapour concentration of the pesticide in the air at the deposit surface on the leaves is calculated from the vapour pressure by using the General Gas Law:

$$C_{a,s} = \frac{M \, P_{act}}{R \, T}$$ (Eq. 5)

with:

$C_{a,s}$	=	concentration of the pesticide in the air at the surface (kg m^{-3})
M	=	molar mass (kg mol^{-1}).

4.4　Effect of temperature on volatilisation

The rate of pesticide volatilisation can be expected to be higher as the temperature is higher, because then the vapour pressure above the deposit is higher. Further, the adsorption to surfaces is lower at a higher temperature, while the tendency to escape from the aqueous phase (if present) is higher.

The volatilisation of a herbicide from glass slides in a chamber increased threefold when temperature was increased from 20 to 30 ^{0}C (McCall et al., 1986a).

The rate of volatilisation of fenitrothion from a glass surface in a laboratory chamber at 30 ^{0}C was 2.9 times as high as that at 20 ^{o}C (Hashimoto, 1989). Temperature has much effect on the rate of volatilisation because it has a great effect on the vapour pressure of the pesticide.

The effect of temperature on the volatilisation of 2,4-D-butyl ester (^{14}C–labelled) from barley leaves in a glass chamber was studied by Breeze et al. (1992). In the measuring period of 6 hours, the rate of herbicide volatilisation was much higher as the temperature was higher (range of 19.3 to 29.5 ^{0}C).

Stork et al. (1997) studied the effect of temperature on pesticide volatilisation from bean plants grown on a lysimeter, with a wind tunnel on top. The volatilisation of fenpropimorph increased from 37% of the dose at 21 ^{0}C to 54% at 27 ^{0}C. For parathion-methyl, volatilisation increased from 60% of the dose at 14 ^{o}C to 73% at 9 ^{0}C.

The volatilisation of fenpropimorph from plants grown on a lysimeter in a wind tunnel was studied also by Ophoff et al. (1999). The volatilisation of this fungicide from bean and radish plants in the first 24 hours was distinctly higher at a temperature which was 6 to 8 ^{0}C higher.

In the first 6 hours after application the volatilization of parathion-methyl from bean plants in a climate chamber was 34% of the dose at 15 ^{0}C, while it was 46% at 20 ^{0}C (Maurer, 1995; Kubiak, 1999).

Schweizer et al. (2000) studied the volatilisation of parathion-methyl, bromoxynil and fluroxypyr from bean plants in a wind tunnel, under well-controlled conditions. They found a strong increase in volatilisation when temperature was increased from 20 ^{0}C to 30 ^{0}C.

The volatilisation rate of a pesticide at different temperatures can be simulated using a computation model. It will be interesting to check whether the differences in volatilisation rate for different temperatures can be explained from the differences in vapour pressure. Because of the strong effect of temperature on vapour pressure, volatilisation tends to benefit more from a higher temperature than the competing processes (Ophoff et al., 1999).

4.5   Effect of conditions in the deposit on volatilisation

Just after spraying, pesticide deposit on the leaves is wet and the same holds for rainy periods. A question is whether moisture condition influences pesticide volatilisation. What is the extent of saturation of the aqueous phase and how does volatilisation from wet deposit compare with that from dry deposit?

The relative humidity of the air at various days may differ and it often shows a day (lower) and night (higher) cycle. A question is whether this influences the rate of pesticide volatilisation from the deposit on the leaves.

The volatilisation flux of a pesticide in the field was found to be highest in the morning hours of a particular day, when the plants were wetted by heavy dew (Willis et al., 1980). A light rain shower seemed to have a similar effect of increasing volatilisation. However, different conditions changed at the same time, which made the situations rather complex.

Schweizer et al. (2000) studied the volatilisation of parathion-methyl, bromoxynil and fluroxypyr from bean plants in a wind tunnel, under well-controlled conditions. Increase of relative humidity of the air from 50% to 70% had divergent effects: it increased the volatilisation of parathion-methyl, whereas it decreased the volatilisation of bromoxynil and fluroxypyr. It would be interesting to study the nature of these effects: acting in a direct way or via the influence on one or more competing processes.

4.6   Research needs

Values given for the vapour pressure of pesticides can only be trusted when they are determined according to well-described methods meeting the requirements of the OECD (1995). It may be difficult to trace older values of the vapour pressure back to the original source. Making estimates of the vapour pressure may be helpful in rejecting doubtful values. In case of uncertainty, a new and well documented determination of vapour pressure is needed.

Up to now, no quantitative relationship has been found between moisture condition of the deposit and volatilisation rate of a pesticide. No instances are known in which the moisture condition of the deposit has been measured. Only in a few cases, observations on the wet or dry status (as far as visible) of the deposit is available. This is an area with a high need for detailed experimental research; it is not mature for modelling yet.

5 Transport in the air

5.1 Diffusion through a laminar air-boundary layer

The resistance in the air to the volatilisation of substances may be (partly) described in terms of an equivalent thickness of a laminar air-boundary layer (Majewski, 1990). In this layer with laminar air flow, the pesticide has to diffuse from the deposit surface to the turbulent air with fast removal of the substance. This vapour diffusion is considered to be the rate-limiting process. The thickness of the air boundary layer (of the order of only 1 mm) may be expected to vary in space and time. Its value is influenced by parameters like surface roughness, wind speed and atmospheric turbulence.

Air flow through a plant canopy is rather complex, so there may be no single equivalent value of the thickness of the air boundary layer for all heights in the canopy. A typical aspect of leaf surfaces is that they move in the wind.

Coefficients for the diffusion of pesticides in air can be calculated using the FSG method as described by Tucker & Nelken (1982). Examples of diffusion coefficients calculated in this way are given in Table 2.

Table 2. Coefficients for the diffusion of pesticides in the air (at 20 ⁰C) calculated by the FSG method as described by Tucker & Nelken (1982).

Pesticide	Molar mass (g mol⁻¹)	Diffusion coefficient (m² d⁻¹)
fenpropimorph	303.5	0.36
parathion-methyl	263.2	0.50
quinoxyfen	308.1	0.42

The coefficient D_a for pesticide diffusion in air at the prevailing temperature is calculated (Tucker & Nelken, 1982) according to:

$$D_a = D_{a,ref}\left(\frac{T}{T_{ref}}\right)^{1.75}$$
(Eq. 6)

with:
D_a = diffusion coefficient of pesticide in air $(m^2\,d^{-1})$
$D_{a,ref}$ = diffusion coefficient in air at reference temperature $(m^2\,d^{-1})$

Volatilisation of pesticide from the deposit surface on the leaves is determined by vapour diffusion through the laminar air boundary layer. The potential rate of volatilisation of pesticide from the deposit/leaf surface is calculated by:

$$J_{vol,pot} = D_a\frac{\left(C_{a,s} - C_{a,t}\right)}{d_{lam}}$$
(Eq. 7)

with:

$J_{vol,pot}$ = potential flux of volatilisation from the surface (kg m^{-2} d^{-1})
$C_{a,t}$ = concentration (kg m^{-3}) in the turbulent air just outside the laminar air layer, (set at zero)
d_{lam} = equivalent thickness of the laminar air boundary layer (m).

All the areic quantities, such as fluxes, are expressed per m^2 field surface (not plant surface).

In the present stage of model development, values for the thickness of the laminar air-boundary layer, d_{lam}, have to be obtained by calibration. This is done by computer simulation of well-defined experiments. Examples of values of d_{lam} derived by simulation of experiments up to now are given in Table 3.

Table 3. Values of the equivalent thickness of the laminar air-boundary layer, d_{lam}, obtained by computer simulation of well-defined experiments.

Type of study	Pesticide	Plants	Temperature in first day (^{0}C)	Air flow rate in first day (m s^{-1})	Value of d_{lam} (mm)	Reference
Wind tunnel	Fenpropi-morph	Bean (1)	23 to 30	1.0	0.5	Leistra & Wolters (2004)
idem	idem	Bean (2)	14 to 19	1.0	0.5	idem
idem	idem	Radish	20 to 29	0.9 to 1.9	0.5	idem
idem	idem	Sugar beet	5 to 25	0.1 to 0.9	1.0	idem

For the time being, the thickness of the laminar air boundary layer is a quantity to be calibrated in the computation. Its starting value can be taken to be e.g. 1.0 mm. As more values of d_{lam} are obtained from detailed simulation of well defined experiments, this parameter gets a higher predictive value.

The actual rate of pesticide volatilisation is described by taking into account the mass of pesticide on the plants:

$$J_{vol,act} = f_{mas} \, J_{vol,pot} \qquad \qquad \text{(Eq. 8)}$$

with:

$J_{vol,act}$ = actual rate of pesticide volatilization (kg m^{-2} d^{-1})
f_{mas} = factor for the effect of pesticide mass on the plants (-)

The factor f_{mass} is defined in Eq. 2.

5.2 Effect of wind speed and turbulence

Pesticide volatilisation from plants may be expected to increase with increasing wind speed. More unstable climatic conditions, with more air turbulence, may also be expected to increase volatilisation. Both factors probably decrease the equivalent thickness of the air boundary layer with laminar flow, in which the pesticide moves by diffusion.

Loss rates (mainly by volatilisation) of lindane and dieldrin from watch glasses in a room at 20 °C were increased about ten times by forced ventilation (Dobbs & Cull, 1982), as compared to the loss at the normal air flow in the room.

Increase of the air flow (from 0.4 to 1.6 km h^{-1}) in a chamber slightly increased the rate coefficient for herbicide volatilization (McCall et al., 1986a).

The volatilisation of fenitrothion from glass plates in a laboratory chamber (20 °C) was higher as the air velocity was higher (Hashimoto, 1989).

The effect of air circulation by a fan on the volatilisation of 2,4-D-butyl ester (^{14}C-labelled) from barley plants in a glass volatilisation chamber was studied by Breeze et al. (1992). In a period of 6 hours with operating fan, the volatilisation of the herbicide was four times that in the chamber without operating fan.

The rate of volatilisation of lindane from plants in a laboratory system increased as the air velocity increased from 0.4 to 2.0 m s^{-1} (Waymann & Rüdel, 1995).

Enhanced exchange of air within the bean canopy in a wind tunnel increased the volatilization of penconazole from 37% to 56% of the dose (Maurer, 1995; Kubiak, 1999).

5.3   Research needs

The laminar air boundary layer model is strongly simplified, but it may play a role in (many) situations in which the details needed for more complex modelling are missing. Representative values are needed for the equivalent thickness of the laminar air boundary layer under divergent weather conditions. For this purpose, additional well defined experiments with micro-agro-ecosystems and in the field have to be simulated using the model.

In further module development, the canopy may be divided into some layers. The relative thickness of the air boundary layer for each of the canopy layers has to be estimated then (greater thickness expected for deeper layers).

Under field conditions, various climatic factors may change at the same time (e.g. in a daily cycle). This makes it impossible to study the isolated effect of such a factor on volatilization. The only possibility is to study the effect of the climatic factor in controlled experimental systems.

More advanced procedures for describing pesticide transport in the air, especially under field conditions, are also needed. Van den Berg & Leistra (2004) describe an approach on the basis of of atmospheric resistances: a boundary layer resistance and an aerodynamic resistance.

6 Penetration into the leaves

6.1 Adsorption

Some pesticide in the deposit may become adsorbed to the leaf surface. Possibly, this occurs mainly when the leaf surface is wet (water as transport medium). In principle, pesticide adsorption in wet condition can be estimated using a parameter like the coefficient for octanol/water partitioning. However, pesticide solubility in the aqueous phase may be enhanced by the constituents in the formulation. In this study, adsorption to the plant surface is considered to be quickly reversible. Because of the great effect of deposit condition on adsorption and the assumed quick reversibility, pesticide adsorbed to the leaf surface is assigned to the 'deposit' class, described earlier. Pesticide penetration into the leaves described in the present section is considered to be an irreversible process (for the time being).

One has to be careful in the distinction of the pesticide fractions a) residing at the plant surface (deposit, adsorbed) and b) penetrated into the plant. In various publications, the fraction of pesticide in the epicuticular waxes is considered to be 'sorbed', so not 'taken up' (de Ruiter et al., 2004). The 'sorbed' fraction may be measured by cellulose acetate film stripping or by washing with chloroform (which dissolves waxes). In the present study, the 'sorbed' pesticide fraction is considered to be 'penetrated' into the leaves, as it is not directly available for volatilisation. In further model development, the 'sorbed' pesticide could be assigned to a class of reversibly penetrated compound, that may diffuse backwards to the leaf surface which is followed by volatilisation etc.

6.2 Experimental information

Experimental information on the penetration of a particular pesticide into plant leaves may be available, because this process is important for its effectiveness (Bentson, 1990; de Ruiter et al., 2004). Various pesticides have systemic activity, which means that they exert their activity after penetration into and translocation within the plants.

The behaviour of the systemic herbicide clopyralid (vapour pressure 1.33 mPa at 24 ^{0}C; Tomlin, 2003) sprayed on plants in a lysimeter + wind tunnel combination was studied by Stork et al. (1998a). Penetration of this systemic herbicide into the plant leaves, followed by translocation and metabolism within the plants, were found to be major processes. They measured only a low extent of volatilization: 0.7% of the dose in 6 days. These results illustrate the possible importance of penetration as a process competing with volatilisation. However, in view of the low pKa-value of clopyralid (pKa = 2; Tomlin, 2003), a large fraction may have been present in anion form at the plant surface (presumably less volatile than the undissociated acid).

The systemic fungicide fenpropimorph showed substantial penetration (18 to 53% of the dose after 3.8 days) into the leaves of bean, sugar beet and radish (Ophoff et al., 1999). In cases in which the volatilization was lower (due to a lower temperature), a higher percentage of the dose penetrated into the leaves. This illustrates that the competition by penetration depends on the environmental conditions.

De Ruiter et al. (2004) compiled a review of studies on the uptake of herbicides (and a few other pesticides) by plant leaves. They defined the quantity FUP50 as the period required for foliar uptake of 50% of the applied amount. Many FP50 values were in the range from a few hours to a few days, but others were longer than the experimental period. On the basis of the details in the experiments, they attempted to derive relationships between FUP50 and factors expected to determine the rate of uptake (see below).

6.3   Physico-chemical properties of the pesticide

The extent of penetration into the leaves is highly dependent on the physico-chemical properties of the pesticide. For non-charged compounds, especially molecular size and polarity are important characteristics (Bentson, 1990). Various weak acid and weak basic pesticides show good penetration into plants, followed by translocation to the action sites.

The relation between the rate of penetration into plant leaves and the physico-chemical properties of the pesticides is not always clear (Briggs & Bromilow, 1994). Sometimes there is a relation with their octanol/water partitioning P_{ow}. Penetration of pesticides in "liquid form" (affected by melting point but possibly also by the formulation) can be expected to be much better than that in "solid form". Briggs & Bromilow (1994) suggest the existence of a special "aquatic route" for penetration of pesticides with high solubility in water.

Uptake by leaves seems to be optimal for compounds of intermediate polarity (Falk, 1994). Compounds with a low melting point form amorphous deposits with better leaf contact and thus better penetration than compounds with high melting point forming crystals.

De Ruiter et al. (2004) attempted to relate the uptake of pesticides (mainly herbicides) to their physico-chemical properties. They selected the results from experiments in which no formulation was used. In many cases, the uptake was low. The time for 50% uptake only showed a weak tendency to increase (with very high spreading) with increasing log(Pow). The effect of a low melting point of the pesticide (with more chance of a fluid condition in the deposit) was also not clear.

Some pesticides show very slow penetration into the leaves: the fraction of chlorothalonil on the leaves of potato plants hardly decreased in the course of a week (van den Berg et al., 1995). Further, volatilisation of chlorothalonil continued at

about the same (low) level for several days. Caux et al. (1996) characterised chlorothalonil to be non-systemic, as it is not readily absorbed by plant leaves.

6.4 Properties of the leaf surface

Foliar penetration of a pesticide may depend greatly on plant species (Bentson, 1990); thickness, composition and structure of the cuticle play a part. Further, the moisture condition of the leaf surface is important, as penetration may be enhanced by hydratation of cuticle components.

In their review of uptake studies, de Ruiter et al. (2004) found a tendency of the uptake by monocotyledons and some dicotyledons (pea, rape, strawberry) to be faster than that by most dicotyledons.

Besides plant species, other factors may have an influence on pesticide penetration into the leaves: plant variety, stage of development, previous growing conditions, etc. (Bentson, 1990). The 'hardening' of plants growing under dry conditions, by the formation of a thicker cuticle and wax layer, is a well-known phenomenon.

A review of the composition and structure of leaf surfaces in relation to pesticide uptake has been given by Falk (1994). Many areas of the outer surface of the cuticle are quite lipophilic. Besides, there are more polar regions and pathways through the cuticle, which seem to be suitable for the movement of some systemic herbicides. Under certain conditions, pesticides could even penetrate into the leaves via the stomata.

Various characteristics of the plants may have an effect on both pesticide penetration and volatilisation: stage of development, structure of the plants, properties of the leaf surface, growing conditions, etc. A detailed plant growth model would be needed for modelling all the characteristics in course of the growing season.

6.5 Effect of the formulation

Pesticide penetration into the leaves can be promoted by using particular formulations (Willis & McDowell, 1987; Bentson, 1990). Unfortunately, information on the composition of such formulations and their effect is usually not published (confidential data of the company).

The uptake of the herbicide glufosinate (^{14}C-labelled) by leaves of barley and barnyard grass was studied by Köcher & Kocur (1993). When applied in a solution in water, there was little penetration into the leaves (herbicide remained washable with water) and there was no distinct herbicidal effect. Combined application of glufosinate with a wetting agent highly increased the uptake in the leaves and the herbicidal effect showed up. This result is explained from a much better spreading of the liquid on the leaves, allowing substantial uptake within 2 to 4 hours.

Roggenbuck et al. (1993) studied the effect of an organosilicone adjuvant on the penetration of acifluorfen and bentazone in the leaves of velvetleaf. Penetration was increased to about 88% of the dose at 0.25 h after application, as compared to less than 5% penetration of the herbicides alone.

Possible mechanisms for surfactant induced enhanced uptake of pesticides by leaves were discussed by Stock & Holloway (1993). Potential sites for surfactant action are both, the surface of the cuticle and the cuticle itself. A surfactant may affect the condition of the pesticide in the deposit in different ways, thus improving the contact with the leaf. Increase of permeation of the pesticide into the cuticle is also considered to be an important mechanism of adjuvant action. The cuticle may be heterogeneous, with preferential pathways of uptake for polar and non-polar pesticides, respectively. They concluded that different surfactants have different effect on different pesticides applied to different target species. It is unlikely that there is a unifying mechanism for uptake activation. In practice, the mixture of substances in a formulation is often more complex than in the simplified model systems.

Mineral oils and seed oils form a well-known type of additives for herbicides. They improve the spreading of the spray liquid on the leaf surfaces and promote herbicide penetration through the cuticle (Gauvrit & Cabanne, 1993). There is a risk that the selectivity of the herbicide application decreases, leading to (severe) phytotoxic symptoms in the crop.

In his review on adjuvants for use with foliar fungicides, Steurbaut (1993) describes various mechanisms for improved uptake:
- improvement of the coverage of the leaves with fungicide deposit
- enhancement of penetration of systemic fungicides into the leaves
- reduction of losses by alkaline hydrolysis, phototransformation etc.
- reduction of wash-off by rainfall

Contact-acting fungicides should be present as a 'stable' deposit at fhe leaf surface (no need for penetration into the leaves).

Most pesticides seem to require an adjuvant in the formulation for substantial penetration into the leaves (Briggs & Bromilow, 1994). However, it is often difficult to explain the mode of action of the adjuvants because their physico-chemical properties and behaviour are not fully known. Some adjuvants might even volatilise quite rapidly, which reduces the duration of their action.

In their review of literature data, de Ruiter et al. (2004) compiled the effect of an (extra) adjuvant added to the pesticide (in aqueous solution or formulated) on the rate of uptake. In many cases without addition of (extra) adjuvant, the rate of uptake was low. In the presence of the adjuvant, the time for 50% uptake by the leaves was decreased to an average of 15 hours.

A surfactant may enhance penetration into the leaves by improving the contact between the pesticide deposit and the leaves. Some spray formulations can even

disrupt the epicuticular wax layer. An example is the enhanced penetration of atrazine into weed leaves by adding crop oil concentrate (COC) to the spray liquid (McCall et al., 1986b).

6.6   Effect of deposit condition

The rate of penetration of a pesticide into the leaves can be especially high just after application, as long as the spray liquid on the leaves is wet. The uptake of pesticide tends to be less when the deposit dries faster. In the later stages, penetration at high air humidity is often greater than that at low humidity (Willis & McDowell, 1987). Slight rainfall or dew rewetting the herbicide deposit can improve its penetration into the leaves and thus its activity (Gerber et al., 1983; Willis & McDowell, 1987). Water seems to be needed as medium for promoting transport from the deposit to the foliage.

McCall et al. (1986b) and Bentson (1990) also state that the penetration of a pesticide from a deposit into the leaf is promoted by a wet condition of deposit and leaf surface. Slow drying of the deposit leads to higher uptake of pesticide by the leaves than fast drying. The aqueous phase seems to act as an effective transport medium to a large part of the leaf surface. Moist conditions may also affect the permeability of the leaf surface, allowing greater penetration of a pesticide (Bentson, 1990).

McCall et al. (1986b) modelled the behaviour of atrazine after application to weed plants. Only the herbicide present in solution state on the leaves was considered to be available for penetration. For this concept, the condition of the deposit and the transfer between the solid and solution states have to be considered.

Different methods for measuring leaf wetness (and possibly deposit wetness) are available and these give different results. It should be investigated which method is most representative for the moisture condition in the deposit. A model for the simulation of leaf wetness duration has been described by Hoppmann & Wittich (1997), in relation to the risk of infection of the leaves by a parasitic fungus.

The penetration of the fungicide famoxadone (^{14}C-labelled; applied in aqueous suspension) in grape leaves was studied by Andrieu et al. (2000). Vapour pressure 6.4 10^{-4} mPa (20 $^{\circ}$C), solubility in water 52 μg/L and log(K_{ow}) = 4.65 (pH7). When the plants were kept under moist condition, 12% (4 days), 4% (7 days) and 4% (12 days) of the dose could be released by vortexing with water (40 s). At the same times, 79%, 75% and 74%, respectively, could be stripped (in the wax layer) from the leaves by cellulose acetate. When the plants were kept under dry conditions, 51% (4 days), 37% (7 days) and 35% (12 days) of the dose could be vortexed-off with water. At the same times, 96%, 92% and 95% respectively, could be stripped with cellulose acetate. Volatilisation and (photo)transformation seemed to be slow processes. The presence of water was essential for substantial penetration of famoxadone into the wax layer. However, the fungicide is hardly translocated in the plants (no systemic activity).

The uptake of 2,4-D-butyl ester (^{14}C-labelled) by barley leaves was not affected very much by the temperature in the range of 22 to 27 ºC (Breeze et al., 1992).

6.7 Lack of quantitative information

Knowledge on the penetration of pesticides into plants is rather empirical. Development of the theory is hampered by a series of factors such as:
- the presence of a mixture of substances in the deposit (common physical laws hold for pure substances);
- lack of public information on the substances in the formulation (confidential domain);
- the lack of observations on the distribution and status of the pesticide deposit;
- the differences and variability in the properties of the plant surfaces (even within species);
- the complexity of the penetration process, including different mechanisms;
- the differences and variability in the environmental conditions;
- the nature of an effect may be known, but no quantitative relationship is available.

Summarising, it can be stated that the prospects for mechanistic modelling of pesticide penetration into plants are not favourable in the near future. Some exercices in detailed modeling have been made, but soon the lack of input data and of checks on the results became evident.

6.8 Description in the module

Pesticide penetration into the leaves is influenced by many factors, but no quantitative relationships are known. Therefore, the description of the process in the plant module can be kept simple. The rate of pesticide penetration into the leaves is calculated by:

$$R_{pen} = k_{pen} A_p \qquad \text{(Eq. 9)}$$

With
R_{pen} =   rate of pesticide penetration into the leaves (kg m^{-2} d^{-1})
k_{pen} =   rate coefficient of penetration (d^{-1}).

The coefficient k_{pen} is one of the quantities to be calibrated in the computation on the basis of the measurements or it is derived from other studies on pesticide and formulation.

As the conditions often change with time in the studied situations, the rate coefficient k_{pen} can be introduced into the computations as a function of time.

6.9 Proposal for classification of penetration rates

Direct measurements on the rate of penetration of pesticides into plants are usually not available. Quantitative predictions on such penetration on the basis of process theory do not seem to be available. A major problem is that, besides the physico-chemical properties of the pesticide, the substances in the formulation may have a great effect on penetration. An attempt can be made to classify (formulated) pesticides into e.g. five classes with respect to their propensity to penetrate into the plants. A representative rate coefficient can be assigned to each of the classes, as a first approximation of the rate of penetration.

The following five main classes of penetration rate are distinguished:
1) very fast penetration: half-life   = 0.04 d (1 h; k_{pen} = 17 d^{-1});
2) fast penetration: half-life   = 0.21 d (5 h; k_{pen} = 3.3 d^{-1});
3) moderate penetration rate: half-life   = 1.0 d (k_{pen} = 0.69 d^{-1});
4) slow penetration: half-life   = 5.0 d (k_{pen} = 0.14 d^{-1});
5) very slow penetration: half-life   = 25 days (k_{pen} = 0.03 d^{-1}).

If the above classification is too rough, one of the boundaries between the classes could be selected: half-life = 0.13 d (3 h; k_{pen} = 5.5 d^{-1}), half-life = 0.63 d (15 h; k_{pen} = 1.1 d^{-1}), half-life = 3.0 d (k_{pen} = 0.23 d^{-1}), half-life = 15 d (k_{pen} = 0.05 d^{-1}).

In this way the available empirical knowledge on penetration is translated into a rate coefficient. The classification allows for penetration into the plants to be included in the computations, as a process competing with volatilisation.

Of course, one should be aware of the uncertainty of this approach and of the effect on the computed volatilisation of the pesticide. If the rate of penetration is critical in view of the environmental assessment of the pesticide, special experiments will be needed.

Examples of values of rate coefficient k_{pen}, derived by computer simulation of well-defined experiments (calibration), are presented in Table 4. According to the classification above, fenpropimorph is a fast-penetrating fungicide.

Table 4. Values of rate coefficient k_{pen} for the penetration of pesticides into plants, obtained by computer simulation of well-defined experiments.

Type of study	Pesticide	Plant	Temperature in first day (^{0}C)	Rate coefficient k_{pen} (d^{-1})	Corresponding half-life (d)	Reference
Wind tunnel	Fenpropimorph, ^{14}C-labelled	Beans (1)	23 to 30	1.7	0.41	Leistra & Wolters (2004)
Idem	Idem	Beans (2)	14 to 19	2.8	0.25	Idem
Idem	Idem	Radish	20 to 29	4.8	0.14	Idem
idem	Fenpropimorph, non-labelled	Sugar beet	5 to 25	2.1	0.33	Idem

6.10 Research needs

Knowledge on the penetration of pesticides into plants has a rather empirical nature. For each pesticide (or related substances), research data have to be traced. Additional information may be present in confidential files of the company. If the information on pesticide penetration into plants is essential for the environmental assessment, data from the company file have to be made available or special experiments have to be carried out. In this type of research, the use of radiolabeled material is essential to establish the material balance of the various processes at the plant surface.

In experiments, different fractions of plant residue should be measured: a) rinsable with polar sovent (water), b) rinsable with less polar sovent and c) total extraction. Such measurements should give a picture of the extent to which the pesticide penetrates into the plants. Further study is needed on how the fractions of the pesticide measured in the experiments relate to the states defined in the computation module.

Some theoretical studies on pesticide penetration into plants have been carried out. However, soon the lack of input data became apparent. Further, well-defined experiments for checking the results of the computations seem to be scarce.

Research on the effect of the physico-chemical properties of the pesticide on penetration into the plants has to be continued. The theory may be different for non-charged compounds, weak acids and weak bases. A research problem is that often a mixture of substances is present in the deposit.

Knowledge on the properties of the surface of plant species is needed for the present type of research. However, additional factors like plant variety and (previous) growth conditions play a part. Further, the properties of the plant surface may be influenced by substances in the formulation of the trade product.

Research on the effect of environmental conditions on pesticide penetration into the plants has to be continued. As expected, moisture condition of the deposit plays an important role in pesticide penetration into the leaves, via water as the transport medium. To allow simulation in the module, a quatitative relationship is needed for this factor. This requires accurate measurements of the moisture condition of the deposit and, if possible, prediction on the basis of weather data. The deposit could dry somewhat more slowly than the non-covered leaf surface.

The prospects for classification of the rate of penetration in the five classes has to be tested for some well-studied pesticide-plant combinations. A question is whether a more refined classification (e.g. in ten classes) is possible.

The development of a more advanced computation model for pesticide penetration into plant leaves requires quantitative relationships of general validity. Unfortunately, such relationships are not available. Factors like pesticide properties, formulation constituents, plant properties and environmental conditions interact in a very

complicated way. Model development is only possible for simplified cases under well-controlled conditions, such as for simple mixtures of compounds and isolated cuticles. Possible quantitative relationships seem only valid for the specific conditions of the experiment.

7 Washoff by rainfall

7.1 General description

Under rainy conditions, part of the pesticide deposit will be washed from the leaves. It is well-known that much rainfall shortly after application decreases herbicide activity (Gerber et al., 1983; McCall et al., 1986b). The extent of this process depends on factors like the properties of the pesticide, the properties of the formulation (e.g. sticking agents), the condition of the deposit and the time after spraying. The extent to which the effectiveness of a pesticide is maintained in washoff situations is characterized by its rainfastness. Substantial washoff of the deposit of a pesticide as a competing process may be expected to result in a drastic reduction in its volatilisation rate.

In practice, the idea of "rainfastness' has a wider meaning than the resistance of a pesticide to washoff from the deposit by rain. The idea includes the penetration of the pesticide into the leaves, as a mechanism of protection against washoff. Rainfastness is usually related to the extent to which the effectiveness in control of the target organism is maintained when it rains. Such research does not distinguish the contributions to the rainfastness by deposit resistance to washoff and plant penetration.

In their review, Willis & McDowell (1987) discussed a few decades of research on washoff of dislodgeable pesticide residue from plants by rainfall. The susceptibility of the residue to washoff is greatest when rain falls within 24 hours after application. Pesticide removal by rain is greatest with the first few mm of rainfall in a shower. Washoff decreases when the time interval between spraying and rainfall increases. Dust and wettable powder formulations may be more susceptible to washoff than emulsions.

Various washoff studies have been carried out with rainfall shortly after spraying of the pesticide on the plants. An example is the study of Willis et al. (1988) on carbaryl washoff after spraying on a cotton crop, as wettable powder. Already at 2 h after spraying, the simulation of 25 mm of rain was started. By far the highest concentrations of carbaryl were measured in the first few mm of washoff water (around 50 mg/L), which can be compared with the solubility of carbaryl in pure water of 120 mg/L at 20 °C (Tomlin, 2003). On average 63% of the carbaryl on/in the plants was washed off by the 25 mm of rain. There was a tendency of somewhat higher washoff concentration at the lower rainfall intensities.

7.2 Effect of solubility in water

Willis et al. (1986) studied washoff of permethrin after spraying cotton plants in the field. The simulated rainfall of 25 mm (at different intensities) was applied at 2 h after

spraying. The initial concentration of permethrin in washoff water was around 5 mg/L, which is much higher than its solubility in water of 0.006 mg/L (20 ^{0}C; Tomlin, 2003). Approximately 35% of the amount on/in the plants was washed off by 25 mm of rain, independent of rainfall intensity.

Washoff of the pesticides with rainfall can be compared with their solubility in water, e.g. as reported by Tomlin (2003). Washoff by 15 mm of rainfall at 1 hour after spraying ranged from 83 to 95% of the deposit for dichlorvos (w.s. 18 000 mg/L), dimethoate (w.s. 23 300 mg/L), malathion (w.s. 145 mg/L) and quinalphos (w.s. 17.8 mg/L) (Chen & Wan, 1997). Washoff of cypermethrin (w.s. 0.004 mg/L) was 74% under these conditions. So the rate of pesticide washoff from the leaves by rainfall is not a simple function of its solubility in water. Washoff may occur by both, dissolution in the water and detachment of particles by the rain drops, with a possible effect of the formulation. The rate of washoff becomes lower as the time between spraying and rainfall increases.

Washoff of the poorly soluble fenvalerate (solubility in water < 0.01 mg/L at 25 ^{0}C; Tomlin, 2003) sprayed as emulsifiable concentrate on cotton plants was studied by McDowell et al. (1987). At 2 h after spraying, 25 mm of rainfall was simulated and the washoff water was collected for analysis. In the initial period, the washoff concentrations (around 5 mg/L) were much higher than the solubility of fenvalerate in pure water. By far the highest concentrations were measured for the first 3 mm of rainfall. Averaged for all rainfall intensities (little effect), 38% of the fenvalerate on/in the plants was washed off.

An emulsifiable concentrate of fenvalerate was sprayed on a cotton crop, which was followed by simulated rainfall (51 mm in 1 h) at various times (Willis et al., 1994a). When rain started at 2 h after application, 94% of the dosage was washed off. Fenvalerate concentration in the initial washoff water was about 15 mg/L. This is much higher than the reported solubility in water of < 0.01 mg/L (Tomlin, 2003). Some possible causes were mentioned: a) continued activity of the emulsifying substances and b) washoff of solid material from the deposit. Even at 6 days after application, 35% of the fenvalerate dosage was washed off by 51 mm of rainfall.

Permethrin concentration in the initial washoff ranged from 12 to 15 mg/L (Willis et al., 1994b), which is far above the solubility of the compound in pure water of 0.006 mg/L at 20 ^{o}C (Tomlin, 2003).

There is only limited effect of water solubility of the pesticide on washoff, especially in the first few days after spraying. Even pesticides with a very low solubility in water can show substantial washoff by rainfall. In various cases, the initial concentration in washoff water was much higher than the (low) water solubility of the pesticide. Possibly, constituents in the formulation (e.g. emulsifying substances) still have an effect on the transfer of the pesticide to the flowing water. Further, deposit particles may be detached from the deposit by the impact of the raindrops. In the latter process, it would be expected that larger drops have more effect than smaller drops.

7.3   Effect of the formulation

The rainfastness of maneb and mancozeb applied in different formulations to potato and pea plants was studied by Kudsk et al. (1991). Rainfall was simulated at 24 h after fungicide spraying in the glasshouse. Rainfastness of the suspension concentrate (SC) application was found to be better than that of the wettable powder (WP) application. For WP, 3 mm of rain reduced the plant residue to e.g. 40% of the pre-rainfall residue and 9 mm of rain reduced it to e.g. 20%. When the particles in the WP formulation were pulverised by milling, better rainfastness was obtained than with the coarser particles.

The effect of extra adjuvants in the formulation on rainfastness depended on the plant species (Kudsk et al., 1991). Oil adjuvants (especially vegetable oil) improved rainfastness of maneb on pea plants (with distinct wax layer), e.g. retention after 9 mm of rain was increased from 14% to 90% of the pre-rain residue. The latex sticker improved rainfastness of maneb WP on potato plants (with little wax on leaves).

Roggenbuck et al. (1993) measured the effect of an organosilicone adjuvant on the absorption of ^{14}C-labelled acifluorfen and bentazone by weed leaves. The absorption was much increased to about 88% of the dose at 0.25 hour after application. The rapid penetration into the cuticle explained the rainfastness of the herbicides when exposed to simulated rainfall at 0.25 and 1 hour after application.

The effect of two adjuvants on washoff of imazaquin herbicide (w.s. 60 to 120 mg/L at 25 ^{0}C; Tomlin, 2003) from two weed species was studied by Reddy & Locke (1996). Rain (25 mm in 20 min) was applied at 1 h and 24 h after spraying. With rain after 1 h, much of the imazaquin was washed off in all treatments. With rain after 24 h the adjuvant had some effect: e.g. washoff from the sensitive weed species was reduced from 88% of the plant residue (no adjuvant) to around 60% of the residue (with adjuvant). Even in the presence of the adjuvant, much time was needed for substantial penetration of imazaquin into the leaves.

7.4   Effect of condition of the deposit

In pesticide deposits on the plant surface, the emulsifying substance (or combinations) can still be active. Such a substance may enhance the transfer of the active ingredient to the running water and thus promote washoff.

Part of the deposit may consist of small particles, e.g. after application of a wettable powder. Such particles may be detached from the leaves by the mechanical action of the rain drops and thus be washed off.

Rainfastness of the fungicide famoxadone sprayed on grape leaves was studied by Andrieu et al. (2000), by using a bioassay (qualitative results). Properties: vapour pressure 6.4 10^{-4} mPa (20 ^{0}C), solubility in water 52 µg/L and log(K_{ow}) = 4.65 (pH7). After keeping the plants under moist condition for 24 hours, 30 mm of rainfall was

simulated. The effectiveness of the fungicide was not affected. In comparison, the performance of mancozeb was reduced by e.g. 68%.

7.5   Effect of time interval

Drops with chlorothalonil (w.s. of 0.81 mg/L at 25 ^{0}C; Tomlin, 2003) were placed on the leaves of potato plants in a greenhouse (Bruhn & Fry, 1982b). Washoff by 10 mm simulated rainfall was dependent on the time interval between fungicide application and sprinkling: 66% (rain after 3 h drying of deposit on same day), 55% (rain after 1 day) and 36% (rain after 7 days) of the residue on/in the leaves just before rain started.

Washoff of parathion-methyl (w.s. 55 mg/L at 20 ^{0}C) and fenvalerate (w.s. < 0.010 mg/L) at 25 ^{0}C) sprayed as emulsifiable concentrates on cotton plants in the field was studied by McDowell et al. (1985). At various times after spraying (range of 2 to 146 h) the simulation of 51 mm of rainfall in about 1 h was started. The percentage of the total plant residue of parathion-methyl washed off decreased from 73% after 2 h to 0.2% after 146 h. For fenvalerate, washoff decreased from 12% after 2 h to 6% after 146 h.

Washoff of malathion from cotton plants was studied after ultra-low-volume application at 0.99 kg/ha (Willis et al., 1992b). The plants were sprinkler-irrigated to a total amount of 51 mm in 1 hour. When irrigated within the first 50 hours after application, washoff was 62% of the amount of malathion on/in the plants released to methanol; thereafter it was on average 37%. Half of the total washoff was caused by the first 4.8 to 6.5 mm of irrigation. Willis et al. (1992b) also studied the washoff of permethrin (dosage 0.11 kg/ha) from cotton plants by sprinkler irrigation. When irrigated within the first 50 hours after application, washoff was 59% of the amount of permethrin on/in the plants released to methanol; thereafter it was on average 26%. Again, half of the total washoff was caused by the first 4.8 to 6.5 mm of irrigation. Soybean oil as carrier did not reduce permethrin washoff.

The effect of time interval between spraying and simulated rainfall on washoff was studied by Willis et al. (1992a). They sprayed methyl-parathion and fenvalerate in oil on cotton plants in the field and started rainfall simulation (51 mm in 1 h) at different times. The rainfall started at 2 h after spraying washed 96% of the methyl-parathion residue from the plants, while rainfall after 146 h washed 12% of the residue. For fenvalerate, these figures were 80% of the plant residue after 2 h and 34% of the residue after 146 h. Pesticide penetration into the leaves (included in the residue analysis) was considered to be a main cause of the decline in washability of the pesticides.

Washoff of permethrin and sulprofos with 51 mm in 1 h at various times after spraying was studied by Willis et al. (1994b). For permethrin, the percentage washed from the plants decreased from 52% (rain started after 2 h) to 14% (rain started after 146 h). The figures for sulprofos were: a percentage of 92% washoff for rainfall after

2 h which decreased to 50% for rainfall after 146 h. The increased resistance to washoff can result from a greater fraction being absorbed into the cuticular layer with time. With rain after 2 h, 80% of the total washoff of permethrin was reached with the first 6 mm of rain, while with rain after 146 h this extent of washoff was reached with 24 mm of rain.

Willis et al. (1994a) studied the effect of time interval between spraying and simulated rainfall (51 mm in 1 hour) for azinphos-methyl and fenvalerate applied as emulsifiable concentrates to cotton plants in the field. Washoff water was collected and analysed for the pesticides. When rainfall was started after 2 h, 95% of the plant residue of azinphos-methyl was washed off; this decreased to 45% washoff after 146 h. For fenvalerate, these figures were 94% of the plant residue after 2 h and 35% of the residue after 146 h. For all times combined, the first 50% of washoff already occurred with the first 2.4 mm of rainfall.

All research data indicate that the washability of a pesticide by rainfall decreases with time after spraying. A main cause is that an increasing part of the pesticide penetrates into the leaves. The plant analyses include both, pesticide left in the deposit and that penetrated into the leaves. Further, the well exposed fraction of the deposit will dissipate more rapidly (volatilisation, phototransformation) than deposit enclosed or protected by plant parts. No research has been found on the effect of change in deposit condition with time on pesticide washability.

7.6   Effect of rainfall intensity

Parathion-methyl in EC formulation was sprayed on cotton plants in the field. At 2 hours after spraying, the plants were sprinkler-irrigated with 24 mm of water at different intensities (McDowell et al., 1984). On average 88% of the residue on the plants at the start of the irrigation was washed off; most of it (e.g. 70% of the total loss) already with the first 5 mm. The intensity of the irrigation had little effect; washoff was determined mainly by the amount of irrigation water.

Kudsk et al. (1991) varied the intensity of simulated rainfall in their studies of rainfastness of maneb. Washoff of the wettable powder (WP) formulation of maneb increased when rain intensity was increased in the range 3, 9 and 27 mm/h. This effect was explained from the greater mechanical impact of the larger rain droplets at the higher intensity. The effect of this increase was greater on the WP formulation than on the suspension concentrate (SC) formulation of maneb (which was more rainfast).

The effect of rainfall intensity on washoff shows considerable variation. In the study of Willis et al. (1988), washoff concentration of carbaryl tended to be higher at the lower rainfall intensity. This could be related to the additional time available for dissolution and transfer to the water flow. Comparatively high washoff at higher rainfall intensities could be explained from the mechanical impact of the raindrops

on the deposit causing more particles to be washed off. Most authors considered rainfall intensity to have less effect on washoff than the amount of rainfall.

Washoff of formulated carbaryl from soybean plants at different rain intensities was studied by Willis et al. (1996). At 24 h after spraying the crop, 25 mm of rain was simulated to fall at different intensities. Carbaryl washoff ranged from 47% of the plant residue at 105 mm/h to 75% of the residue at 13 mm/h. This difference was explained from the longer contact time between the deposit and the flowing water.

7.7 Washoff by a rain shower

FOCUS (2003) made a proposal for calculation of the mass of pesticide washed off from the plant canopy by a rain shower:

$$\text{Final mass on plants} = (\text{initial mass on plants}) *$$
$$\exp[-(\text{foliar washoff coefficient}) * (\text{layer of rainfall})] \qquad \text{(Eq. 10)}$$

The foliar washoff coefficient (cm^{-1}) is the fraction of the mass of pesticide on the plants washed off by 1 cm of rain. This equation has been taken from the RZWQM documentation (Root Zone Water Quality Model; Hanson et al., 1998).

The foliar washoff coefficient is calculated from the solubility of the pesticide in water:

$$\text{Foliar washoff coefficient} = 0.016 * (\text{solubility in water})^{0.3832} \qquad \text{(Eq. 11)}$$

Pesticide solubility in water is expressed in mg L^{-1}.

Table 5 gives the values for the foliar washoff coefficient calculated with Eq. 9.2 for a range of solubilites in water.

Table 5. Foliar washoff coefficients calculated for pesticides with a range of solubilites in water

Solubility in water (mg L^{-1})	Foliar washoff coefficient (cm $^{-1}$)
0.1	0.0066
1.0	0.016
10.0	0.039
100	0.093
1000	0.23
10 000	0.55

The default value of the foliar washoff coefficient is set at 0.5 cm^{-1}, which corresponds to a water solubility of 8000 mg L^{-1}. This value is considered to be a worst case with respect to the mass washed from the canopy.

Some questions arise with respect to this proposal:
• The washoff equation is based on the mass of the pesticide <u>on</u> the plants, thus on the dislodgeable residue, which is conceptually correct. However, all data found in

the literature up to now are expressed on the basis of dislodgeable plus plant-penetrated residue.

- The values of the foliar washoff coefficient are low, considering the high washoff values measured in the first period (e.g. on the first day) after spraying. Within this period, much of the pesticide is expected to be present in the deposit.
- Other factors like the influence of special additives in the formulation and the condition of the deposit are not considered.

In conclusion it is important to search for the original basic data on which the washoff equation was based. Further, details are needed on the way in which the equations were derived. The first impression, based on the literature review in this chapter, is that if the equations are applied to the dislodgeable residue on the plants, washoff will be often under-estimated.

7.8   Quantities and equations

The rate of pesticide washoff from the leaves by (simulated) rainfall is set dependent on rainfall intensity and a wash-off coefficient:

$$R_w = k_w W_r A_p \qquad \text{(Eq. 12)}$$

with:
R_w =   rate of pesticide washoff from the leaves (kg m^{-2} d^{-1})
k_w =   coefficient for pesticide washoff (mm^{-1})
W_r =   rainfall intensity (mm d^{-1}).

7.9   Proposal for a classification

Various factors are known to affect pesticide washoff with rainfall from plants. However, no relationships are available for a mechanistic and quantitative description of this process. Only a rough classification of washoff based on the experimental results seems to be possible at present. It is proposed to classify washoff in a certain situation in one of the following five classes:
1) k_w = 0.09 mm^{-1} (e.g. 90% washoff with 10 mm rainfall);
2) k_w = 0.07 mm^{-1} (70% with 10 mm);
3) k_w = 0.05 mm^{-1} (50% with 10 mm);
4) k_w = 0.03 mm^{-1} (30% with 10 mm);
5) k_w = 0.01 mm^{-1} (10% with 10 mm).

If this classification is too rough, a value at the boundary of two classes can be selected. In this classification it is assumed that the crop is only sprayed if no rain is expected in the first period of e.g. 6 hours. It should be noted that in some experiments rainfall was simulated to occur very soon after spraying, which may result in very high washoff.

7.10 Research needs

The effect of various factors on pesticide washoff from plants has to be studied further. Solubility of the pesticide in water may be expected to have an effect, but no quantitative relationship is known. The same holds for the possible effect of the octanol/water partitioning coefficient P_{ow}. There is no systematic information on the effect of the formulation on washoff. Substances may have been added to a pesticide product to enhance rainfastness. Much of this type of information may be confidential company property. The time after application at which the rain falls has an effect on washoff, but a relationship of more general validity is lacking. The condition of the deposit changes in time (e.g. by drying), but more information on this aspect is needed. Rate of washoff for the layers in the canopy may be different, as water flow through the lower layers is more heterogeneous.

8 Transformation on the plant surface

8.1 General description

Pesticides deposited on leaf surfaces may be subject to transformation, especially to photochemical transformation. Direct phototransformation can occur if the pesticide absorbs light at wavelengths in the sunlight spectrum (> 290 nm). Indirect phototransformation involves reaction of the pesticide with natural compounds formed by sunlight irradiation. A well-known example is the formation of OH radicals by sunlight. For effective plant-applied pesticides, phototransformation should not be fast as this impedes their usefulness. However, several pesticides show some extent of phototransformation on leaf surfaces, according to the survey on this topic by Leistra (1998).

The contribution of phototransformation to the fate of a pesticide on plants can be studied in a micro-agro-ecosystem, e.g. with a light source simulating the sunlight spectrum. In the presence of such light (simulated day in August), Müller et al. (1997) found a distinct fraction of transformation products of ^{14}C-labelled parathion-methyl on/in the leaves after 24 hours. By contrast, no transformation was measured in the dark.

The chance of direct phototransformation can be derived from the absorption of light in the sunlight spectrum by the compound in a natural medium, e.g. water (Chen & Wan, 1997). Such absorption data have been published for various pesticides. The extent of light absorption and the quantum yield of the reaction at this absorption are important characteristics. Further, the rate of phototransformation has to be related to sunlight intensity as a function of time.

Indications for indirect phototransformation of fenpropimorph on leaves were found by Stork et al. (1998b) and Ophoff et al. (1999) in experiments with lysimeter plus wind tunnel. Filtering the inlet air by activated carbon resulted in lower amounts of transformation products. It seems that substances participating in the photochemical reactions were filtered out.

It is likely that the rate of pesticide phototransformation decreases with increasing depth in the canopy, because of shadow action. The decrease in light intensity with depth can be described with an extinction equation, with corresponding extinction coefficient (Hicks et al., 1987). This equation can be applied to both direct (beam) sunlight and indirect (diffuse) sunlight.

(Photo)transformation of pesticides on plant leaves may lead to products (possibly also toxic), that also show volatilisation. An example is the photo-oxidation of parathion to paraoxon, which is also highly toxic.

8.2 Quantities and equation

The rate of pesticide transformation on the plant surface by solar irradiation is described by first-order kinetics:

$$R_{ph} = k_{ph} A_p \qquad \text{(Eq. 13)}$$

with:
R_{ph} = rate of phototransformation on the leaves (kg m^{-2} d^{-1})
k_{ph} = rate coefficient of phototransformation (d^{-1}).

The rate coefficient k_{ph} is set dependent on the intensity of solar irradiation:

$$k_{ph} = \left(\frac{I_{act}}{I_{ref}} \right) k_{ph,ref} \qquad \text{(Eq. 14)}$$

with:
I_{act} = actual solar irradiation intensity (W m^{-2})
I_{ref} = reference solar irradiation intensity (500 W m^{-2})
$k_{ph,ref}$ = rate coefficient of phototransformation at reference irradiation intensity (d^{-1}).

8.3 Proposal for a classification

The coefficient $k_{ph,ref}$ is one of the quantities to be calibrated in the computation on the basis of the measurements or it has to be derived from other studies on the pesticide. Usually, direct measurements on the phototransformation of a pesticide on plant surfaces are not available. Types of information that may be available are:
• photolysis in water, purified or natural;
• phototransformation on artificial surfaces;
• phototransformation on soil or other natural surfaces;
• phototransformation in air.
These types of measurements give an indication whether phototransformation on plant surfaces may occur. However, translation of rates between such media does not seem to be possible yet.

The rate of phototransformation on plant surfaces may show a wide variation. Possible factors are: a) the substances in the formulated product; b) the substances at the plant surface, c) the substances in the local air, etc.

An attempt could be made to classify a pesticide in one of five classes of vulnerability to phototransformation on plant surfaces, on the basis of available research data. The following representative values of the rate coefficient $k_{ph,ref}$ are assigned to each of these classes:
1) very fast phototransformation: half-life   = 0.04 d (1 h; $k_{ph,ref}$ = 17 d^{-1});
2) fast phototransformation: half-life   = 0.21 d (5 h; $k_{ph,ref}$ = 3.3 d^{-1});
3) moderate rate of phototransformation: half-life = 1.0 d ($k_{ph,ref}$ = 0.69 d^{-1});

4) slow phototransformation: half-life $\quad\quad$ = 5.0 d ($k_{ph,ref}$ = 0.14 d^{-1});
5) very slow phototransformation: half-life $\quad$ = 25 days ($k_{ph,ref}$ = 0.03 d^{-1}).

If the above classification is too rough, one of the boundaries between the classes could be selected: half-life = 0.13 d (3 h; $k_{ph,ref}$ = 5.5 d^{-1}), half-life = 0.63 d (15 h; $k_{ph,ref}$ = 1.1 d^{-1}), half-life = 3.0 d ($k_{ph,ref}$ = 0.23 d^{-1}), half-life = 15 d ($k_{ph,ref}$ = 0.05 d^{-1}).

If the rate of phototransformation at plant surfaces is critical in the environmental evaluation, special measurements should be made.

Examples of values of $k_{ph,ref}$ derived from computer simulations of well-defined experiments with micro-agro-ecosystems are given in Table 6.

Table 6. Values of the rate coefficient $k_{ph,ref}$ for phototransformation on plant surfaces at reference sunlight radiation, derived by computer simulations of well-defined experiments

Type of study	Pesticide	Plant	Radiation regime	Rate coefficient $k_{ph,ref}$ (d^{-1})	Reference
Wind tunnel, inlet air filtered	Fenpropimorph, ^{14}C-labelled	Bean (1)	Natural sunlight, inside wind tunnel	1.1	Leistra & Wolters (2004)
Wind tunnel, inlet air not filtered	Idem	Bean (2)	Idem	13.8	Idem
Idem	Idem	Radish	Idem	6.0	Idem
idem	Fenpropimorph, non-labelled	Sugar beet	idem	1.6	idem

According to these data, the rate of phototransformation of fenpropimorph in non-filtered air is classified as "fast to very fast", with a representative rate coefficient $k_{ph,ref}$ of 5.5 d^{-1}. This value could be used as a first estimate for field conditions.

8.4 Research needs

Research data on the photochemical transformation of pesticides on plant surfaces are very scarce. Thus, an important research question is how results on the phototransformation of a pesticide under standard conditions, e.g. photolysis in water, can be translated to rates of phototransformation on plant surfaces.

There are many environmental factors which affect the rate of phototransformation. Quantitative information on their effect has to be obtained in experiments under well-controlled conditions. More studies with radiolabelled compounds in micro-agro-ecosystems are needed. The use of radiolabelled material in such ecosystems is essential for estimating the material balance of the processes.

In photochemistry, many reaction mechanisms are possible. It is not possible yet to predict their importance in the field and thus their rate coefficient.

The light spectrum in a volatilization chamber etc. is often different from that in the field. Walls of common glass types filter out the shorter UV wavelengths in sunlight (e.g. 290 to 390 nm), which are often most active in the phototransformation of pesticides. In any study, the sunlight spectrum and intensity should be compared with the range of the values under field conditions.

9 Mass conservation equation

The equation for the conservation of mass of pesticide on the plant surface reads:

$$\frac{dA_p}{dt} = -J_{vol,act} - R_{pen} - R_w - R_{ph}$$
(Eq. 15)

with:
t   = time, d.

All areic quantities in this equation are expressed on the basis of m^2 field surface. The definition of the two deposit classes of a) well-exposed deposit and b) poorly exposed deposit requires the use of two mass conservation equations, one for each of these classes.

10 Example of the estimation of input data

Directly measured input data are often not available for several quantities to be used in the computer simulation of pesticide behaviour at plant surfaces. Probably, the best input data are obtained from the simulation of well-defined wind tunnel experiments with plants, in which radiolabelled pesticides are used. However, this type of experiment has only be carried out for a few pesticides. The input data for most of the pesticides have to be estimated from a wide range of divergent types of experiment. The processes at the plant surface are so complex that a detailed simulation is not possible yet. The effect of many factors on the rate of the processes is not quantitatively known. For the time being, comparatively simple descriptions are used. Nevertheless, the input data have to be collected carefully, by necessity often on the basis of empirical data. In Appendix 3, an example is given of the estimation of input data for a pesticide, i.c. the extensively studied insecticide chlorpyrifos.

11 General discussion

The volatilization of pesticides can be studied in different types of experiment, ranging from experiments with volatilization chambers, via semi-field experiments (micro-agro-ecosystems) to field experiments. Each experimental set-up has its advantages and disadvantages. The effect of single factors on the rate of volatilization can only be studied using chambers or wind tunnels in which the conditions can be controlled. Quantitative study of the factors affecting volatilization in combination with a simulation model can be helpful in the translation of results from smaller-scale experiments to a range of field conditions.

Several aspects of the behaviour of a pesticide can be studied simultaneously in a micro-agro-ecosystem, using radiolabelled compound. Chemical analyses for different compartments in the course of the experiment can give a rather complete picture of the processes. Attempts can be made to simulate the outdoor conditions closely in the ecosystems. Further, the isolated effect of an environmental factor can be studied. Such experiments can be utilised to derive rate coefficients and relations to be used in modelling the transfer and transformation processes under field conditions.

Residue analyses for the plants in the framework of volatilisation studies should be rather specific (Smelt et al., 1997; 2003). The fraction of the residue available for volatilisation (dislodgeable residue) should be measured separately. Possibly, the fraction on/in the cuticle and the fraction penetrated into the plant cell region can also be distinguished.

Henry's Law coefficient (often mentioned as a factor) only seems to be a logical parameter in volatilisation studies for the periods in which the deposit on the leaves is wet. It should be noted that the affinity of the pesticide for the aqueous phase may be strongly influenced by constituents in the formulation.

As vapour pressure is a very important pesticide characteristic in volatilisation, the reliability of reported values should be checked. Sometimes even strongly divergent values are reported or cited for a certain pesticide. It may be necessary to make new measurements according to official guidelines, e.g. that of the OECD (1995). Another aspect is that vapour pressures hold for pure substances. In practice, often mixtures will occur (e.g. with formulation constituents), so the possible effect of the admixtures on vapour pressure should be considered.

The formulation of the pesticide product may have an effect on pesticide volatilisation from the deposit. In some cases, the common EC and WP formulations had little effect on volatilisation, but in other cases there was a difference. It seems that special formulations have to be developed to reduce volatilisation to a large extent, while maintaining the effectiveness of the pesticide.

A general aspect is that the physico-chemical properties of pesticides have been measured for pure substances (where relevant in pure phase). Examples are the solubility of the compound in water and the Henry coefficient for partitioning between air and water. However, pesticides are often not present as the pure substance (in pure phase). The presence of other substances in the water may affect these characteristics drastically. This makes prediction of their behaviour on the basis of physico-chemical properties rather uncertain (Bedos et al., 2002).

The formulation has often much effect on the behaviour of a pesticide in the plant canopy. However, the information on the composition of the trade product is intellectual property of the registration holder/applicant. So it is usually not publicly known which substances have been added for specific effects on pesticide behaviour and efficacy. Especially in critical cases of environmental assessment, it is needed that such information is made available by the registration holder/applicant.

Literature

Andrieu, N., J.L. Genet, G. Jaworska & G. Bompeix, 2000. Behaviour of famoxadone deposits on grape leaves. Pest Manag. Sci. 56: 1036-1042.

Bedos, C., P. Cellier, R. Calvet, E. Barriuso & B. Gabrielle, 2002. Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: Overview. Agronomie 22: 21-33.

Bentson, K.P., 1990. Fate of xenobiotics in foliar pesticide deposits. Reviews Environ. Contam. Toxicol. 114: 125-161.

van den Berg, F., G. Bor, R.A. Smidt, A.E. van de Peppel-Groen, J.H. Smelt, T. Müller & T. Maurer, 1995. Volatilization of parathion and chlorothalonil after spraying onto a potato crop. Report 102. DLO Winand Staring Centre, Wageningen.

van den Berg, F., R. Kubiak, W.G. Benjey, M.S. Majewski, S.R. Yates, G.L. Reeves, J.H. Smelt, A.M.A. van der Linden, 1999. Emission of pesticides into the air. Water Air Soil Pollut. 115: 195-218.

van den Berg, F. & M. Leistra, 2004. Improvement of the model concept for volatilisation of pesticides from soils and plant surfaces in PEARL. Description and user's guide for PEARL 2.1.1-C1. Alterra, Wageningen, The Netherlands.

Breeze, V.G., J.C. Simmons & M.O. Roberts, 1992. Evaporation and uptake of the herbicide 2,4-D-butyl applied to barley leaves. Pestic. Sci. 36: 101-107.

Briggs, G.G. & R.H. Bromilow, 1994. Influence of physicochemical properties on uptake and loss of pesticides and adjuvants from the leaf surface. In: Interactions between adjuvants, agrochemicals and target organisms. Ernst Schering Research Foundation Workshop 12: 1-26. P.J. Holloway, R. Rees & D. Stock (eds). Springer Verlag, Berlin.

Bruhn, J.A. & W.E. Fry, 1982a. A statistical model of fungicide deposition on potato foliage. Phytopathology 72: 1301-1305.

Bruhn, J.A. & W.E. Fry, 1982b. A mathematical model of the spatial and temporal dynamics of chlorothalonil residues on potato foliage. Phytopathology 72: 1306-1312.

Caux, P.Y., R.A. Kent, G.T. Fan & G.L. Stephenson, 1996. Environmental fate and effects of chlorothalonil – A Canadian perspective. Critical Reviews Environ. Sci. Technol. 26: 45-93.

Chen, Z. & H. Wan, 1997. Degradation of pesticides on plant surfaces and its prediction – A case study on tea plant. Environ. Monitoring Assessment 44: 303-313.

Cooper, R.J., J.J. Jenkins & A.S. Curtis, 1990. Pendimethalin volatility following application to turfgrass. J. Environ. Qual. 19: 508-513.

Dearden, J.C., 2003. Quantitative structure-property relationships for prediction of boiling point, vapor pressure, and melting point. Environ. Toxicol. Chem. 22: 1696-1709.

Falk, R.H., 1994. Influence of formulation and adjuvants on the foliar location and physical form of the active ingredient. In: Interactions between adjuvants, agrochemicals and target organisms. Ernst Schering Research Foundation Workshop 12: 53-82. P.J. Holloway, R. Rees & D. Stock (eds). Springer Verlag, Berlin.

FOCUS, 2003. Foliar washoff coefficient. In: FOCUS surface water scenarios. Final report, p. 202. May 2003.

Gauvrit, C. & F. Cabanne, 1993. Oils for weed control: uses and mode of action. Pestic. Sci. 37: 147-153.

Gerber, H.R., A. Nyffeler & D.H. Green, 1983. The influence of rainfall, temperature, humidity, and light on soil- and foliage-applied herbicides. Aspects Applied Biology 4: 1-14.

Gottschild, D., J. Siebers & H.G. Nolting, 1995. The volatilisation and depsition of plant protection products. Publishing and Documentation Service, Council of Europe, Strasbourg, France.

Grain, C.F., 1982. Vapor pressure. In: Handbook of chemical property estimation methods, Environmental behaviour of organic compounds. Chapter 14, 19 pages. WJ Lyman, WF Reehl & DH Rosenblatt (eds). McGraw-Hill Book Company, New York.

Harper, L.A., L.L. McDowell, G.H. Willis, S. Smit & L.M. Southwick, 1983. Microclimate effects on toxaphene and DDT volatilization from cotton plants. Agronomy Journal 75: 295-302.

Hartley, G.S. & I.J. Graham-Bryce, 1980. Behaviour of pesticides in air. In: Physical principles of pesticide behaviour. G.S. Hartley & I.J. Graham-Bryce (eds). Vol 1: 337-385. Academic Press, New York.

Hashimoto, A., 1989. A kinetic study on the evaporation of pesticides on glass surface in air current. J. Pestic. Sci. 14: 457-464.

Hicks, B.B., D.D. Baldocchi, T.P Meyers, R.P. Hosker & D.R. Matt, 1987. A preliminary multiple resistance routine for deriving dry depositon velocities from measured quantities. Water Air Soil Pollut. 36: 311-320.

Hoppmann, D. & K.P. Wittich, 1997. Epidemiology-related modelling of the leaf-wetness durarion as an alternative to measurements, taking Plasmopara viticola as an example. Zeitschift Pflanzenkrankheiten Pflanzenschutz 104: 533-544.

Köcher, H. & J. Kocur, 1993. Influence of wetting agents on the foliar uptake and herbicidal activity of glufosinate. Pestic. Sci. 37: 155-158.

Kubiak, R., 1999. Praxisrelevante Untersuchungen zum Verhalten von Pflanzenschutzmitteln in der Umwelt. Schriftenreihe Agrarwissenschaft Band 6, D 386. Verlag Dr Köster, Berlin.

Kudsk, P., S.K. Mathiassen & E. Kirknel, 1991. Influence of formulations and adjuvants on the rainfastness of maneb and mancozeb on pea and potato. Pestic. Sci. 33: 57-71.

Leistra, M., 1998. Extent of photochemical transformation of pesticides on soil and plant surfaces. Environmental Planning Bureau Series 5. DLO Winand Staring Centre, Wageningen, The Netherlands.

Leistra, M., A.M.A. van der Linden, J.J.T.I. Boesten, A. Tiktak & F. van den Berg, 2001. PEARL model for pesticide behaviour and emissions in soil-plant systems; Descriptions of the processes in FOCUS PEARL v. 1.1.1. Alterra rapport 13, Alterra, Wageningen, The Netherlands. RIVM report 711401 009. RIVM Bilthoven, The Netherlands.

Leistra, M. & A. Wolters, 2004. Computations on the volatilisation of the fungicide fenpropimorph from plants in a wind tunnel. Water Air Soil Pollut. 157: 133-148.

Majewski, M.S., 1990. Sources, movement and fate of airborne pesticides. In: Pesticide Chemistry, Proc. 7th Intern. Congress Pestic. Chem., IUPAC, Hamburg. H. Frehse (Ed.). Pages 307-317. VCH, Weinheim.

Maurer, T., 1995. Entwicklung einer Messapparatur zur Erfassung flüchtiger organische Stoffe in der Gasfase und Validierung des Messsystems durch Untersuchung des Volitalitätsverhaltens ausgewählter Pflanzenschutzmittel. Dissertation, Univ. Kaiserslautern, Deutschland.

McCall, P.J., L.E. Stafford & P.D. Gavit, 1986a. Compartmental model describing the foliar behavior of tridiphane on Giant Foxtail. J. Agric. Food Chem. 34: 229-234.

McCall, P.J., L.E. Stafford, P.S. Zorner & P.D. Gavit, 1986b. Modeling the foliar behavior of atrazine with and without crop oil concentrate on Giant Foxtail and the effect of tridiphane on the model rate constants. J. Agric. Food Chem. 34: 235-238.

McDowell, L.L., G.H. Willis, L.M. Southwick & S. Smith, 1984. Methyl parathion and EPN washoff from cotton plants by simulated rainfall. Environ. Sci. Technol. 18: 423-427.

McDowell, L.L., G.H. Willis, S. Smith & L.M. Southwick, 1985. Insecticide wash-off from cotton plants as a function of time between insecticide application and rainfall. Trans. Amer. Soc. Agric. Engin. 28: 1896-1900.

McDowell, L.L., G.H. Willis, L.M. Southwick & S. Smith, 1987. Fenvalerate wash-off from cotton plants by rainfall. Pestic. Sci. 21: 83-92.

Müller, T., T. Maurer & R. Kubiak, 1997. Volatilization and metabolism of pesticides under simulated outdoor conditions. Environ. Monitoring Assessment 44: 541-547.

OECD, 1995. Guideline for the testing of chemicals. No 104. Vapor pressure. 16 pages. Organisation for Economic Cooperation and Development, Paris.

Ophoff, H., F. Führ, A Stork & J.H. Smelt, 1999. Volatilization of fenpropimorf under simulated field conditions after application onto different plants. Proc. XI Symp. Pesticide Chemistry, Cremona, Italy, pages 199-209.

Porskamp, H.A.J., J.M.G.P. Michielsen, H. Stallinga, P. van Velde & J.C. van de Zande, 2003. Depositie en emissie bij bespuiting van aardappelen. Nota P 2003-37. IMAG, Wageningen.

Reddy, K.N. & M.A. Locke, 1996. Imazaquin spray retention, foliar washoff and runoff losses under simulated rainfall. Pestic. Sci. 48: 179-187.

Roggenbuck, F.C., D. Penner, R.F. Burow & B. Thomas, 1993. Study of the enhancement of herbicide activity and rainfastness by an organosilicone adjuvant utilizing radiolabelled herbicide and adjuvant. Pestic. Sci. 37: 121-125.

de Ruiter, H., C. Kempenaar & G. Blom, 2004. Folair absorption of crop protection agents: influence of CPA properties, formulation and plant species. Report 77, Plant Research International, Wageningen.

Schweizer, A., C. Turgut & K. Hurle, 2000. Untersuchungen zur Verflüchtigung von Pflanzenschutzmitteln von Pflanzenoberflächen in Abhängigkeit von Temperatur und relativer Luftfeuchte. Z. Pflanzenkr. Pflanzenschutz, Sonderheft XVII: 791-798.

Smelt, J.H., R.A. Smidt, F. van den Berg, A.M. Matser, A. Stork & H. Ophoff, 1997. Volatilization of fenpropimorph and clopyralid after spraying onto a sugar beet crop. Report 136. DLO Winand Staring Centre, Wageningen.

Smelt, J.H., R. Aalderink, F. van den Berg & J.H. Weststrate, 2003. Volatilisation of chlorpyrifos and fenpropimorph from a potato crop, measurements with different methods. Alterra, Wageningen, The Netherlands.

Smit, A.A.M.F.R., F. van den Berg & M. Leistra, 1997. Estimation method for the volatilisation of pesticides from fallow soil. Environmental Planning Bureau Series 2. DLO Winand Staring Centre, Wageningen, The Netherlands

Smit, A.A.M.F.R., M. Leistra & F. van den Berg, 1998. Estimation method for the volatilization of pesticides from plants. Environmental Planning Bureau Series 4, DLO Winand Staring Centre, Wageningen.

Spencer, W.F., T.D. Shoup, M.M. Cliath, W.J Farmer & R. Haque, 1979. Vapor pressures and relative volatility of ethyl and methyl parathion. J. Agric. Food Chem. 27: 273-277.

Steurbaut, W., 1993. Adjuvants for use with foliar fungicides. Pestic. Sci. 38: 85-91.

Stock, D. & P.J. Holloway, 1993. Possible mechanisms for surfactant-induced foliar uptake of agrochemicals. Pestic. Sci. 38: 165-177.

Stork, A., H. Ophoff & F. Führ, 1997. Windkanal zur Erfassung von Umwelt-chemikalien im Agrarökosystem. Jahresbericht 1996: 73-83. Forschungszentrum Jülich.

Stork, A., H. Ophoff, J.H. Smelt & F. Führ, 1998a. Volatilization of clopyralid and terbuthylazine under field conditions: Comparison of field and wind tunnel experiments. Zeitschrift Pflanzenkrankheiten Pflanzenschutz, Sonderheft XVI: 745-755.

Stork, A., H. Ophoff, J.H. Smelt & F. Führ, 1998b. Volatilization of pesticides. Measurements under simulated field conditions. In: The lysimeter concept. F. Führ, R.J. Hance , J.R. Plimmer & J.O. Nelson (Eds). ACS Symposium Series 699: 21-39. American Chemical Society, Washington DC.

Taylor, A.W., D.E. Glotfelty, B.C. Turner, R.E. Silver, H.P. Freeman & A. Weiss., 1977. Volatilization of dieldrin and heptachlor residues from field vegetation. J. Agric. Food Chem. 25: 542-548.

Taylor, A.W., 1978. Post-application volatilization of pesticides under field conditions. J. Air Pollut. Control Assoc. 28: 922-927.

Tinsley, I.J., 1979. Chemical concepts in pollutant behavior. John Wiley & Sons, New York.

Tomlin, C.D.S., 2003. The pesticide manual. A world compendium. 13th ed. British Crop Protection Council, Omega Park, Alton, Hampshire, UK.

Tucker W.A. & L.H. Nelken, 1982. Diffusion coefficients in air and water. In: Handbook of chemical property estimation methods. Environmental behaviour of organic compounds. W.J. Lyman (ed.). McGraw Hill Book Company, New York.

Watanabe, T., 1993. Relationship between volatilization rates and physico-chemical properties of some pesticides. J. Pestic. Sci. 18: 201-209.

Wayman, B. & H. Rüdel, 1995. Inlfluence of air velocity, application dose, and test size on the volatilisation of lindane. Anal. Chem. 58: 371-378.

Willis, G.H., L.L. McDowell, S. Smit, L.M. Southwick & E.R. Lemon, 1980. Toxaphene volatilization from a mature cotton canopy. Agronomy Journal 72: 627-631.

Willis, G.H., L.L. McDowell, S. Smith & L.M. Southwick, 1986. Permethrin washoff from cotton plants by simulated rainfall. J. Environ. Qual. 15: 116-120.

Willis, G.H. & L.L. McDowell, 1987. Pesticide persistence on foliage. Reviews Environ. Contam. Toxicol. 100: 23-73.

Willis, G.H., L.L. McDowell, S. Smith & L.M. Southwick, 1988. Rainfall amount and intensity effects on carbaryl washoff from cotton plants. Trans. Amer. Soc. Agric. Engin. 31: 86-90.

Willis, G.H., L.L. McDowell, L.M. Southwick & S. Smith, 1992a. Washoff of ultra-low-volume-oil-applied insecticides from cotton plants as a function of time between application and rainfall. J. Environ. Qual. 21: 373-377.

Willis, G.H., L.L. McDowell, S. Smith & L.M. Southwick, 1992b. Foliar washoff of oil-applied malathion and permethrin as a function of time after application. J. Agric. Food Chem. 40: 1086-1089.

Willis, G.H., L.L McDowell, S. Smith & L.M. Southwick, 1994a. Azinphosmethyl and fenvalerate washoff from cotton plants as a function of time between application and initial rainfall. Arch. Environ. Contam. Toxicol. 27: 115-120.

Willis, G.H., L.L. McDowell, S. Smith & L.M. Southwick, 1994b. Permethrin and sulprofos washoff from cotton plants as a function of time between application and initial rainfall. J. Environ. Qual. 23: 96-100.

Willis, G.H., S. Smith, L.L. McDowell & L.M. Southwick, 1996. Carbaryl washoff from soybean plants. Arch. Environ. Contam. Toxicol. 31: 239-243.

Woodrow, J.E., J.N. Seiber & L.W. Baker, 1997. Correlation techniques for estimating pesticide volatilization flux and downward concentrations. Environ. Sci. Technol. 31: 523-529.

Appendix 1 Effect of formulations and admixtures on volatilisation

In various experiments, the effect of the formulation on the volatilisation of a pesticide has been studied. In other cases, the volatilisation of a pesticide from a mixture of pesticides has been investigated. This Appendix gives a brief survey of the results of such studies, which forms the basis for tentative conclusions on the effect of other substances on the volatilisation of a pesticide.

Formulations with pesticides

The rate of volatilisation of parathion-methyl from the technical material on a glass surface (25 °C) was compared with that from an emusifiable concentrate (46%) (Spencer et al., 1979). Volatilisation rates from both dried deposits were found to be almost the same.

Crop oil concentrate (COC) was added to an EC-formulated herbicide applied to glass plates in a chamber (McCall et al., 1986a). This increased the half-life of volatilization from 3.5 hours to 11.5 hours (keeper effect). However, different amounts of COC on plants had little effect on herbicide volatilization rate.

The effect of seven commercial and potential adjuvants on the volatilisation of 2,4-D iso-octyl ester was studied by Schubert et al. (1993). The mixtures were sprayed on short grass and after 30 min a Perspex chamber (1 m^3) was placed on the surface. The air was sampled by pumping and trapping on PUF plugs. Three adjuvants resulted in an increased volatilisation of 2,4-D ester in the first measuring hour. Some other adjuvants had no effect and only one decreased volatilisation in this hour. In the second measuring hour there were several cases with decreased volatilisation, as compared to 2,4-D ester without adjuvant. Possibly the decrease in volatilisation was caused by the increase in plant penetration of 2,4-D ester in the presence of adjuvant.

Parathion-methyl in EC and WP formulation, respectively, was sprayed on bean plants grown on a lysimeter provided with a wind channel on top (Stork et al., 1997). In a period of 6 to 7 days, the volatilisation from WP formulation (73% of the dose) was somewhat higher than that from EC formulation (60%). With the latter formulation, penetration of pesticide into the plants, as competing process, is expected to be faster.

The volatilisation of parathion-methyl from dwarf beans in a lysimeter + wind tunnel combination was studied by Stork et al. (1998). The insecticide was applied in two formulations. There was only a small difference in the volatilisation of the insecticide from the deposits of the WP (76% of the dose) and EC (67%) formulations in 4 days (this difference may have been caused by a competing process).

[14]C-labelled pyrimethanil was applied to glass slides in different forms, after which the loss (mainly by volatilisation) was measured by LSC (Green et al., 1998). When the fungicide was applied in combination with matrix-forming materials, the effect on its loss was small. Only when applied as an organic salt (with fatty acids), loss of the fungicide was reduced substantially.

Volatilization of endosulfan from an EC formulation was found to be distinctly higher than that from two WP formulations (Kubiak, 1999).

The loss of triadimefon from Petri dishes (presumably by volatilisation) in the dark at 40 °C and at an air flow of 0.5 m/s was studied by Da Silva et al. (2001). When the fungicide was applied as a suspension of the formulation (Bayleton 5), 17% of the dose was left after 16 hours (dark). When applied as a solution of the pure compound, 5% was left after 16 hours. So the effect of the formulation on volatilisation was only moderate. After the first 4 hours with approximately first-order volatilisation kinetics, the process proceeded comparatively slowly.

Mixtures of pesticides

The rates of loss (mainly by volatilisation) of lindane, dieldrin and pentachlorophenol from watch glasses were measured in a room at 20 °C (Dobbs & Cull, 1982). When applied as a mixture (in a solvent) to the glass, the rate of loss of each compound was similar to that of the compound applied alone.

Solutions of various combinations of two pesticides were added to watch glasses, the solvent was evaporated and the glasses were placed in a temperature cabinet (20 °C) with circulating air (Dobbs et al., 1984). In two cases there was an interaction in the loss (mainly by volatilisation) of the compounds:
- for chemicals having very different vapour pressures;
- for combinations of liquids and high-melting solids.

Tentative conclusion

The general tendency is that the influence of common formulations like emulsifiable concentrates (EC) and wettable powders (WP) on pesticide volatilisation is small. Special formulations can be developed to reduce pesticide volatilisation. A major problem/challenge is that these should also maintain or even improve pesticide effectiveness.

Literature

Da Silva, J.P., A.M. Da Silva & I.V. Khmelinskii, 2001. Dissipation of triadimefon on the solid/gas interface. Chemosphere 45: 875-880.

Dobbs, A.J. & M.R. Cull, 1982. Volatilization of chemicals. Relative loss rates and the estimation of vapour pressures. Environ. Pollution B3: 289-298.

Dobbs, A.J., G.F. Hart & A.H. Parsons, 1984. The determination of vapour pressures from relative volatilization rates. Chemosphere 13: 687-692.

Green, S.A., R.J. Williams & D. Stock, 1998. Influence of formulants and salt formation on volatization and activity of pyrimethanil. Pestic. Sci. 54: 313-314.

Kubiak, R., 1999. Praxisrelevante Untersuchungen zum Verhalten von Pflanzenschutzmitteln in der Umwelt. Schriftenreihe Agrarwissenschaft Band 6, D 386. Verlag Dr Köster, Berlin.

McCall, P.J., L.E. Stafford & P.D. Gavit, 1986a. Compartmental model describing the foliar behavior of tridiphane on Giant Foxtail. J. Agric. Food Chem. 34: 229-234.

Schubert, C.L., D.J. Erasmus, L.P. Vandyk, V. Gray & K Lovell, 1993. Adjuvants and volatility of hormone herbicides. Pestic. Sci. 38: 179-183.

Spencer, W.F., T.D. Shoup, M.C. Cliath, W.J. Farmer & R. Haque, 1979. Vapor pressures and relative volatility of ethyl and methyl parathion. J. Agric Food Chem. 27: 273-278

Stork, A., H. Ophoff & F. Führ, 1997. Windkanal zur Erfassung von Umwelt-chemikalien im Agrarökosystem. Jahresbericht 1996: 73-83. Forschungszentrum Jülich.

Stork, A., H. Ophoff, J.H. Smelt & F. Führ, 1998. Volatilization of pesticides. Measurements under simulated field conditions. In: The lysimeter concept. F. Führ, R.J. Hance , J.R. Plimmer & J.O. Nelson (Eds). ACS Symposium Series 699: 21-39. American Chemical Society, Washington DC.

Appendix 2   Reliability of values for the vapour pressure: example for parathion-methyl

The values given for the vapour pressure of pesticides have to be evaluated critically. For a number of pesticides, even (strongly) different values are given. Other values may be doubtful, e.g. because they do not correspond to the volatilisation behaviour of the pesticide (relative to others). The origin of a value for the vapour pressure may be not clear. Gradually, the reliability of vapour pressures should improve, because the guidelines of the OECD (1995) have to be followed in the determination now.

The problem with the reliability of vapour pressure values is illustrated for parathion-methyl. The values given for its vapour pressure are compiled in Table A2.1, together with their sources.

Table A2.1. Values given for the vapour pressure of parathion-methyl

Vapour pressure (mPa)		Reference	Source for reference
Reported	**Translated to 20 ^{0}C**		
1.29 mPa at 20 ^{0}C	1.29 mPa	Gückel et al. (1973)	Handbooks from 1963 and 1971
2.29 mPa at 25 ^{0}C	1.13 mPa	Spencer et al. (1979)	Determination with gas-saturation method
1.3 mPa at 20 ^{0}C	1.3 mPa	Müller et al. (1995)	Industrieverband Agrar (1990)
2.3 mPa at 25 ^{0}C	1.20 mPa	Kromer et al. (1999)	Spencer et al. (1979)
0.41 mPa at 25 ^{0}C	0.2 mPa at 20 ^{0}C	Tomlin (2003)	Not given

Table A2.1 shows that four values for the vapour pressure of parathion-methyl, translated to 20 ºC, are in the range of 1.1 to 1.3 mPa. Probably, the most reliable value is 1.13 mPa (20 ºC), which was fully documented in a scientific journal. There seem to be two original sources, but the 'handbook' source could not be traced back up to now. The vapour pressure given by Tomlin (2003 source not given) is much lower than the other four values.

The vapour pressures of parathion(-ethyl) compiled in Table A2.2, translated to 20 ºC, are in the range of 0.6 to 0.9 mPa. Parathion-methyl has a similar structure with a lower molar mass, so its vapour pressure is expected to be higher than that for parathion(-ethyl). Thus the vapour pressures for parathion(-ethyl) in Table A2.2 support the range of 1.1 to 1.3 mPa given for parathion-methyl in Table A2.1.

Table A2.2. Values given for the vapour pressure of parathion(-ethyl)

Vapour pressure (mPa)		Reference	Source for reference
Reported	**Translated to 20 ^{0}C**		
0.76 mPa at 20 ^{0}C	0.76 mPa	Gückel et al. (1973)	Handbooks from 1963 and 1971
1.29 mPa at 25 ^{0}C	0.63 mPa	Spencer et al. (1979)	Determination with gas-saturation method
0.89 mPa at 20 ^{0}C	0.89 mPa	Tomlin (2003)	Not given

The conclusion is that the vapour pressure of 0.2 mPa for parathion-methyl (20 °C), as given by Tomlin (2003), is the least reliable value. Tomlin (2003; page xvi) states that, in case of different values for the vapour pressure, the lowest figure has normally been chosen for presentation in the Manual.

Another compound with a similar structure is fenitrothion, which has a slightly higher molar mass than parathion-methyl. On the basis of this, fenitrothion would be expected to have a somewhat lower vapour pressure than parathion-methyl. Surprisingly, Tomlin (2003) reports a much higher vapour pressure of 18 mPa for fenitrothion at 20 °C (source not given). Such a higher value seems unlikely; it could only be explained from comparatively weak molecular interaction forces for fenitrothion.

Vapour pressures of parathion-methyl were calculated using two methods given by Grain (1982). The first method used the reported boiling point of 427 K at a low pressure of 136 Pa (Tomlin, 2003). This yielded a vapour pressure of 1.5 mPa at 20 °C for parathion-methyl. The second method used the boiling point of 611 K at atmospheric pressure for parathion-methyl, as calculated according to Rechsteiner (1982). This resulted in a vapour pressure of 1.2 mPa at 20 °C for parathion-methyl. Thus the calculated values support the 'measured' values in the range of 1.1 to 1.3 mPa at 20 °C given in Table A2.1. It should be noted that the quality of the results of these calculations methods is dependent on the availability of accurate boiling points for the substance.

A calculation method for the vapour pressure of organophosphate pesticides was presented by Tsuzuki et al. (2000). Varieties of this method resulted in calculated vapour pressures of 1.4 and 1.8 mPa for parathion-methyl at 20 °C. This is somewhat higher than the range of 1.1 to 1.3 mPa (20 °C) given in Table A2.1.

Remark. Vapour pressure estimates have a rather wide range of uncertainty.

Literature

Grain, C.F., 1982. Vapor pressure. In: Handbook of chemical property estimation methods, Environmental behaviour of organic compounds. Chapter 14, 19 pages. WJ Lyman, WF Reehl & DH Rosenblatt (eds). McGraw-Hill Book Company, New York.

Gückel, W, G Synnatschke & R Rittig, 1973. A method for determining the volatility of active ingredients used in plant protection. Pestic. Sci. 4: 137-147.

Industrieverband Agrar, 1990. Wirkstoffe in Pflanzenschutzmitteln. Physikalisch-chemische und toxicologische Daten. Seiten 311-313. Industrieverband Agrar EV, BLV Verl. Ges., München.

Kromer, T., H. Ophoff, F. Führ & A Stork, 1999. Photodegradation and volatilisation of parathion-methyl on glass and soil dust under laboratory conditions. Proc. XI Symposium Pesticide Chemistry, Cremona, Italy, p. 363-374.

Müller, T., T. Maurer & R. Kubiak, 1995. Metabolism and volatilisation of parathion-methyl under simulated outdoor conditions. Med. Fac. Landbouww. Univ. Gent 60: 541-547.

OECD, 1995. Guideline for the testing of chemicals. No 104. Vapor pressure. 16 pages. Organisation for Economic Cooperation and Development, Paris.

Rechsteiner, CE, 1982. Boiling point. In: Handbook of chemical property estimation methods, Environmental behaviour of organic compounds. Chapter 12, 55 pages. WJ Lyman, WF Reehl & DH Rosenblatt (eds). McGraw-Hill Book Company, New York.

Spencer, W.F., T.D. Shoup, M.M. Cliath, W.J. Farmer & R Haque, 1979. Vapor pressures and relative volatility of ethyl and methyl parathion. J. Agric. Food Chem. 27: 273-278.

Tomlin, C.D.S., 2003. The pesticide manual. A world compendium. British Crop Protection Council. Omega Park, Alton, Hampshire, UK.

Tsuzuki, M., 2000. Thermodynamic estimation of vapor pressure for organophosphorus pesticides. Environ. Toxicol. Chem. 19: 1717-1726.

Appendix 3 Estimation of input parameters for the canopy processes. Example: chlorpyrifos

Introduction

When using the module for pesticide behaviour in the crop canopy, input data are needed on the processes in the canopy. Only vapour pressure is an input datum that is measured or estimated directly, which results in a distinct value. The rate parameters for plant penetration, wash-off by rainfall and phototransformation are not measured directly. They have to be derived from a wide variety of experimental data. In principle, they can also be derived from theoretical studies, if available and applicable. Because of the highly complex pesticide-canopy system and the large variation of the conditions in time, only the order of magnitude of the rate parameters can be estimated.

A classification of the rate parameters into five groups will often be the maximum degree of quantification which is feasable. The five classes for the rate parameter of a certain process may be indicated as follows:
1) high rate, 2) substantial rate, 3) intermediate rate, 4) limited rate, and 5) low rate.
A representative rate coefficient could be assigned to each of these classes.

This proposal for deriving semi-quantitave input data is applied to the organophosphate insecticide chlorpyrifos, for which a lot of reseach has been published.

Vapour pressure

The vapour pressure of chlorpyrifos is reported to be in the range of 2.4 to 2.7 mPa at 25 °C (Racke, 1993; cited company data). Tomlin (2003) reports the vapour pressure of chlorpyrifos to be 2.7 mPa at 25 °C.

Volatilisation of chlorpyrifos form inert surfaces was measured under constant air flow at 30 °C (Racke, 1993). Rapid volatilisation from glass etc. occurred, with half-lives of less than 1 day.

Corn plants were sprayed at a rate of 1.12 kg chlorpyrifos per ha and placed in a growth chamber (30 °C) with constant air flow of 0.22 m/s (Racke, 1993). Within 2 days, 79% of the chlorpyrifos dose had volatilised from the corn leaf surfaces. Volatilisation is considered to be the major route for the loss of chlorpyrifos from plants.

Volatilisation of chlorpyrifos from a filter paper strip was measured by Meikle et al. (1983) in the dark (25 °C). At an air flow rate of 0.3 km/h, the half-life due to

volatilisation was found to be 7.8 hours. The authors expect that volatilisation is the primary process in the loss of chlorpyrifos from plant leaves in the field.

The vapour pressure of 2.7 mPa at 25 ^{0}C can be translated to 1.4 mPa at 20 ^{0}C, using Eq. 4 in Section 4.3. Smit et al. (1998) derived an empirical relationship between cumulative volatilisation of a pesticide from plants (in 7 days) and its vapour pressure at 20 ^{o}C on the basis of many literature data:

$$Log(CV) = 1.528 + 0.466 \log(VP)$$

with
CV   = cumulative volatilisation (% of dosage);
VP   = vapour pressure (mPa).

In this way, cumulative volatilisation of chlorpyrifos from plants is estimated to be 39% of the dosage. So the substantial volatilisation of chlorpyrifos in some experiments can be explained from its vapour pressure.

Rate of penetration into the plants

Chlorpyrifos is known to be an insecticide with contact and ingestion activity (Racke, 1993; Tomlin, 2003). Respiratory contact via the vapour phase enhances its activity. Its systemic properties in plant systems (uptake, translocation) are poor. It is not meaningful to add substances to the formulation that promote penetration into the plants. However, because of the non-polar character of chlorpyrifos [log(Pow) about 5; Racke, 1993], there will be affinity for interaction with cuticula and wax layer on the leaf surfaces.

There is a limited extent of penetration of chlorpyrifos into the plants, e.g. about 10% of the dose at 1 day after application (Racke, 1993). One of the causes is that volatilisation is the dominant process shortly after application. A first stage with rapid decrease of the mainly dislodgeable plant residue is followed by a second stage with much slower decrease of the mainly penetrated residue (at a rather low level).

On the basis of the available information, chlorpyrifos penetration into the plants is classified as "slow" (Section 6.9). On the entire scale of $k_{pen} = 0.03$ to 17 d^{-1} for the five classes, the first estimate of k_{pen} for chlorpyrifos is taken to be 0.14 d^{-1} (half-life of penetration of 5 d).

Rate of washoff by rainfall

No detailed studies have been found in the literature on the washoff of sprayed chlorpyrifos from plants by rainfall. Some studies report application to turf of golf courses, which was followed immediately by irrigation to wash the insecticide to the soil where the insect lavae had to be controlled. This was found to lower the content of chlorpyrifos on the grass. Even after a short drying period for the deposit (e.g. 1.5

hour), washoff from the plants was substantially less. It should be noted that spraying in agriculture is not done when rain is expected to fall in the first few hours or even longer after application.

The solubility of chlorpyrifos was reported to be in the range of 0.94 to 2 mg L^{-1} at 23 to 25 ^{0}C (Racke, 1993) and circa 1.4 mg L^{-1} at 25 ^{0}C (Tomlin, 2003). On the basis of these low values, washoff is classified to occur at a "limited rate" (Section 7.9). In the total range of 0.01 to 0.09 mm^{-1}, the washoff coefficient is then taken to be 0.03 mm^{-1} for chlorpyrifos (30% of the deposit washed of with 10 mm of rain).

Rate of phototransformation

Results of studies on the phototransformation of pesticides must be evaluated critically. The wavelength spectrum should correspond to that of sunlight reaching the earth's surface (about 300 to 800 nm) and translation of the results on the basis of light intensity may be needed. No other substances (e.g. solvents) should have been be added to the natural medium, as they may act as photosensitisers.

Chlorpryifos in water only shows slight absorption of light at wavelengths around 300 nm in the sunlight spectrum (Barcelo, 1993). On the basis of this, direct photolysis may be expected to be slow.

The half-lives for the photolysis of chlorpyrifos in phosphate-buffered aqueous solution (pH 5 to 8; 25 ^{0}C) were in the range of 13 to 22 days (Meikle et al., 1983).

The direct photolysis of chlorpyrifos in water by simulated sunlight was found to be very slow and the same is expected to hold for indirect photolysis mediated by OH radicals in natural waters (Armbrust, 2000).

Hebert et al. (2000a, 2000b) studied the direct and indirect phototransformation of chlorpyrifos in air in a glass chamber at elevated temperatures (60 to 80 ^{0}C). They found indications for substantial rates of both direct (in pure air) and indirect (reaction with OH radicals) phototransformation.

Phototransformation of chlorpyrifos was not inhibited when applied in wax to a surface (Meikle et al., 1983). It's half-life was found to be 3.1 days, which was much shorter than that in aqueous solution in the same study. However, Walia et al. (1988) found that chlorpyrifos applied to plant leaves and exposed to sunlight underwent only very slow phototransformation.

In his review, Racke (1993) appraised the rate of phototransformation of chlorpyrifos in the field to be distinctly lower than measured in various laboratory systems (with e.g. photosensitisers or photocatalysers).

Results of monitoring studies at locations remote from the application area of chlorpyrifos may give an indication of its stability in atmospheric conditions

(interacting with aqueous and terrestrial systems). Chlorpyrifos was measured to occur in marine ice in the Bering Sea and Chukchi Sea, west of Alaska, and in arctic fog in these areas (Chernyak et al., 1996). Such a monitoring study indicates that chlorpyrifos is only slowly transformed under atmospheric conditions.

In summary, the measurements on the phototransformation of chlorpyrifos resulted in a wide range of low to intermediate rates, with an indication of some transformation in/on waxy material. On the basis of this, phototransformation on the leaves is classified to occur 'slowly' (Section 8.3), with a rate coefficient $k_{ph,ref}$ of 0.14 d^{-1} (on the scale of 0.03 to 17 days) (half-life of 5 d). It should be noted that the overall half-life of phototransformation in the field (with day-night sunlight rithm) becomes distinctly longer then.

General remark

The derivation of input data for a pesticide in plant canopies may be facilitated when a high-quality summary of the physico-chemical properties and its environmental behaviour is available. This can be a published review, a Summary for national registration or an EU Monograph.

Literature

Armbrust, K.L., 2000. Pesticide hydroxyl radical rate constants: measurements and estimates of their importance in aquatic environments. Environ. Toxicol. Chem. 19: 2175-2180.

Barcelo, D., G. Durand & N.D. Bertrand, 1993. Photodegradation of the organophosphorus pesticides chlorpyrifos, fenamiphos and vamidothion in water. Toxicol. Environ. Chem. 38: 183-199.

Chernyak, S.M., C.P. Rice & L.L. McConnell, 1996. Evidence of currently used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi seas. Marine Pollution Bulletin 32: 410-419.

Hebert, V.R., C. Hoonhout & G.C. Miller, 2000a. Use of stable tracer studies to evaluate pesticide photolysis at elevated temperatures. J. Agric. Food Chem. 48:1916-1921.

Hebert, V.R., C. Hoonhout & G.C. Miller, 2000b. Reactivity of certain organophosphorus insecticides toward hydroxyl radicals at elevated air temperatures. J. Agric. Food Chem. 48: 1922-1928.

Meikle, R.W., N.H. Kurihara & D.H. Devries, 1983. Chlorpyrifos – The photodecomposition rates in dilute aqueous solution and on a surface, and the volatilisation rate from a surface. Archives Environ. Contam. Toxicol. 12: 189-193.

Racke, K.D., 1993. Environmental fate of chlorpyrifos. Reviews Environ. Contam. Toxicol. 131: 1-150.

Smit, A.A.M.F.R., M. Leistra & F. van den Berg, 1998. Estimation method for the volatilization of pesticides from plants. Environmental Planning Bureau Series 4, DLO Winand Staring Centre, Wageningen.

Tomlin, C.D.S., 2003. The pesticide manual. A world compendium. 13th ed.. British Crop Protection Council, Omega Park, Alton, Hampshire, UK.