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VOLATILIZATION OF PESTICIDES FROM SOIL AND PLANTS AFTER SPRAYING

J.W. Jansma, J.B.H.J. Linders

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PREFACE

The Uniform System for the Evaluation of Substances (USES) (RIVM, VROM, WVC, 1994) is a harmonized system for making a rapid general risk evaluation for a wide range of substances, like new substances, existing substances and pesticides.
USES incorporates methods for the assessment of plant protection products developed by the former CTB[1] Environment Support Group.
The exposure assessment starts with an estimate of the emissions to water, soil and air during the various life-cycle stages of the substance and of its subsequent distribution. The result of the exposure assessment determines the Predicted Environmental Concentrations (PECs).
In general, the PECs are compared to "no-effect" levels for organisms in the environment. Following calculation by USES these hazard quotients are subsequently compared to criteria on the tolerability of pesticides using so-called decision trees. In combination with expert judgement these decision trees are the basis for the approval decision.
In the model calculations in USES the rate of volatilization of pesticides from soil and plants is not calculated and also not taken into account for further calculations. In order to improve the model a literature search on the volatilization of pesticides is done. This report is the result of this search.

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[1] Commissie Toelating Bestrijdingsmiddelen

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SUMMARY

This report discusses the volatilization of pesticides from the soil surface, from within the soil and from plants.

Not only during, but mainly also after, application of pesticides part of the applied substance volatilizes. The rate of volatilization is different for each substance and is in the first instance linked up with the vapour pressure of the substance. Beside it factors like temperature, water solubility, adsorption to soil or plant surfaces, soil moisture, air flow and the concentration of the pesticide are important.

A large amount of measured volatilization data of pesticides are collected from literature and presented in tables. Data obtained from field studies and from laboratory studies are presented in different tables. Data for volatilization from within the soil, from the soil surface and from the plant surface are also split up in different tables.

Literature data concerning models for estimating the volatilization of pesticides are also collected. Many models found are not useful because input parameters are not available.

For estimating the rate of volatilization from the soil surface the so called "Dow-method" is proposed. Vapour pressure, water solubility and adsorption to soil are the factors in this model that are supposed to influence the volatilization substantially.

As a first step to validate the "Dow-method" some values calculated with this method are compared with measured values. In general the agreement of these values was within a factor of 7.

A useful model to estimate the volatilization of pesticides incorporated in soil and volatilization from plant surfaces could not be found.

Finally an overview of percentages volatilized substance, calculated with the "Dow-method" at 1 and 4 days after application, is given for a large number of pesticides.

SAMENVATTING

Dit rapport bespreekt de vervluchtiging van bestrijdingsmiddelen vanaf en vanuit de grond en vanaf de plant.

Niet alleen tijdens toepassing van bestrijdingsmiddelen, maar vooral ook daarna, verdampt een deel van de toegediende stof. De mate van vervluchtiging verschilt per stof en hangt in eerste instantie samen met de dampdruk van de stof. Daarnaast spelen factoren als temperatuur, wateroplosbaarheid, adsorptie aan grondoppervlak of plant, bodemvochtigheid, luchtstroom en de concentratie van de stof een rol.

Uit de literatuur is een groot aantal gegevens verzameld omtrent gemeten hoeveelheden vervluchtiging van bestrijdingsmiddelen per tijdseenheid. Deze gegevens zijn gepresenteerd in tabellen. Gegevens van veldstudies en laboratoriumstudies zijn in afzonderlijke tabellen gezet. Gegevens over vervluchtiging vanuit de grond, vanaf het grondoppervlak en vanaf de plant zijn ook opgesplitst over verschillende tabellen.

Daarnaast zijn literatuurgegevens verzameld omtrent modellen waarmee de mate van vervluchtiging van bestrijdingsmiddelen geschat kan worden. Veel van de gevonden modellen zijn vanwege niet beschikbare invoerparameters niet bruikbaar.

Voor het schatten van de vervluchtiging van bestrijdingsmiddelen vanaf het grondoppervlak wordt het gebruik van de zgn. "Dow-methode" voorgesteld. Bij deze methode zijn dampdruk, wateroplosbaarheid en adsorptie aan grond factoren die geacht worden de mate van vervluchtiging daadwerkelijk te beinvloeden.

Als eerste aanzet om de "Dow-methode" te valideren zijn enkele hiermee berekende waarden vergeleken met gemeten waarden. Over het algemeen bleek de overeenkomst tussen deze waarden binnen een factor 7 te blijven.

Voor de vervluchtiging van in de grond ingewerkte bestrijdingsmiddelen en voor de vervluchtiging vanaf planten werd geen bruikbaar model gevonden.

Tenslotte wordt voor een groot aantal bestrijdingsmiddelen een overzicht gegeven van de met de "Dow-methode" berekende percentages vervluchtigde stof, 1 en 4 dagen na toepassing.

1. INTRODUCTION

Spray application is one of the most familiar operations connected with pesticide use (Plimmer, 1990). When spraying an agricultural field, soil and plants are the main targets. Some of the pesticide however will reach the surface water as a result of drift and run-off. Another fraction will become airborne during the application process, by evaporation from the applied surface or by movement on windblown, contaminated dust particles (Harper et al., 1976).

The fate of pesticides in soil and water is extensively investigated. Residues of pesticides on crops are a main item in view of public health. However, pesticides in air is not a main topic yet. What happens to pesticides after they enter the atmosphere is of considerable importance, but very little is known about their ultimate fate. Photochemical alteration, adsorption on dust particles, fallout (dry deposition), and rainout (wet deposition) of airborne pesticides are areas of research needing attention (Spencer et al., 1973).

Since the early sixties post-application losses of pesticides by volatilization have been increasingly recognized as a pathway for general environmental contamination and as a process limiting their effectiveness. Volatilization and subsequent aerial transport is thought to be a major pathway of pesticide disappearance from application sites (Willis et al., 1983). Taylor (1978) stated that "volatilization rates from plant or moist soil surfaces can be very large, with losses approaching 90% within 3 days for more volatile compounds". Although pesticides range in volatility from fumigants, such as gaseous methyl bromide, to herbicides, with vapour pressures below 10^{-6} Pa, the same physical and chemical principles govern their rates of volatilization. In the sixties and seventies the influence of several physical and chemical parameters on volatilization of pesticides was investigated. The vapour pressure of the pesticide is the major factor influencing the volatilization rate. The effective vapour pressure may differ from the vapour pressure of the chemical itself as a result of such factors as adsorption on soil or other surfaces, temperature, soil water content, air movement and the nature of the pesticide (Spencer et al., 1973).

In this report the process of volatilization from soil and plant surfaces will be discussed.

In chapter 2 the factors influencing volatilization are discussed. Most articles discussing the influence of physical and chemical parameters on the volatilization process were published in the sixties and seventies. In more recent articles most authors refer to this relatively old literature.

All measured rates of volatilization found in literature from both laboratory and field experiments are given in tables in chapter 3.

In order to estimate the rate of volatilization of pesticides a model is suggested in chapter 4. The validity of this model is tested by comparing calculated and measured values.

Volatilization rates for c. 100 pesticides are calculated in chapter 5, using the model suggested in chapter 4.

2. FACTORS INFLUENCING VOLATILIZATION

Thomas (1990) defines volatilization as the process by which a compound evaporates in the vapour phase to the atmosphere from another environmental compartment.

2.1 Volatilization from soil

Graham-Bryce and Hartley (1980) predicted that the losses by evaporation from 1 ha of inert surface would be 2.02 kg/month for lindane, 1.35 kg/year for DDT and 0.04 kg/year for simazine. Plimmer (1990) also mentioned seasonal losses of 0.199 kg/ha for dieldrin and 0.383 kg/ha for heptachlor. The applied amount of pesticide is not given by these authors.

The rate at which a chemical volatilizes from soil is affected by many factors, such as soil properties, chemical properties, and environmental conditions. These factors, which are interrelated, can be placed into the following catergories (Spencer et al., 1973):

- factors affecting the movement away from the evaporating surface into the atmosphere
- factors which affect the vapour density of the pesticide
- factors which control the rate of movement to the evaporating surface.

2.1.1 Pesticide movement away from the evaporating surface

According to Hartley (1969) the rate of movement away from the evaporating surface is a diffusion-controlled process. Close to the evaporating surface the air is relatively still. The vapourizing substance is transported from the surface through this stagnant air layer only by molecular diffusion. Diffusion away from the surface is related to the vapour density and the molecular weight of the pesticide. Changes in temperature will influence both vapour density and the diffusion process itself.

The thickness of this stagnant air layer above the evaporating surface depends on the air flow rate. Parochetti and Warren (1966) found that for propham and chlorpropham vapour losses increased with increasing air-flow rate and temperature.

Hartley (1969) and Hamaker (1972) studied the codistillation process in detail and concluded that codistillation does not apply to pesticide volatilization. Pesticide and water molecules volatilize from water or moist surfaces independently of each other. Pesticide volatilization will occur, whether water is evaporating or not.

2.1.2 Pesticide vapour density

Vapour density is the concentration of a chemical in the air. When the concentration reaches a maximum, the vapour is saturated. Every chemical has a characteristic saturation vapour pressure which varies with temperature. The vapour pressure is also influenced by adsorption on soils and other surfaces. The reduction of the vapour pressure of a pesticide in soil is dependent mainly upon the nature of the pesticide, the soil pesticide concentration, the soil water content and the soil properties such as organic matter and clay content.

2.1.2.1 Nature of the pesticide

Vapour pressure, solubility in water, type of basic nucleus (i.e. phenyl, alkyl, pyridine, etc.) and number, kind, and position of functional groups are important properties of a chemical that influence the volatilization of these chemicals. Subtle differences in chemical structure within the same type of pesticide can result in a relatively large change in vapour pressure. For example, atrazine has a vapour pressure of $4.0 * 10^{-5}$ Pa at 30 °C. When the ethane group is replaced by an isopropyl group (propazine), the vapour pressure decreases to $3.9 * 10^{-6}$ Pa at 30 °C. Another example is the difference between o,p'-DDT and p,p'-DDT, with vapour pressures of 7.3 * 10^{-4} and 9.7 * 10^{-5} Pa at 30 °C, respectively. (Guenzi and Beard, 1974)

2.1.2.2 Pesticide adsorption to soils

Adsorption of a pesticide to the inorganic and organic fractions of a soil may be the result of chemical adsorption (Coulombic forces), physical adsorption (van der Waals forces) and hydrogen bonding. (Guenzi and Beard, 1974)

Adsorption reduces the chemical activity and thus also the volatilization rate of the compound. The amount of soil organic matter is the most important soil factor determining the amount of adsorption of weakly polar or nonionic pesticides. Spencer (1970) found that the volatilization rate of dieldrin was inversely related to the organic matter content in the five soils he tested. For more polar or ionic pesticides clay minerals play an increasingly important role in effects on adsorption and volatilization. For example, some organic cations like diquat or paraquat are adsorbed by clays up to the cation-exchange capacity of the clays. The clay content plays a minor role with weakly polar compounds when sufficient water is present to cover the mineral surface. Factors such as concentration of the pesticide in the soil, the soil water content, the relative humidity of the air and temperature will influence the rate of adsorption to soil (Spencer et al., 1973).

2.1.2.3 Soil pesticide concentration

Soil surface applications, or pesticides precipitating on the soil surface from foliar applications, can result in relatively high concentrations of pesticides at the evaporating surface. For example, a 1 kg/ha application is equivalent to c. 150 mg/kg in the surface 0.5 mm of soil.

At relatively low pesticide concentrations the vapour density of the pesticide in soil will increase with concentration and will reach a saturation vapour density, equal of that of the pesticide without soil. For lindane in moist Gila silt loam the saturation vapour density is reached at a concentration of 55 mg/kg. With dieldrin, the rate of volatilization increased with increasing soil concentration until the soil dieldrin concentration reached approximately 25 mg/kg, which is the concentration required in Gila silt loam to give a saturated vapour density at 20 °C. This relatively low soil concentration needed for a saturated vapour in moist soil indicates that weakly adsorbed pesticides such as lindane will be subject to relatively high rates of loss by volatilization, especially following application to the soil surface. Incorporation of the pesticide in the soil, which is commonly done for volatile herbicides such as trifluralin and EPTC, will reduce the volatilization rate because the concentration at the evaporating surface is lower (Farmer et al., 1972; Spencer et al., 1969; Guenzi and Beard, 1974).

2.1.2.4 Soil water content

Pesticides volatilize much more rapidly from wet than from dry soils because the polar water molecules are strong competitors for adsorption sites on the soil, especially to nonpolar organic compounds (Petersen et al., 1994). Once the soil surface is saturated with just one molecular layer of water, the vapour density of the pesticide in the soil air is greatly increased. Additional soil water does not influence the tendency of the compound to leave its sorbed site. About 2.8% water is needed in a Gila silt loam to achieve a monomolecular layer (Spencer et al., 1973). When water evaporates, the compound sorbs onto the dry soil. Thus, volatilization of the compound is enhanced by the presence of water, not its evaporation (Thomas, 1990).

The highest volatilization losses from a moist soil surface are near solar noon or early afternoon. Losses are very small at night. If the surface layer of the soil becomes dry, volatilization losses are dramatically reduced. During the day volatilization is low. In the evening and morning volatilization will increase because dew and upward movement of soil moisture makes the soil

surface moist. (Glotfelty et al., 1984; Whang et al., 1993)
Passing moist air over moist soil will result in little water loss. Therefore pesticide volatilization will continue for a long time. However, with dry air (low relative humidity), the soil dries rapidly and pesticide vapour pressure is decreased within a relatively short time. Passing air with a high relative humidity over a dry soil increases its water content.

The drying effect, decreasing the volatilization, is reversible, since rewetting the air-dry soil will increase the vapour density again to its original maximum value.

The amount of pesticide volatilizing from a soil in a certain time is related to the water holding capacity of the soil since the soil initially dries at a uniform rate and total pesticide volatilization is related to the time needed to dry the soil sufficiently (Spencer et al., 1973). However, if the concentration of a compound in soil becomes high enough that its chemical activity approaches that of the pure compound, the presence or absence of water will not affect its volatilization rate (Thomas, 1990).

The soil water content at which the vapour density begins to decrease depends upon the soil and the sorption competition with water. The more strongly adsorbed the compound is, the higher the water content will be at which an appreciable decrease in vapour density will occur (Spencer et al., 1973).

2.1.2.5 Temperature

The overall effect of an increasing temperature on a soil-pesticide system is an increasing volatilization of the pesticide. Temperature affects the volatilization of a given pesticide from soil by a direct influence on the vapour density of the pesticide and by temperature influences on the physical and chemical properties of the soil. (Guenzi and Beard, 1974)

However, an increase of temperature may also increase the drying rate of the soil surface. Depending on the result of the temperature effect on soil drying and the effect on vapour pressure, volatilization will increase or decrease (Deming, 1963).

2.1.2.6 Air flow rate

Windspeed, turbulence, and relative humidity, play an important role in the overall loss of pesticides by volatilization in the field. The rate of air flow can influence pesticide volatilization directly and indirectly. The direct effect of increased air movement involves a more rapid removal of pesticide vapours from the soil surface, and results in an increased movement of pesticide vapours to the soil surface. (Guenzi and Beard, 1974)

Farmer et al. (1972), Igue et al. (1972), and Harris and Lichtenstein (1961) found more volatilization of chlorinated insecticides with increased flow rates.

Grass et al. (1994) measured the volatilization of trifluralin from the soil surface at three air velocities (0.4, 1.0, and 1.8 m/s). Respective percentages of volatilized trifluralin over the first 24 hours were 70, 64, and 73% (temperature 20-21 °C, relative humidity 49%).

If the relative humidity of the air is not 100%, increases in air flow will hasten the drying of the soil. This indirect effect alters the soil-water content, which has an effect on the volatilization. (Guenzi and Beard, 1974)

Grass et al. (1994) also measured the influence of air humidity on the volatilization of trifluralin. At a relative air humidity of 31, 49, and 78% the measured percentage of volatilized trifluralin over the first day was 66, 64, and 96%, respectively (temperature 20 °C, air velocity 1.0-1.2 m/s).

2.1.3 Pesticide movement towards the evaporating surface

The rate of loss by volatilization depends on soil concentration-vapour density relationships at the soil surface. Volatilization of soil incorporated pesticides is therefore mainly dependent upon desorption of the pesticide from the soil and upward movement to the soil surface. According to Letey and Farmer (1974) there are two general mechanisms whereby pesticides move to the evaporating surface, i.e. diffusion and mass flow. The total rate of movement is the summation of diffusion and mass flow.

2.1.3.1 Diffusion

Diffusion is the process by which material is transported as a result of random molecular motion caused by the molecule's thermal energy. The random molecular motions gradually cause the molecules to become uniformly distributed in the system. (Letey and Farmer, 1974)
Diffusion occurs whenever a concentration gradient is present. Movement is always from a higher to a lower concentration. An increase in difference in gradient will increase the diffusion rate. Volatilization of a pesticide depletes the pesticide from the soil surface. Additional pesticide in the soil will diffuse upward to replace that volatilized.
In general the diffusion rate of a pesticide is controlled by temperature, soil bulk density, pesticide concentration and the soil water, organic matter, and clay contents.
Diffusion can occur along four major pathways; one in the vapour phase and three in nonvapour phases: air-water interface, water-water pathway and water-solid interface. Only small quantities are in the vapour phase compared with the amount in solution or adsorbed on the soil. However, as coefficients of diffusion in air are several thousands times greater than those for water or surface diffusion, total mass transport by diffusion through the vapour phase can be approximately equal to that through nonvapour phases (Thomas, 1990). Diffusion through the soil or the soil water is a slow process but movement by diffusion also takes place in the absence of evaporating water.

2.1.3.1.1 soil water content

Shearer et al. (1973) and Ehlers et al. (1969a) measured lindane diffusion through Gila silt loam soil at different water contents. Essentially no diffusion occurred in dry soil. Diffusion increased rapidly with increasing water content and reached a maximum at approximately 4% water content. After increasing the water content above 4% Shearer et al. (1973) found a decline in total diffusion until 30% water content when an increase in diffusion occurred with increasing water. Vapour diffusion decreased slightly as water content increased from 4 to 20% and then decreased rapidly at water contents above 20%. The shape of the curve found by Ehlers et al. (1969a) was somewhat different from that of Shearer et al. (1973), possibly due to a different concentration used.
Scott and phillips (1972) measured the diffusion of several herbicides through Lanton silty clay loam at three different soil water contents. The diffusion coefficients for prometone, atrazine, simazine, prometryne, diphenamid, and chloropropham all increased as the soil water increased. Trifluralin was not greatly affected by soil water content. As trifluralin is the most volatile of the herbicides tested, the diffusion results are explained by vapour phase diffusion.
Leistra (1972) concluded that soil water content is one of the most important factors influencing the diffusion of fumigants. The diffusion rate is usually high in dry soils and the movement is slow in wet soils. Thus, an increasing soil water content decreases the diffusion rate.

2.1.3.1.2 adsorption

Lindstrom et al. (1968) measured the diffusion of 2,4-D in a number of water-saturated soils with an adsorption coefficient ranging from 0.4 - 23.0. They found that the effective diffusion coefficient is reduced by adsorption of the chemical to soil. Walker and Crawford (1970) found an obvious inverse relationship between measured diffusion coefficients and adsorption for propazine and prometryne.

2.1.3.1.3 bulk density

The general overall effect of increasing bulk density is to decrease the diffusion coefficient. This is especially true for compounds which have a significant amount of diffusion in the vapour phase, as increasing bulk density decreases the air-filled porosity of the soil. (Letey and Farmer, 1974)

Ehlers et al. (1969b) reported a decrease in the apparent diffusion coefficient of lindane as the bulk density of the Gila silt loam was increased. The water content was maintained at 10% (weight basis) so that the air-filled porosity decreased as the bulk density increased.

Farmer et al. (1973) studied the influence of bulk density on diffusion and volatilization of dieldrin from soil. The volatilization of dieldrin tended to decrease as bulk density increased. The principal effect of bulk density was that of limiting the vapour phase movement of dieldrin to the soil surface.

Call (1957a) found that an increase in the bulk density (1.39 to 1.62 g/cm^3) resulted in a decrease of the measured apparent diffusion coefficient of ethylene dibromide (from 4.49 * 10^{-4} to 2.67 * 10^{-4} cm^2/sec).

2.1.3.1.4 temperature

Temperature has a very significant effect on the rate of diffusion. Diffusion coefficients tend to increase with increasing temperature. Vapour density increases significantly as temperature increases. The general overall effect of increasing temperature is an increase in diffusion. (Letey and Farmer, 1974)

Ehlers et al. (1969b) reported an exponential increase in the apparent diffusion coefficient for lindane after increasing the temperature from 20 to 40 °C.

Lavy (1970) found an increase in the diffusion coefficient for atrazine, simazine, and propazine when the temperature was increased from 5 to 25 °C. The overall diffusion coefficient increased 10-fold as the temperature increased from 20 to 40 °C.

An increase of the diffusion coefficient of ethylene dibromide with increasing temperature was measured by Call (1957b).

2.1.3.2. Mass flow in water moving to the surface

Mass flow occurs as a result of external forces. The pesticide is considered to be either dissolved or suspended in water, present in the vapour phase, or adsorbed on solid mineral or organic components of the soil. Mass flow of the pesticide therefore is the result of the mass flow of water and/or soil particles with which the pesticide molecule is associated. Mass flow due to air movement in soil is considered negligible. (Letey and Farmer, 1974)

When water evaporates from the soil surface the suction gradient produced results in an upward movement of water. Pesticides in the soil solution can move upward with the water by mass flow with the evaporating water. This proces is called the wick effect.

The magnitude of the wick effect is related to water evaporation rate, vapour pressure of the pesticide, and the concentration of the pesticide in the soil solution. The concentration in the soil solution will depend upon the adsorption characteristics and the water solubility of the pesticide and other factors affecting partitioning between the water, air, and soil phases in the soil. The wick effect enhances volatilization much more in wet soils because the degree of enhancement is related to the water evaporation rate.

When the evaporation rate of the water is higher than the volatilization rate of the pesticide, for example when the surface of the soil is dry, the pesticide will accumulate at the soil surface. After rewetting of the soil the pesticide can volatilize after all.

2.1.3.2.1 temperature

Temperature may influence the volatility of soil-incorporated pesticides through its effect on movement of the pesticide to the surface by diffusion or by mass flow in the evaporating water, or through its effect on the soil water adsorption-desorption equilibrium.

Experiments of Samuel and Pillai (1989) showed a fivefold increase in volatilization for the strongly adsorbing pesticide DDT when the temperature was raised from 15 to 45 °C. Basile (1986) found a twofold increase in volatilization of 1,3-D over a period of 3 days when the temperature was raised from 5° C to 15° C.

Higher temperatures decrease adsorption and thus increase the availability of free residues for volatilization.

Temperature gradients in soil may also influence pesticide volatilization because of the effect on temperature gradients on water and pesticide movement. When exposed to a temperature gradient, water in soil will move from points of high temperature to points of low temperature (Nielsen et al., 1972). In the same way, pesticides move from higher to lower temperature zones in the soil. Based on this theory, an upward transport of the pesticide can be expected at night, when the temperature at the surface of the soil is lower than in the subsoil, and a downward movement of the pesticide is expected during the day, when the temperature at the surface will be higher than in the subsoil. Although the process undoubtedly occurs, experimental evidence is still lacking (Spencer et al., 1973).

2.1.3.2.2 Henry's law constant

Chemicals with low Henry's law constants will tend to accumulate at the soil surface when water is evaporating, resulting in an increased volatilization with time. Volatilization of chemicals with high Henry's law constants is within the soil; no accumulation at the soil surface will occur. (Spencer et al., 1988) For compounds with a dimensionless Henry's law constant > $2.65 * 10^{-5}$ volatilization decreases with time under all conditions whether water is evaporating or not. Compounds with a dimensionless Henry's law constant << $2.65 * 10^{-5}$ move faster to the surface in evaporating water than they can volatilize through the boundary layer. Therefore the concentration at the soil surface increases under evaporative conditions and the volatilization rate increases with time. (Jury et al., 1984)

2.1.3.2.3 adsorption

Although many factors contribute to mass transport of pesticides through soil by water, the most important factor appears to be adsorption between the pesticide and soil. (Letey and Farmer, 1974)

Ashton (1961), Hamaker et al., (1966) and Harris (1966, 1967) found an inverse order between pesticide movement in soil and adsorption. An increase in soil organic matter content causes an increase in adsorption coefficient for pesticides which accounts for a decreased depth of leaching. Similarly, an increase in clay content of soil has been reported to both increase the adsorption coefficient and decrease the mobility of pesticides.

2.2 Volatilization from plants

Willis and McDowell (1987) mention weather factors like rain, wind, temperature, sunlight and relative humidity to affect the rate of pesticide disappearance from foliage.
Rain has the most dramatic effect on residues, especially if it occurs within 24 hours after pesticide application. Rainfall amount appears to have a greater effect than rainfall intensity on washoff of emulsifiable concentrate formulations of insecticides from cotton plants. (McDowell et al., 1987)
The primary effect of wind on pesticide disappearance from foliage is through turbulent transfer of volatilized pesticide from plant surfaces to the atmosphere. (Spencer et al., 1973)
Temperature affects pesticide disappearance from foliage through its influence on pesticide vapour pressure and volatility. (Harper et al., 1983)
Sunlight affects pesticide disappearance through photochemical alteration of the pesticide. (Crosby, 1972)
High relative humidity has been reported to both increase pesticide persistence on plants by facilitating foliar absorption and decrease persistence by favoring volatilization. (Willis and McDowell, 1987)
Willis et al. (1992) performed field experiments in which the disappearance of methyl parathion from cotton plants was measured. Overall, cumulative wind was the best predictor of methyl parathion disappearance from cotton foliage. Increased wind is an indicator of greater turbulence and greater volatile loss of pesticides from plant surfaces. This was also found by Willis et al. (1983). Cumulative temperature above 16 °C and cumulative solar radiation were the two best predictors. Increased air temperature results in increased pesticide vapour pressure and subsequent volatile loss from soil (Spencer et al., 1973) and plant (Harper et al., 1983) surfaces. Solar radiation is a measure of the energy available to drive the various heating and energy-consuming processes (primarily volatilization).

It is estimated that c. 20% of the total amount of active ingredient applied will volatilize from the plant into the atmosphere (Ministerie van L.N.V., 1991). Grover et al. (1985) found the same amount of volatilization for 2,4-D-isoctyl. Cliath et al. (1980) reported amounts of 75%.

According to Baas (1994) volatilization from plants is mainly influenced by:
- windspeed and stability of the atmosphere
- nature of the leaf surface
- vapour pressure of the active ingredient
- the application technique
- temperature
- plant foliage amount.

Huygen (1986) assumes that the sprayed solution consists of fine droplets that are deposited on the plant. After evaporation of the solvent the active ingredient on the plant will remain in more or less round spots. The diameter of these spots depends on droplet size distribution, application method and the structure of the leaf. The rate of volatilization of the pesticide is given by the total surface of evaporation and the vapour density. The active ingredient is not assumed to get attached to the plant surface.

Que Hee and Sutherland (1975) examined the volatilization of 2,4-D-esters from plant leaves contained in small chambers at constant temperature. Uptake and evaporation were found to be competing processes, and the relative rate of each depended upon the size of the herbicide droplet. Small droplets had faster rates of evaporation. Large ones had faster rates of uptake.

Breeze et al. (1992) did experiments to measure evaporation from leaves of barley plants under different conditions of temperature, lighting and boundary layer conductance. The conclusions from these experiments were that evaporation was strongly dependent upon temperature (evaporation rate was 8 times higher at 29.5 °C than at 19.3 °C). Furthermore evaporation from leaves in the dark increased by > 80% of the value in the light at the same temperature. Boundary layer conductance affected the rate of evaporation because values were lower in uncirculating air than in circulating air, even though the leaf temperature was higher.

2.2.1 Uptake by plant leaves

Uptake rates appeared to be inversely related to temperature, probably because evaporation was small at low temperature and so there was more herbicide available for uptake. Light or darkness had little effect. It is unclear why uptake was low in the absence of air circulation, with most of the herbicide remaining in the surface deposit.

Uptake of 2,4-D-butyl by leaves of barley was generally a more rapid (about 2.5 times faster) process than evaporation. It should be stated that the rate of uptake of 2,4-D-butyl is high compared to other compounds (see table 2.2.1).

Table 2.2.1 Rates of herbicide uptake by plant leaves (Breeze et al., 1992).

compound	species	dose (mg/plant)	period (h)	uptake (ng $cm^{-2}h^{-1}$)	reference
fluazifop	green foxtail	0.1	12	4000	Grafstrom, 1988
2,4-D acid	hemp dogbane	0.03	12	1600	Schultz, 1980
glyphosate	hemp dogbane	0.02	12	250	Schultz, 1980
haloxyfop-methyl	quackgrass	0.007	96	69	Wilhm, 1986
chlorsulfuron	wild garlic	0.017	12	39	Leys, 1988
metsulfuron	wild garlic	0.012	12	36	Leys, 1988
diclofop-methyl	cultivated oat	0.0064	24	33	Kafiz, 1988

From the table one can assume that the dose is also an important factor regulating the uptake of pesticides by plant leaves.

Most of the herbicide that penetrated the plant (95%) remained in the leaf to which it was applied. (Breeze, 1992)

3. MEASURED RATES OF VOLATILIZATION

Many authors reported measured volatilization rate data for experiments they performed in the laboratory or in the field. These reported rates of volatilization, as far as they could be found, are given in six tables. Data for volatilization from the soil surface (table 3.1 and 3.2), volatilization of incorporated pesticides (table 3.3 and 3.4) and volatilization from plants (table 3.5 and 3.6) are given. Data from field and laboratory experiments are given in separate tables.
The substances in the tables are sorted alphabetically. Furthermore the values and sorted numerically on the length of the measuring period.
All data in the tables are given by the author in the literature referred to. Due to variation in e.g. temperature the vapour pressure may not always be the same for one single substance.

Table 3.1 Measured rates of volatilization of pesticides **from the soil surface, field studies**.

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
alachlor	21	19	2.9E-3	May	USA	3.36	dry and hot weather	Glotfelty, 1989
alachlor	35	14		spring	USA	4.2	no-till field, >50% residue cover	Wienhold, 1994
alachlor	35	9		spring	USA	4.2	tilled corn field	Wienhold, 1994
atrazine	4	0.9	4.0E-5	13 April	USA	2.5	no-till corn field	Whang, 1993
atrazine	4	0.7	4.0E-5	13 April	USA	2.5	tilled corn field	Whang, 1993
atrazine	21	2.4	8.8E-5	May	USA	2.52	dry and hot weather	Glotfelty, 1989
atrazine	26	2.5	4.0E-5	13 April	USA	2.5	no-till corn field	Whang, 1993
atrazine	26	1.9	4.0E-5	13 April	USA	2.5	tilled corn field	Whang, 1993
atrazine	35	9		spring	USA	2.8	no-till field, >50% residue cover	Wienhold, 1994
atrazine	35	4		spring	USA	2.8	tilled corn field	Wienhold, 1994
chlordane	2.1	2	1.3E-3	14 June	USA	0.84	dry soil surface	Glotfelty, 1984
chlordane	2.5	50	1.3E-3	8 Aug	USA	0.72	moist soil surface	Glotfelty, 1984
chlorpropham	50	49		May	USA	?	bare soil, soybean planted	Turner, 1978
chlorpyrifos	4	23	2.5E-3	13 April	USA	5.6	no-till corn field	Whang, 1993
chlorpyrifos	4	7	2.5E-3	13 April	USA	5.6	tilled corn field	Whang, 1993
chlorpyrifos	26	49	2.5E-3	13 April	USA	5.6	no-till corn field	Whang, 1993
chlorpyrifos	26	12	2.5E-3	13 April	USA	5.6	tilled corn field	Whang, 1993
dacthal	1.4	2	3.3E-4	8 Aug	USA	5.11	moist soil surface	Glotfelty, 1984
deltamethrin	1	24	2E-6	25 May	BRD	1.13	dry and hot weather	Boehncke, 1990
deltamethrin	3.1	52	2E-6	25 May	BRD	1.13	dry and hot weather	Boehncke, 1990
dieldrin	50	18	2.8E-6	1 Sept	USA	12-14	moist soil	Willis, 1972
dieldrin	150	18	2.8E-6	1 Sept	USA	12-14	moist soil	Willis, 1972
dieldrin	150	7	2.8E-6	1 Sept	USA	12-14	dry soil	Willis, 1972
dieldrin	150	2	2.8E-6	1 Sept	USA	12-14	flooded soil	Willis, 1972

Table 3.1 Measured rates of volatilization of pesticides from the soil surface, field studies (continued).

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
fonofos	4	48	2.8E-2	13 April	USA	5.3	no-till corn field	Whang, 1993
fonofos	4	18	2.8E-2	13 April	USA	5.3	tilled corn field	Whang, 1993
fonofos	26	62	2.8E-2	13 April	USA	5.3	no-till corn field	Whang, 1993
fonofos	26	27	2.8E-2	13 April	USA	5.3	tilled corn field	Whang, 1993
heptachlor	0.25	50	4E-2	8 Aug	USA	3.55	moist soil surface	Glotfelty, 1984
heptachlor	2.1	14-40	4E-2	14 June	USA	3.75	dry soil surface	Glotfelty, 1984
heptachlor	6	90	4E-2	8 Aug	USA	3.55	moist soil surface	Glotfelty, 1984
lindane	0.25	50	8.4E-3	10 June	USA	1.1	moist soil surface	Glotfelty, 1984
lindane	1	28	5E-3	25 May	BRD	2.2	dry and hot weather	Boehncke, 1990
lindane	2.1	12	8.4E-3	14 June	USA	0.62	dry soil surface	Glotfelty, 1984
lindane	3.1	32	5E-3	25 May	BRD	2.2	dry and hot weather	Boehncke, 1990
lindane	6	90	8.4E-3	10 June	USA	1.1	moist soil surface	Glotfelty, 1984
simazine	21	1.3	2E-6	May	USA	2.52	dry and hot weather	Glotfelty, 1989
toxaphene	21	31	1.3E-4	May	USA	3.78	dry and hot weather	Glotfelty, 1989
trifluralin	0.13-0.3	50	1.5E-2	June/Aug	USA	2.8	moist soil surface	Glotfelty, 1984
trifluralin	2.1	2-25	1.5E-2	14 June	USA	2.5	dry soil surface	Glotfelty, 1984
trifluralin	2.5-7	90	1.5E-2	June/Aug	USA	2.8	moist soil surface	Glotfelty, 1984

Table 3.2 Measured rates of volatilization of pesticides **from the soil surface, laboratory studies**.

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
atrazine	1	0.1		-	-	normal	air dry peat soil, 20 °C	Dörfler, 1991
atrazine	1	<0.07		-	-	normal	40% MWHC, peat soil, 20 °C	Dörfler, 1991
atrazine	1	0.07		-	-	normal	air dry sandy soil, 20 °C	Dörfler, 1991
atrazine	1	0.5		-	-	normal	40% MWHC, sandy soil, 20 °C	Dörfler, 1991
lindane	1	5.8		-	-	normal	air dry peat soil, 10 °C	Dörfler, 1991
lindane	1	3.1		-	-	normal	40% MWHC, peat soil, 10 °C	Dörfler, 1991
lindane	1	11.8		-	-	normal	air dry peat soil, 20 °C	Dörfler, 1991
lindane	1	4.3		-	-	normal	40% MWHC, peat soil, 20 °C	Dörfler, 1991
lindane	1	3.2		-	-	normal	air dry sandy soil, 10 °C	Dörfler, 1991
lindane	1	13.7		-	-	normal	40% MWHC, sandy soil, 10 °C	Dörfler, 1991
lindane	1	9.8		-	-	normal	air dry sandy soil, 20 °C	Dörfler, 1991
lindane	1	22.6		-	-	normal	40% MWHC, sandy soil, 20 °C	Dörfler, 1991
trifluralin	0.04	13	1.37E-2	-	-	0.75	air velocity 0.4 m/s, 20 °C, rel. humidity 49%	Grass, 1994
trifluralin	1	70	1.37E-2	-	-	0.75	air velocity 0.4 m/s, 20 °C, rel. humidity 49%	Grass, 1994
trifluralin	0.04	14	1.37E-2	-	-	0.75	air velocity 1.0 m/s, 20 °C, rel. humidity 49%	Grass, 1994
trifluralin	1	64	1.37E-2	-	-	0.75	air velocity 1.0 m/s, 20 °C, rel. humidity 49%	Grass, 1994
trifluralin	0.04	20	1.37E-2	-	-	0.75	air velocity 1.8 m/s, 20 °C, rel. humidity 49%	Grass, 1994
trifluralin	1	73	1.37E-2	-	-	0.75	air velocity 1.8 m/s, 20 °C, rel. humidity 49%	Grass, 1994

Table 3.2 Measured rates of volatilization of pesticides from the soil surface, laboratory studies (continued).

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
trifluralin	0.04	16	1.37E-2	-	-	0.75	15 °C, rel. hum. 49%, 1 m/s	Grass, 1994
trifluralin	1	80	1.37E-2	-	-	0.75	15 °C, rel. hum. 49%, 1 m/s	Grass, 1994
trifluralin	0.04	14	1.37E-2	-	-	0.75	21 °C, rel. hum. 49%, 1 m/s	Grass, 1994
trifluralin	1	64	1.37E-2	-	-	0.75	21 °C, rel. hum. 49%, 1 m/s	Grass, 1994
trifluralin	0.04	25	1.37E-2	-	-	0.75	30 °C, rel. hum. 49%, 1 m/s	Grass, 1994
trifluralin	1	78	1.37E-2	-	-	0.75	30 °C, rel. hum. 49%, 1 m/s	Grass, 1994
trifluralin	0.04	14	1.37E-2	-	-	0.75	rel. humidity 31%, 1 m/s, 20 °C	Grass, 1994
trifluralin	1	66	1.37E-2	-	-	0.75	rel. humidity 31%, 1 m/s, 20 °C	Grass, 1994
trifluralin	0.04	29	1.37E-2	-	-	0.75	rel. humidity 78%, 1 m/s, 20 °C	Grass, 1994
trifluralin	1	96	1.37E-2	-	-	0.75	rel. humidity 78%, 1 m/s, 20 °C	Grass, 1994

Table 3.3 Measured rates of volatilization of pesticides **incorporated in soil, field studies**.

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
dieldrin	164	3.6		3 May	USA	5.6	bare soil, incorporated in 0-7.5 cm, maize planted	Taylor, 1976
heptachlor	164	6.8		3 May	USA	5.6	bare soil, incorporated in 0-7.5 cm, maize planted	Taylor, 1976
triallate	7	10	2.6E-2	May	CAN	2.2	heavy clay	Grover, 1988
triallate	28	13	2.6E-2	May	CAN	2.2	heavy clay	Grover, 1988
triallate	67	18	2.6E-2	May	CAN	2.2	heavy clay	Grover, 1988
trifluralin	7	12	1.5E-2	May	CAN	1.1	heavy clay	Grover, 1988
trifluralin	28	17	1.5E-2	May	CAN	1.1	heavy clay	Grover, 1988
trifluralin	67	24	1.5E-2	May	CAN	1.1	heavy clay	Grover, 1988
trifluralin	9	9.5		15 June	USA	1.12	bare soil, incorporated in 0-7.5 cm, soybean planted	White, 1977
trifluralin	35	20		15 June	USA	1.12	bare soil, incorporated in 0-7.5 cm, soybean planted	White, 1977
trifluralin	90	3.4	1.5E-2	May	USA	1.12	bare soil, incorporated in 0-7.5 cm, soybean planted	Taylor, 1978
trifluralin	120	22		15 June	USA	1.12	bare soil, incorporated in 0-7.5 cm, soybean planted	White, 1977

Table 3.4 Measured rates of volatilization of pesticides **incorporated in soil, laboratory studies**.

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
aldrin	1	3	4.9E-5	-	-	12.5	30°C, moisture content unknown	Lichtenst., 1970
azinphos-methyl	1	0	< 1E-7	-	-	12.5	30°C, moisture content unknown	Lichtenst., 1970
cycloate	1	43	8.3E-1	-	-	45.5	temp./moisture content unknown	Ekler, 1988
DDT	84	10.4		-	-	5	30 °C	Hussain, 1994
DDT	42	9.6		-	-	5	35 °C	Hussain, 1994
DDT	42	16.4		-	-	5	45 °C	Hussain, 1994
diazinon	1	0.1	2.8E-4	-	-	12.5	30°C, moisture content unknown	Lichtenst., 1970
dieldrin	1	0.3	1.4E-6	-	-	12.5	30°C, moisture content unknown	Lichtenst., 1970
dieldrin	1	4		-	-	50	30°C, air flow 8 ml/s	Farmer, 1972
dieldrin	1	10		-	-	1	30°C, air flow 8 ml/s	Farmer, 1972
dieldrin	1	11		-	-	5	30°C, air flow 8 ml/s	Farmer, 1972
dieldrin	1	12		-	-	10	30°C, air flow 8 ml/s	Farmer, 1972
dieldrin	7	38		-	-	5	30°C, air flow 8 ml/s	Farmer, 1972
dieldrin	7	40		-	-	10	30°C, air flow 8 ml/s	Farmer, 1972
dieldrin	12	34		-	-	5	30°C, air flow 2 ml/s	Farmer, 1972
dieldrin	12	36		-	-	10	30°C, air flow 2 ml/s	Farmer, 1972
dieldrin	12	49		-	-	10	30°C, air flow 8 ml/s	Farmer, 1972
dieldrin	12	50		-	-	5	30°C, air flow 8 ml/s	Farmer, 1972
dieldrin	14	7		-	-	50	20°C, air flow 2 ml/s	Farmer, 1972
dieldrin	14	14		-	-	50	20°C, air flow 8 ml/s	Farmer, 1972
dieldrin	14	18		-	-	1	20°C, air flow 2 ml/s	Farmer, 1972
dieldrin	14	20		-	-	5	20°C, air flow 2 ml/s	Farmer, 1972
dieldrin	14	20		-	-	10	20°C, air flow 2 ml/s	Farmer, 1972
dieldrin	14	26		-	-	1	20°C, air flow 8 ml/s	Farmer, 1972
dieldrin	14	30		-	-	10	20°C, air flow 8 ml/s	Farmer, 1972
dieldrin	14	32		-	-	5	20°C, air flow 8 ml/s	Farmer, 1972

Table 3.4 Measured rates of volatilization of pesticides incorporated in soil, laboratory studies (continued).

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
DDT	1	2		-	-	1	30°C, air flow 8 ml/s	Farmer, 1972
DDT	1	2		-	-	5	30°C, air flow 8 ml/s	Farmer, 1972
DDT	1	2		-	-	10	30°C, air flow 8 ml/s	Farmer, 1972
DDT	1	1		-	-	50	30°C, air flow 8 ml/s	Farmer, 1972
DDT	7	9		-	-	5	30°C, air flow 8 ml/s	Farmer, 1972
DDT	7	9		-	-	10	30°C, air flow 8 ml/s	Farmer, 1972
p,p' DDT	1	< 0.1	3E-7	-	-	12.5	30°C, moisture content unknown	Lichtenst., 1970
dyfonate	1	0.9	2E-4	-	-	12.5	30°C, moisture content unknown	Lichtenst., 1970
EPTC	1	78	4.5	-	-	45.5	temp./moisture content unknown	Ekler, 1988
lindane	1	0.8	9.4E-6	-	-	12.5	30°C, moisture content unknown	Lichtenst., 1970
lindane	1	25		-	-	1	30°C, air flow 8 ml/s	Farmer, 1972
lindane	1	29		-	-	5	30°C, air flow 8 ml/s	Farmer, 1972
lindane	1	33		-	-	10	30°C, air flow 8 ml/s	Farmer, 1972
lindane	1	30		-	-	50	30°C, air flow 8 ml/s	Farmer, 1972
lindane	7	60		-	-	5	30°C, air flow 8 ml/s	Farmer, 1972
lindane	7	63		-	-	10	30°C, air flow 8 ml/s	Farmer, 1972
lindane	14	7.6	1.33E-4	-	-	4.2	sterile soil, water evaporation 0.55 cm/d	Spencer, 1988
lindane	14	5.5	1.33E-4	-	-	4.2	sterile soil, no water evaporation	Spencer, 1988
parathion	1	< 0.1	2.3E-5	-	-	12.5	30°C, moisture content unknown	Lichtenst., 1970
prometon	14	7.6	1E-7	-	-	15	sterile soil, water evaporation 0.55 cm/d	Spencer, 1988
prometon	14	1.5	1E-7	-	-	15	sterile soil, no water evaporation	Spencer, 1988
triallate	1	0.6		-	-	10	sandy loam, 100% rel.hum.	Jury, 1980
triallate	1	0.7		-	-	10	silt loam, 100% rel.hum.	Jury, 1980
triallate	29	3		-	-	10	sandy loam, 100% rel.hum.	Jury, 1980
triallate	29	3.7		-	-	10	silt loam, 100% rel.hum.	Jury, 1980
triallate	29	3.8		-	-	10	sandy loam, 100% rel.hum.	Jury, 1980
triallate	29	3.8		-	-	10	silt loam, 100% rel.hum.	Jury, 1980

Table 3.4 Measured rates of volatilization of pesticides incorporated in soil, laboratory studies (continued).

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
vernolate	1	64	1.4	-	-	45.5	temp./moisture content unknown	Ekler, 1988
1,3-D	2	37	4655	-	-	300	sandy clay, 2.78% o.m.	Basile, 1986
1,3-D	2	30	4655	-	-	300	sandy silt, 1.27% o.m.	Basile, 1986
1,3-D	2	40	4655	-	-	300	sand, 0.015% o.m.	Basile, 1986
1,3-D	2	35	4655	-	-	120	sandy clay	Basile, 1986
1,3-D	2	40	4655	-	-	240	sandy clay	Basile, 1986
1,3-D	2	24	4655	-	-	360	sandy clay	Basile, 1986
1,3-D	3	37	4655	-	-	300	sandy clay, 5°C	Basile, 1986
1,3-D	3	78	4655	-	-	300	sandy clay, 15°C	Basile, 1986
1,3-D	3	71	4655	-	-	300	sandy clay, 25°C	Basile, 1986
1,3-D	6	40	4655	-	-	1200	sandy clay, 27% moisture	Basile, 1986
1,3-D	6	61	4655	-	-	1200	sandy clay, 31% moisture	Basile, 1986
1,3-D	6	65	4655	-	-	1200	sandy clay, 35% moisture	Basile, 1986

Table 3.5 Measured rates of volatilization of pesticides **from plants, field studies**.

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
DDT	11	21	2E-5	27 Aug	USA	1.3	cotton plants, 45% coverage	Willis, 1983
DDT	33	58	2E-5	27 Aug	USA	1.3	cotton plants, 45% coverage	Willis, 1983
deltamethrin	0.04	7	2E-6	20 July	BRD	0.09	green beans	Boehncke, 1990
deltamethrin	0.125	15	2E-6	20 July	BRD	0.09	green beans	Boehncke, 1990
deltamethrin	0.25	39	2E-6	20 July	BRD	0.09	green beans	Boehncke, 1990
deltamethrin	1	71	2E-6	20 July	BRD	0.09	green beans	Boehncke, 1990
deltamethrin	3.1	72	2E-6	20 July	BRD	0.09	green beans	Boehncke, 1990
deltamethrin	0.04	0	2E-6	6 July	BRD	0.09	kohlrabi	Boehncke, 1990
deltamethrin	0.125	0	2E-6	6 July	BRD	0.09	kohlrabi	Boehncke, 1990
deltamethrin	0.25	0	2E-6	6 July	BRD	0.09	kohlrabi	Boehncke, 1990
deltamethrin	1	12	2E-6	6 July	BRD	0.09	kohlrabi	Boehncke, 1990
deltamethrin	3.1	34	2E-6	6 July	BRD	0.09	kohlrabi	Boehncke, 1990
deltamethrin	0.04	0	2E-6	6 July	BRD	0.09	lettuce	Boehncke, 1990
deltamethrin	0.125	36	2E-6	6 July	BRD	0.09	lettuce	Boehncke, 1990
deltamethrin	0.25	42	2E-6	6 July	BRD	0.09	lettuce	Boehncke, 1990
deltamethrin	1	44	2E-6	6 July	BRD	0.09	lettuce	Boehncke, 1990
deltamethrin	3.1	70	2E-6	6 July	BRD	0.09	lettuce	Boehncke, 1990
deltamethrin	0.04	0	2E-6	20 July	BRD	0.09	summer wheat	Boehncke, 1990
deltamethrin	0.125	22	2E-6	20 July	BRD	0.09	summer wheat	Boehncke, 1990
deltamethrin	0.25	23	2E-6	20 July	BRD	0.09	summer wheat	Boehncke, 1990
deltamethrin	1	24	2E-6	20 July	BRD	0.09	summer wheat	Boehncke, 1990
diazinon	0.17	4.9		13 Jan	USA	3.63	peach orchard	Glotfelty, 1990
dieldrin	0.5	12	3.7E-4	12 July	USA	5.6	orchard grass, 100% coverage	Taylor, 1977
dieldrin	30	90	3.7E-4	12 July	USA	5.6	orchard grass, 100% coverage	Taylor, 1977
heptachlor	0.5	46	4E-2	12 July	USA	5.6	orchard grass, 100% coverage	Taylor, 1977
heptachlor	7	90	4E-2	12 July	USA	5.6	orchard grass, 100% coverage	Taylor, 1977

Table 3.5 Measured rates of volatilization of pesticides from plants, field studies (continued).

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
lindane	0.04	45	5E-3	20 July	BRD	0.225	green beans	Boehncke, 1990
lindane	0.125	76	5E-3	20 July	BRD	0.225	green beans	Boehncke, 1990
lindane	0.25	82	5E-3	20 July	BRD	0.225	green beans	Boehncke, 1990
lindane	1	85	5E-3	20 July	BRD	0.225	green beans	Boehncke, 1990
lindane	3.1	90	5E-3	20 July	BRD	0.225	green beans	Boehncke, 1990
lindane	0.04	30	5E-3	6 July	BRD	0.225	kohlrabi	Boehncke, 1990
lindane	0.125	68	5E-3	6 July	BRD	0.225	kohlrabi	Boehncke, 1990
lindane	0.25	82	5E-3	6 July	BRD	0.225	kohlrabi	Boehncke, 1990
lindane	1	91	5E-3	6 July	BRD	0.225	kohlrabi	Boehncke, 1990
lindane	3.1	94	5E-3	6 July	BRD	0.225	kohlrabi	Boehncke, 1990
lindane	0.04	51	5E-3	6 July	BRD	0.225	lettuce	Boehncke, 1990
lindane	0.125	74	5E-3	6 July	BRD	0.225	lettuce	Boehncke, 1990
lindane	0.25	86	5E-3	6 July	BRD	0.225	lettuce	Boehncke, 1990
lindane	1	95	5E-3	6 July	BRD	0.225	lettuce	Boehncke, 1990
lindane	3.1	97	5E-3	6 July	BRD	0.225	lettuce	Boehncke, 1990
lindane	0.04	25	5E-3	20 July	BRD	0.225	summer wheat	Boehncke, 1990
lindane	0.125	69	5E-3	20 July	BRD	0.225	summer wheat	Boehncke, 1990
lindane	0.25	69	5E-3	20 July	BRD	0.225	summer wheat	Boehncke, 1990
lindane	1	77	5E-3	20 July	BRD	0.225	summer wheat	Boehncke, 1990
lindane	3.1	88	5E-3	20 July	BRD	0.225	summer wheat	Boehncke, 1990
mevinphos	0.04	69	8E-2	20 July	BRD	0.43	green beans	Boehncke, 1990
mevinphos	0.125	85	8E-2	20 July	BRD	0.43	green beans	Boehncke, 1990
mevinphos	0.25	93	8E-2	20 July	BRD	0.43	green beans	Boehncke, 1990
mevinphos	1	99	8E-2	20 July	BRD	0.43	green beans	Boehncke, 1990
mevinphos	3.1	100	8E-2	20 July	BRD	0.43	green beans	Boehncke, 1990
mevinphos	0.04	39	8E-2	6 July	BRD	0.43	kohlrabi	Boehncke, 1990
mevinphos	0.125	65	8E-2	6 July	BRD	0.43	kohlrabi	Boehncke, 1990
mevinphos	0.25	75	8E-2	6 July	BRD	0.43	kohlrabi	Boehncke, 1990
mevinphos	1	86	8E-2	6 July	BRD	0.43	kohlrabi	Boehncke, 1990
mevinphos	3.1	98	8E-2	6 July	BRD	0.43	kohlrabi	Boehncke, 1990

Table 3.5 Measured rates of volatilization of pesticides from plants, field studies (continued).

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
mevinphos	0.04	38	8E-2	6 July	BRD	0.43	lettuce	Boehncke, 1990
mevinphos	0.125	83	8E-2	6 July	BRD	0.43	lettuce	Boehncke, 1990
mevinphos	0.25	85	8E-2	6 July	BRD	0.43	lettuce	Boehncke, 1990
mevinphos	1	92	8E-2	6 July	BRD	0.43	lettuce	Boehncke, 1990
mevinphos	3.1	98	8E-2	6 July	BRD	0.43	lettuce	Boehncke, 1990
mevinphos	0.04	50	8E-2	20 July	BRD	0.43	summer wheat	Boehncke, 1990
mevinphos	0.125	83	8E-2	20 July	BRD	0.43	summer wheat	Boehncke, 1990
mevinphos	0.25	82	8E-2	20 July	BRD	0.43	summer wheat	Boehncke, 1990
mevinphos	1	96	8E-2	20 July	BRD	0.43	summer wheat	Boehncke, 1990
mevinphos	3.1	100	8E-2	20 July	BRD	0.43	summer wheat	Boehncke, 1990
toxaphene	4	25		14 Aug	USA	2.24	cotton plants, 100% coverage	Willis, 1980
toxaphene	5	26		5 Sept	USA	2.24	cotton plants, 100%	Willis, 1980
toxaphene	5	10	1.3E-4	16 Aug	USA	2.24	cotton plants, 45% coverage	Willis, 1983
toxaphene	5	19	1.3E-4	27 Aug	USA	3.73	cotton plants, 45% coverage	Willis, 1983
toxaphene	11	17	1.3E-4	16 Aug	USA	2.24	cotton plants, 45% coverage	Willis, 1983
toxaphene	11	33	1.3E-4	27 Aug	USA	3.73	cotton plants, 45% coverage	Willis, 1983
toxaphene	33	53	1.3E-4	27 Aug	USA	3.73	cotton plants, 45% coverage	Willis, 1983

Table 3.6 Measured rates of volatilization of pesticides **from plants, laboratory studies**.

substance	period (days)	volatilized (%)	vap. pressure (Pa)	time of applic.	country	conc. applied (mg a.i./kg)	experimental conditions	reference
atrazine	1	1.3		-	-	15% of normal	oats, leaf temp. 10 °C	Dörfler, 1991
atrazine	1	2.7		-	-	15% of normal	bean, leaf temp. 20 °C	Dörfler, 1991
atrazine	1	2.8		-	-	15% of normal	turnip, leaf temp. 20 °C	Dörfler, 1991
atrazine	1	4.6		-	-	15% of normal	oats, leaf temp. 20 °C	Dörfler, 1991
lindane	1	64		-	-	normal	turnip, leaf temp. 11 °C	Dörfler, 1991
lindane	1	69		-	-	normal	oats, leaf temp. 11 °C	Dörfler, 1991
lindane	1	71		-	-	normal	bean, leaf temp. 20 °C	Dörfler, 1991
lindane	1	82		-	-	normal	turnip, leaf temp. 20 °C	Dörfler, 1991
lindane	1	89		-	-	normal	oats, leaf temp. 20 °C	Dörfler, 1991
lindane (γ-HCH)	4	37		-	-	0.5 mg	garden beans, 16°C, 60% rel. hum.	Starr, 1968
lindane (γ-HCH)	4	37		-	-	0.5 mg	garden beans, 16°C, 70-100% rel. hum.	Starr, 1968
lindane (γ-HCH)	4	79		-	-	0.5 mg	garden beans, 27°C, 40% rel. hum.	Starr, 1968
lindane (γ-HCH)	4	64		-	-	0.5 mg	garden beans, 27°C, 60-80% rel. hum.	Starr, 1968

4. MODELS

Mackay (1991) stated that the best model is the least worse set of simplifying assumptions that yields a model which is not too complex, but at the same time sufficiently detailed to be useful.

4.1 Volatilization from soil

4.1.1 Volatilization from the soil surface

The rate of volatilization of pesticides from soil is controlled by a number of intrinsic factors that depend upon properties of the chemical and of the soil. Spencer (1970) showed that the vapour density of pesticides over soil is proportional to the concentration of pesticides in the soil solution and that the proportionality constant was equal to the ratio of pesticide vapour pressure to solubility. In other words, pesticides in the soil solution obeyed Henry's law. The concentration of pesticide in the soil solution is, in turn, a function of soil organic matter and moisture content, as described by the soil/water adsorption coefficient. Spencer therefore concluded that a knowledge of Henry's law coefficients and soil/water adsorption isotherms could be used to predict pesticide volatility from soil. (Glotfelty et al., 1989)
This concept has been embodied in an empirical rate expression developed by Swann et al., 1982). In this approach, which is appropriate to soil surface applications, the volatilization rate constant (or specific volatilization rate, day^{-1}), K_v, is given by

$$K_v = \frac{Q*P}{K_{om}*S}$$

where:
K_v = volatilization rate constant in day^{-1}
P = vapour pressure in Pa
K_{om} = soil adsorption coefficient in dm^3/kg (organic matter basis)
S = solubility in mg/l
Q = coefficient which equals $5.6 * 10^5$ (empirically determined, assuming 1 mm Hg = 133 Pa and $K_{om} = 1.7 * K_{oc}$)

This method is also known as the Dow method.

Thomas (1990) discussed and compared several models for estimating the rate of volatilization from soil. Thomas (1990) concluded that if the chemical is not distributed throughout the soil, the Dow method, which computes the volatilization rate for a surface-applied chemical, is appropriate.
The only data required are the solubility (S), the vapour pressure (P) and the soil adsorption coefficient (K_{om}) for the chemical.
The half-life (DT_{50}) of the chemical in the soil can be estimated by:

$$DT_{50} = \frac{0.693}{K_v} = \frac{1.24*10^{-6} * K_{om} * S}{P} \quad (days)$$

assuming first order kinetics.

The concentration on the surface at any time can be estimated from

$$c_x = c_o * e^{-K_v * t}$$

where:

c_x = concentration at the soil surface at t = x days
c_o = concentration at the soil surface at t = 0 days
K_v = volatilization rate constant (day^{-1})
t = time (days)

Swann (1982) studied nine chemicals (see table 4.1.1.1) and derived a correlation that could predict the volatilization of these chemicals from a soil surface under laboratory conditions.

Table 4.1.1.1 Chemicals, chemical properties and volatilization rate constants (measured in laboratory and calculated) (Swann, 1982).

chemical	P (mmHg)	S (mg/l)	K_{oc}	measured rate constant (hr^{-1})	calculated rate constant (hr^{-1})	agreement factor
atrazine	8.5E-7	24	150	6.4E-4	4.2E-4	1.5
carbofuran	2.0E-6	415	10	1.2E-3	2.9E-4	4.1
chlorpyrifos	1.9E-5	2	13,000	8.8E-3	1.3E-2	1.5
DDT	2.7E-7	0.0012	240,000	6.9E-4	1.2E-3	1.7
dinoseb	5.0E-5	50	700	1.1E-3	2.6E-3	2.4
diuron	1.9E-6	42	150	2.5E-3	5.3E-4	4.7
lindane	8.0E-5	7	2,500	4.4E-2	1.4E-2	3.1
nitrapyrin	3.0E-3	4	600	6.4E-1	2.2	3.4
trifluralin	1.3E-4	0.6	6,000	2.6E-2	6.6E-2	2.5

Although factors such as soil moisture, soil type, temperature and wind conditions are not incorporated in this simple model, the estimated values are within a factor 5 for the nine pesticides tested.

Swann et al. (1982) also compared field-measured, laboratory measured and calculated (using the Dow method) volatilization half-life values (see table 4.1.1.2).

Table 4.1.1.2 Comparison of field-measured, laboratory measured, and predicted half-life values using the Dow method.

chemical	half-life (days) field	half-life (days) laboratory	half-life (days) predicted	agreement factor field/predicted
chlordane	6.0	-	2.5	2.4
heptachlor	1.5	-	0.4	3.8
lindane	3.0	0.7	2.0	1.5
trifluralin	1.5	1.0	0.4	3.8

Glotfelty et al. (1989) compared measured (field) and calculated (Dow method) volatilization rate constants of some less volatile and more polar pesticides (see table 4.1.1.3).

Table 4.1.1.3 Chemicals, chemical properties and volatilization rate constants (measured in field and calculated with Dow method). (Glotfelty et al., 1989)

chemical	P (mm Hg)	S (mg/l)	K_{oc} (dm3/kg)	measured rate constant (hr^{-1})	calculated rate constant (hr^{-1})	agreement factor
alachlor	2.2E-5[a]	242[a]	82[b]	9.0E-3	4.9E-2	5.4
atrazine	6.6E-7[c]	32[d]	163[e]	1.1E-3	6.0E-3	5.5
simazine	1.5E-8[c]	5[d]	138[e]	0.6E-3	1.0E-3	1.7
toxaphene	1.0E-6[f]	0.4[g]	99,000[h]	1.5E-2	1.0E-3	15.0

[a] Herbicide Handbook, 1974. [b] Average for soils 2-7, Table 3 in Weber and Peter (1982). [c] Friedrich and Stammbach, 1964. [d] Freed, 1976. [e] Rao and Davidson, 1980. [f] Seiber et al., 1981. [g] Sanborn et al., 1976.
[h] McDowell et al., 1981.

The agreement factors found by Glotfelty et al. (1989) are somewhat higher than those found by Swann et al. (1982). Toxaphene was not correctly estimated because it is a mixture having a range of volatilities.

Watanabe (1993) measured the volatilization of 14 pesticides from soils with a water content of a third of saturation and an organic matter content of 5%. He calculated correlation coefficients between volatilization rates and physicochemical parameters (see table 4.1.1.4).

Table 4.1.1.4 Correlation coefficients between volatilization rates and physico-chemical parameters for soil with a water content of a third of saturation and an organic matter content of 5% (Watanabe, 1993).

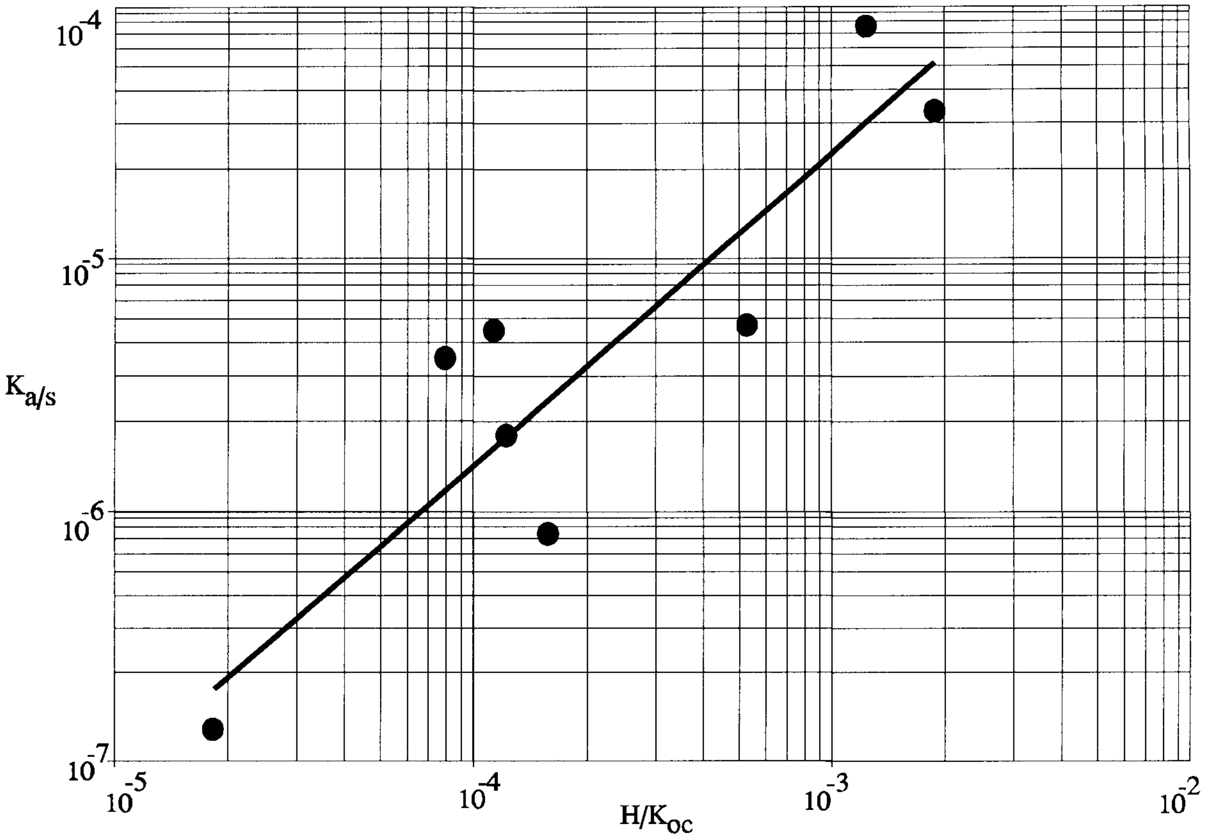
physicochemical parameter(s)	$K_{a/s}$ soil	physicochemical parameter(s)	$K_{a/s}$ soil
H/K_{oc}	0.91*	P/S	0.63
$P/S*K_{oc}$	0.89*	H	0.57
P*Mw	0.79	K_{ow}	0.32
P	0.76	P/S^2	0.31
$P/\sqrt{Mw}$	0.75	Mw	0.23
P/Mw	0.73		

$K_{a/s}$: air/soil partition coefficient, H: Henry constant ($Pa.m^3.mol^{-1}$), K_{oc}: soil adsorption coefficient (K_{oc} * 1.7 = K_{om}), P: vapour pressure, S: water solubility, Mw: molecular weight
* parameters are significantly related statistically (p<0.001)

The $K_{a/s}$ and the $P/(S * K_{oc})$ were significantly related ($r=0.89$, $p<0.01$, $n=8$). $(P * Mw)/(S * Koc) = H / K_{oc}$ was even better significantly related to the $K_{a/s}$ ($r=0.91$, $p<0.01$, $n=8$). The relationship between H / K_{oc} and $K_{a/s}$ is shown in figure 4.1.1.1.

These correlation coefficients support the Dow method, where the same formula is proposed to predict the volatilization from soil. According to Watanabe (1993) it should be better to insert the molecular weight in the formula because of the higher correlation coefficient achieved. In that case the empirically estimated coefficient Q will change.

Figure 4.1.1.1 Relationship between H / K_{oc} and $K_{a/s}$ (Watanabe, 1993).



In order to get more insight in the validity of the Dow method measured volatilization half-life values (field or laboratory) published in literature (see chapter 3, table 3.1 and 3.2) were compared with calculated values (see Table 4.1.1.5).

Table 4.1.1.5 Chemicals, chemical properties and half-life times for volatilization (calculated with the Dow method and measured in the field or the laboratory). included.

chemical	P (Pa)	S (mg/l)	K_{om}[b] (dm3/kg)	calculated DT_{50} (days)	measured DT_{50} (days)[a]	agreement factor
field studies:						
alachlor	2.1E-3[c]	240[c]	117	16.5	161	9.8
atrazine	4.0E-5[d]	30[c]	70	63	313	5.0
chlorpyriphos	2.5E-3[d]	0.4-4[c]	293	0.06-0.6	29.5	49-490
dieldrin	2.8E-6[e]	0.19[f]	100[g]	8.3	174	21
fonofos	2.8E-2[d]	13[c]	>325	0.2	23.5	118
lindane	8.4E-3[h]	7.3[c]	633	0.7	2	2.9
trifluralin	1.5E-2[h]	0.05[c]	3775	0.016	0.85-2.4	53-150
laboratory studies:						
atrazine	4.0E-5[c]	30[c]	70	63	138	2.2
lindane	8.4E-3[h]	7.3[c]	633	0.7	2.7	3.9
trifluralin	1.37E-2[i]	0.05[c]	3775	0.017	0.7	41

[a] Calculated using linear regression, assuming first order kinetics. [b] Mean K_{om} value, derived from Linders et al. (1994) [c] Linders et al. (1994) [d] Whang et al. (1993) [e] Willis et al. (1972) [f] Environmental summary RIVM [g] Default value for "very slightly mobile" [h] Glotfelty et al. (1984) [i] Grass et al. (1994)

Only experiments with moist and no-tilled soil are included. Table 4.1.1.5 gives the necessary input parameters for the calculation of the DT_{50} for volatilization with the Dow method (P, S and K_{om}). When the author did not mention values for these parameters in the article, the values were derived from Linders et al. (1994). A calculated DT_{50} was derived from the input parameters. A measured DT_{50} was derived from the data (period and % volatilized) in table 3.1 and 3.2, assuming first order kinetics. In some cases these data are less reliable because only two or three measuring points were available. Finally an agreement factor is calculated dividing the measured DT_{50} by the calculated DT_{50}.

The agreement factors found are higher than those found by Swann et al. (1982) and Glotfelty et al. (1989). It has to be stated that the calculation of the measured half-life is not very reliable. First it is assumed that the degradation follows first order kinetics and second only one or two time points were available for linear regression.

4.1.2 Volatilization of pesticides incorporated in soil

After incorporation of organic chemicals with relatively high Henry's law constants in soil, the volatilization is controlled more by the rate of movement to the soil surface than by factors controlling volatilization at the soil surface. For chemicals with low Henry's law constants the control of volatilization is within the atmosphere at the soil surface. (Jury et al., 1987)

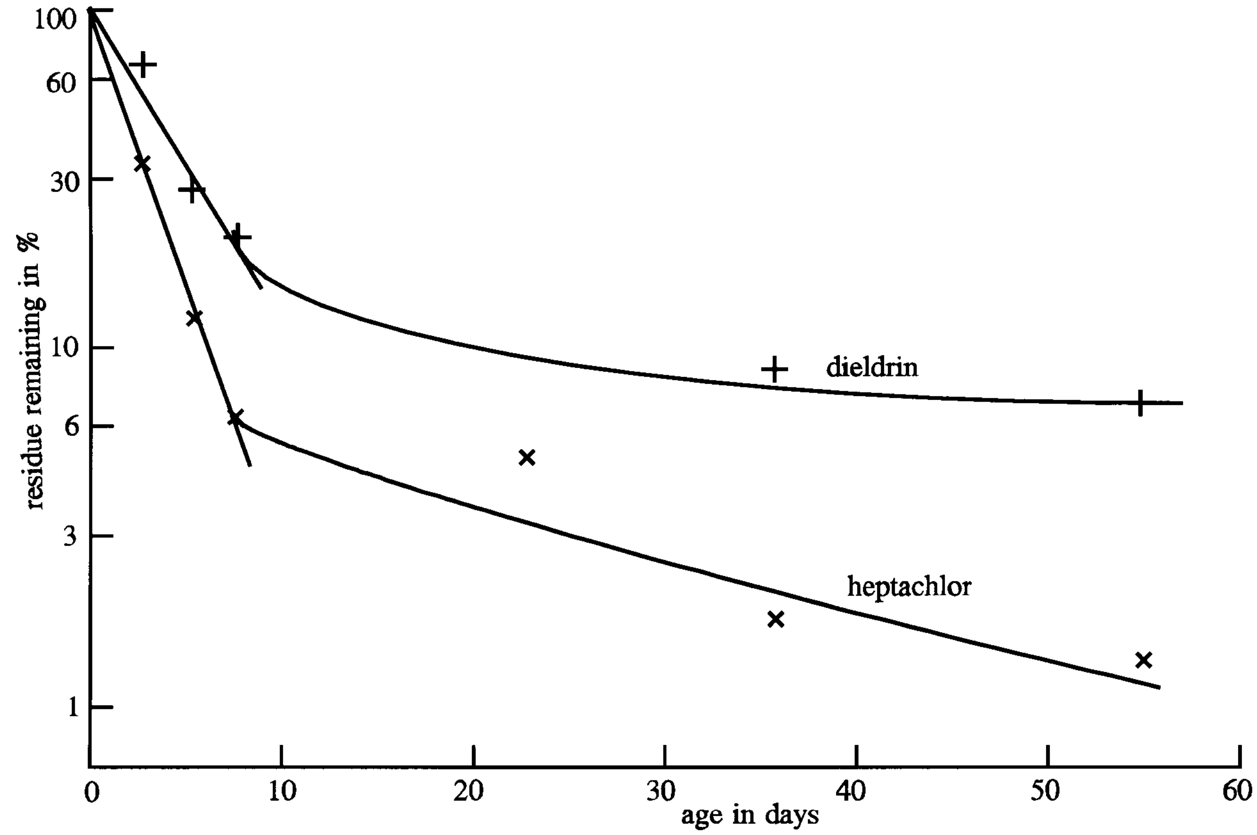
A simple model for estimating the volatilization rate of pesticides incorporated in soil is not available. For less volatile substances the volatilization rate will be low. The amount volatilizing during the first day or the first four days will be low. However, pesticides with higher vapour pressures might have a volatilization rate that can not be neglected.

4.2 Volatilization from plants

4.2.1 Relation between volatilization rate and time

Taylor et al. (1977) measured the volatilization of heptachlor and dieldrin from orchard grass. The losses could be accounted for by volatilization because chemical degradation was negligible. The curves Taylor found are typical for volatilization losses from vegetation. The curves show an initial rapid loss for about one week, during which the rate decreases in proportion to the residue remaining. After this the remaining residue is lost much more slowly.

Figure 4.2.1.1 Loss of dieldrin and heptachlor residues by volatilization from vegetation for 55 days after application (Taylor, 1978).



These curves may be interpreted in terms of the decreasing coverage of the leaf surfaces by the layer of pesticide residue. Initially, during the time the coverage is complete, the loss rate is governed by evaporation through the boundary layer of still air very close to the leaf surface. Provided the vapour pressure of the pesticide residue on the leaf surface is not reduced by chemical adsorption reactions, the volatilization per unit area of the leaf will not be affected by the amount present, since the depth of the solid (or liquid) film of residue will not affect the rate of diffusion to the boundary layer. If the film is not of uniform thickness, rapid volatilization will lead to the formation of shrinking "islands" of residue, and the volatilization rate per unit area will decrease as the remaining islands decrease in size. In practice where pesticides are applied as water-based sprays or wettable powders which are deposited as droplets, complete coverage of leaf surfaces will not be attained. No initial period of constant volatilization per unit area will then exist and the rate will decrease as mentioned. (Taylor et al., 1978)

Harrison et al. (1967) measured volatilization rates of dieldrin and other insecticides from apple trees. He also observed an initial rapid decline in pesticide residues, followed by further volatilization at declining rate.

Watanabe (1993) measured the volatilization of pesticides from the surface of rice plants. He also calculated correlation coefficients between volatilization rates and physicochemical parameters. The K_v for rice plants significantly correlated best with P / (S * K_{oc}) (r=0.83, p<0.01, n=10). The P seems to be the main factor for volatilizability from the leaf surface. The K_{oc} is supposed to be a factor for the wax layer on the leaf surface.

Huygen (1986) assumes that the active ingredient is not attached to the plant surface. This means that the factor K_{oc} is not influencing the volatilization from plant tissue.
When compared to the formula used in the Dow method to measure the volatilization from soil, the volatilization from plants only depends on:

$$K_v = \frac{Q * P}{S}$$

The only question remaining then is: How big is Q ? Perhaps the same value as for soil can be used.

Boehncke et al. (1990) measured volatilization rates of pesticides from several plants under field conditions. The half-life for volatilization (5 measurement points) over the first 3 days was not constant for the four plant species tested. For deltamethrin the half-life varied from 1.75 days on green beans to 5 days on kohlrabi. The half-life for lindane varied from 0.75 days on lettuce to 1.4 days on green beans. Mevinphos showed the shortest half-life on green beans (0.14 days) and the largest on lettuce (0.7 days).
Although these half-life values are not the same, they are all in the same range per substance. Under field conditions small variations can be expected because of the changing circumstances.

In order to get more information on the reliability of the formula proposed, measured and calculated volatilization rates are compared in table 4.2.1.1.

Table 4.2.1.1 Chemicals, chemical properties and half-life times for volatilization from plants (measured in the field and calculated with the adapted Dow method).

chemical	P (Pa)	S (mg/l)[a]	plant species	measured t1/2 (days)[b]	calculated t1/2 (days)[c]	agreement factor
field studies:						
DDT	2E-5[g]	0.0031[f]	cotton, 45% coverage	26	0.0003	8.7E4
deltamethrin	2E-6[d]	<0.002	green beans	1.75	0.002	8.8E2
deltamethrin	2E-6[d]	<0.002	kohlrabi	5	0.002	2.5E3
deltamethrin	2E-6[d]	<0.002	lettuce	2.1	0.002	1.1E3
deltamethrin	2E-6[d]	<0.002	summer wheat	3.2	0.002	6.4E3
diazinon	1.9E-2[a]	40	peach orchard	2.3	0.004	5.8E2
dieldrin	3.7E-4[e]	0.19[f]	orchard grass	9.2	0.001	9.2E3
heptachlor	4E-2[e]	0.056[f]	orchard grass	2.3	2.9E-6	7.9E5
lindane	5E-3[d]	7.3	green beans	1.4	0.003	4.7E2
lindane	5E-3[d]	7.3	kohlrabi	0.9	0.003	3.0E2
lindane	5E-3[d]	7.3	lettuce	0.75	0.003	2.5E2
lindane	5E-3[d]	7.3	summer wheat	1.3	0.003	4.3E2
mevinphos	8E-2[d]	>100000	green beans	0.14	2.7	19
mevinphos	8E-2[d]	>100000	kohlrabi	0.6	2.7	4.5
mevinphos	8E-2[d]	>100000	lettuce	0.7	2.7	3.9
mevinphos	8E-2[d]	>100000	summer wheat	0.16	2.7	17
toxaphene	1.3E-4[g]	0.4[f]	cotton, 100% coverage	9.6	0.006	1.6E3
toxaphene	1.3E-4[g]	0.4[f]	cotton, 100% coverage	11.5	0.006	1.9E3
toxaphene	1.3E-4[g]	0.4[f]	cotton, 45% coverage	41	0.006	6.8E3
toxaphene	1.3E-4[g]	0.4[f]	cotton, 45% coverage	32	0.006	5.3E3

[a] Linders et al. (1994) [b] Calculated by linear regression, assuming first order kinetics [c] Calculated according to the Dow method, assuming K_{oc} is 1 [d] Boehncke et al. (1990) [e] Taylor et al. (1977) [f] Environmental summary RIVM [g] Willis et al. (1983)

The agreement factors in table 4.2.1.1 show that using the same value for Q as used for volatilization from soil is not right. Based on the measured half-life values, the solubility and the vapour pressure the value for Q can be calculated for each substance on each plant species (see table 4.2.1.2).

Table 4.2.1.2 Calculated Q-values per substance and plant species, based on measured half-lives.

compound	Q-value(s)	mean Q-value
DDT	4.1	4.1
deltamethrin	396/138.6/330/216.6	270
diazinon	634	634
dieldrin	38.7	38.7
heptachlor	0.42	0.42
lindane	723/1124/1349/778	994
mevinphos	6187500/1443750/1237500/5414063	3570703
toxaphene	222/185/52/67	132

The geometric mean value for Q (based on the 8 substances in table 4.2.1.1) is 201 (26733 when P is expressed in mm Hg). When this value is used for Q following results can be calculated (see table 4.2.1.3).

Table 4.2.1.3 Chemicals, chemical properties and half-life times for volatilization from plants (measured in the field and calculated with the adapted Dow method, using Q = 26733).

chemical	P (Pa)	S (mg/l)[a]	plant species	measured t1/2 (days)[b]	calculated t1/2 (days)[c]	agreement factor
field studies:						
DDT	2E-5[g]	0.0031[f]	cotton, 45% coverage	26	0.53	49
deltamethrin	2E-6[d]	<0.002	green beans	1.75	3.45	2
deltamethrin	2E-6[d]	<0.002	kohlrabi	5	3.45	1.5
deltamethrin	2E-6[d]	<0.002	lettuce	2.1	3.45	1.6
deltamethrin	2E-6[d]	<0.002	summer wheat	3.2	3.45	1.1
diazinon	1.9E-2[a]	40	peach orchard	2.3	7.3	3.2
dieldrin	3.7E-4[e]	0.19[f]	orchard grass	9.2	1.8	5.1
heptachlor	4E-2[e]	0.056[f]	orchard grass	2.3	0.005	460
lindane	5E-3[d]	7.3	green beans	1.4	5	3.6
lindane	5E-3[d]	7.3	kohlrabi	0.9	5	5.6
lindane	5E-3[d]	7.3	lettuce	0.75	5	6.7
lindane	5E-3[d]	7.3	summer wheat	1.3	5	3.8
mevinphos	8E-2[d]	>100000	green beans	0.14	4310	30786
mevinphos	8E-2[d]	>100000	kohlrabi	0.6	4310	7183
mevinphos	8E-2[d]	>100000	lettuce	0.7	4310	6157
mevinphos	8E-2[d]	>100000	summer wheat	0.16	4310	26938
toxaphene	1.3E-4[g]	0.4[f]	cotton, 100% coverage	9.6	66	6.9
toxaphene	1.3E-4[g]	0.4[f]	cotton, 100% coverage	11.5	66	5.7
toxaphene	1.3E-4[g]	0.4[f]	cotton, 45% coverage	41	66	1.6
toxaphene	1.3E-4[g]	0.4[f]	cotton, 45% coverage	32	66	2.1

[a] Linders et al. (1994) [b] Calculated by linear regression, assuming first order kinetics [c] Calculated according to the Dow method, assuming K_{oc} is 1 [d] Boehncke et al. (1990) [e] Taylor et al. (1977) [f] Environmental summary RIVM [g] Willis et al. (1983)

Five of the 8 substances in table 4.2.1.3 have an agreement factor within a factor 7. DDT, heptachlor and especially mevinphos have much higher agreement factors.

Therefore, it is concluded that more experimental data are needed to give insight in the validity of the used Q-value and the adapted Dow method for plants.

5. CALCULATED VOLATILIZATION RATES

In table 5.1 the calculated volatilization rate from the soil surface is given for several pesticides. The pesticides are selected from Linders et al. (1994). The selection criterion was that a value without a range or a < or > sign for solubility, vapour pressure and mean K_{om} is given in the report. The expected percentages volatilized after 1 and 4 days are calculated using the Dow method. For the calculations a default value of 1 is used for c_o.

Table 5.1 Calculated volatilization rates for several pesticides (volatilization from the soil surface)

compound	solubility (mg/l)	vapour pressure (Pa)	Kom (dm3/kg)	Kv (day-1)	t 1/2 volatilization (days)	% volatilized after	
						1 day	4 days
alachlor	240	2.1E-3	117	0.0421	16	4.1	16
aldicarb	6000	1.7E-2	4.7	0.3390	2	29	74
anilazine	8	9E-6	95	0.0067	103	0.7	2.6
asulam	4000	1E-3	64	0.0022	315	0.2	0.9
atrazine	30	4E-5	70	0.0107	65	1.1	4.2
bromofenoxim	0.1	1.3E-6	565	0.0129	54	1.3	5
bromophos-ethyl	2	6.1E-3	10	171	0.004	100	100
buminaphos	170	0.1	85	3.9	0.2	98	100
bupirimate	22	6.7E-5	300	0.0057	122	0.6	2.3
carbaryl	120	6.65E-1	34	92	0.008	100	100
chlorbromuron	35	5.3E-5	440	0.0019	365	0.2	0.8
chlorfenvinphos	95	5.3E-4	539	0.0058	119	0.6	2.3
chlorothalonil	0.6	7.6E-5	5031	0.0142	49	1.4	5.5
chlorotoluron	70	1.7E-5	133	0.0010	693	0.1	0.4
chloroxuron	3.7	2.3E-7	1048	0.00003	23100	0.003	0.01
chlorpropham	89	1.3E-3	251	0.0327	21	3.2	12
clodinafop-propargyl	2.5	5.3E-6	816	0.0015	462	0.15	0.6
clofentezine	0.029	1.3E-7	139	0.0181	38	1.8	7
cyanamide	872	0.5	0.001	322481	0.2E-5	100	100
cyanazine	171	2.1E-7	55	0.00001	69300	0.001	0.004
cycloxydim	85	1E-2	61	1.08	0.6	66	99
cymoxanil	1000	8E-5	10	0.0045	154	0.45	1.8
cypermethrin (cis/trans)	0.004	2E-7	2137	0.0132	53	1.3	5.1
cyproconazole	140	3E-5	219	0.00055	1260	0.05	0.2
demeton-S-methylsulfon	3300	5E-6	0.001	0.8521	0.8	57	97
desmedipham	7	4E-7	208	0.00015	4620	0.015	0.06
desmetryn	580	1.3E-4	119	0.0011	630	0.1	0.4
dichlofluanid	2	1.3E-4	14	2.6	0.3	93	100
dichlorprop/dichlorprop-P	350	1E-3	0.001	1.61	0.4	80	100
dichlorvos	10000	1.6	87	1.03	0.7	64	99

Table 5.1 Calculated volatilization rates for several pesticides (volatilization from the soil surface) (continued)

compound	solubility (mg/l)	vapour pressure (Pa)	Kom (dm3/kg)	Kv (day-1)	t 1/2 volatilization (days)	% volatilized after 1 day	4 days
dicofol (op/pp)	1.3	2.5E-5	201	0.0538	13	5.2	19
diethatyl-ethyl	120	2.3E-3	99	0.1089	6	10	35
diethofencarb	31	2.2E-7	158	0.00003	23100	0.003	0.01
difenoconazole	3.3	1.2E-8	1840	0.000001	693000	0.0001	0.0004
difenoxuron	20	1.2E-6	343	0.0001	6930	0.01	0.04
dimethoate	2500	1.1E-3	17	0.0146	47	1.45	6
dimethomorph (E)	12	9.7E-7	252	0.0002	3465	0.02	0.08
dimethomorph (Z)	6	1E-6	252	0.0004	1733	0.04	0.16
dinoterb	0.45	1.5E-4	72	2.6	0.3	93	100
DNOC	130	8.7E-3	20.6	1.83	0.4	84	100
ethiofencarb	1900	5E-4	11	0.0135	51	1.3	5
ethofumesate	110	8.6E-5	84	0.0052	133	0.5	2.1
ethoprophos	750	4.7E-2	60	0.5874	1	44	91
etrimfos	40	8.6E-3	17	7.1	0.1	100	100
fenamiphos	400	1E-4	171	0.0008	866	0.08	0.3
fenchlorazole-ethyl	0.9	8.9E-7	215	0.0026	267	0.3	1.0
fenitrothion	30	8E-4	111	0.1351	5	13	42
fenoxaprop-ethyl	0.9	1.9E-6	15	0.0792	9	7.6	27
fenoxaprop-P-ethyl	0.7	5.3E-8	8.7	0.0049	141	0.5	1.9
fenpiclonil	2	4.2E-7	1150	0.0001	6930	0.01	0.04
fenpropathrin	0.33	7.3E-4	616	2.0	0.3	86	100
fenpropidin	350	2.1E-2	1500	0.0225	31	2.2	8.5
fenpropimorph	6.8	3E-3	2075	0.1196	6	11	38
fluroxypyr 1-methylheptyl ester	0.9	1.5E-7	9400	0.0001	6930	0.01	0.04
fluroxypyr	91	4.1E-12	35	0.000001	693000	0.0001	0.0004
flutolanil	9.6	1.8E-3	402	0.2623	3	23	65
furathiocarb	10	8.4E-5	375	0.0126	55	1.3	5
hexaconazole	18	2E-5	605	0.0010	693	0.1	0.4
hexazinone	33000	2.7E-5	16	0.00003	23100	0.003	0.01

Table 5.1 Calculated volatilization rates for several pesticides (volatilization from the soil surface) (continued)

compound	solubility (mg/l)	vapour pressure (Pa)	Kom (dm3/kg)	Kv (day-1)	t 1/2 volatilization (days)	% volatilized after 1 day	4 days
imazamethabenz-methyl (m)	1370	1.3E-3	64	0.0083	83	0.8	3.3
imazamethabenz-methyl (p)	857	1.3E-3	56	0.0152	46	1.5	5.9
imidacloprid	510	2E-7	144	0.000002	346500	0.0002	0.0008
isofenphos	23.8	5.3E-4	155	0.0808	9	7.8	28
lambda-cyhalothrin	0.005	2E-7	180000	0.0001	6930	0.01	0.04
lenacil	6	2.7E-4	20	1.27	0.5	72	99
MCPA	1500	2E-4	29	0.0026	267	0.3	1
metalaxyl	7100	2.9E-4	27	0.0009	770	0.1	0.4
metazachlor	30	4.7E-5	81	0.0109	64	1.1	4.3
methidathion	240	1.3E-4	96	0.0032	217	0.3	1.3
methiocarb	30	3.8E-5	506	0.0014	495	0.15	0.6
methomyl	58000	6.7E-3	12	0.0054	128	0.5	2.1
methylbromide	13.4	1.9E5	2.4	3.3E9	2E-10	100	100
metolachlor	530	1.7E-3	103	0.0175	40	1.7	6.8
metoxuron	678	4.3E-6	166	0.00002	34650	0.002	0.008
monolinuron	570	6E-3	193	0.0307	23	3	12
myclobutanil	142	2.1E-4	355	0.0023	301	0.2	0.9
nuarimol	26	2.7E-6	344	0.0002	3465	0.02	0.08
oxamyl	280000	3.1E-2	2	0.0311	22	3	12
parathion	24	5E-3	1746	0.0671	10	6.5	24
penconazole	77	2.1E-4	1166	0.0013	533	0.1	0.5
pencycuron	0.4	3.3E-10	1000	0.0000005	1386000	0.0001	0.0002
pendimethalin	0.3	4E-3	111	68	0.01	100	100
permethrin	0.2	4.5E-5	340	0.3722	2	31	77
phenmedipham	4.7	1.3E-9	464	0.0000003	2310000	0.00003	0.0001
pirimicarb	2700	4E-3	461	0.0018	385	0.2	0.7
pirimiphos-methyl	5	1.5E-2	202	8.4	0.08	100	100
propachlor	613	3.1E-2	40	0.7110	1	51	94
propaquizafop	2	1.3E-8	242	0.00002	34650	0.002	0.008

Table 5.1 Calculated volatilization rates for several pesticides (volatilization from the soil surface) (continued)

compound	solubility (mg/l)	vapour pressure (Pa)	Kom (dm3/kg)	Kv (day-1)	t 1/2 volatilization (days)	% volatilized after	
						1 day	4 days
propazine	8.6	3.9E-6	58	0.0044	158	0.45	1.7
propiconazole	110	1.3E-4	717	0.0009	770	0.1	0.4
propyzamide	15	1.1E-2	117	3.5	0.2	97	100
prosulfocarb	13.2	6.9E-3	996	0.2952	2	26	69
pyrazophos	4.2	1E-4	376	0.0356	19	3.5	13
pyridathioben (pyridaben)	0.012	2.5E-4	6200	1.9	0.4	85	100
pyrifenox	115	1.9E-3	263	0.0353	20	3.5	13
quizalofop-ethyl	0.3	3E-5	1069	0.0526	13	5.1	19
tebuconazole	32	9.6E-7	613	0.00003	23100	0.003	0.01
terbufos	4.5	3.5E-2	630	6.9	0.1	100	100
thiocyclam hydrogen oxalate	84000	5E-4	12	0.0003	2310	0.03	0.1
thiodicarb	35	5.7E-3	88	1.04	0.7	65	98
thiofanox	5200	2.3E-2	10	0.2488	3	22	63
triapenthenol	68	4.4E-6	86	0.0004	1733	0.04	0.2
triazophos	39	4E-4	208	0.0277	25	2.7	10
trichlorfon	154000	1E-3	11	0.0003	2310	0.03	0.1
tridemorph	10	4E-2	985	2.3	0.3	90	100
triflumizole	12900	1.4E-3	1085	0.00006	11550	0.006	0.02
trifluralin	0.05	1.5E-2	3775	45	0.02	100	100
1,3-dichloropropene	1000	3.2E3	15	119980	0.000006	100	100

6. INCORPORATION IN USES

Based on the results of this report following suggestions are given for incorporation of a volatilization model in USES.

6.1 Volatilization from soil

To estimate the volatilization from the soil surface after application of a pesticide the so-called Dow method is suggested.

6.1.1 Input data

The following input data are required to run this model:
- Vapour pressure (P) in Pa
- Solubility (S) in mg/l
- Soil adsorption coefficient (K_{om}) in dm^3/l.
- Concentration of the pesticide at the soil surface at $t = 0$ days (C_o)
- Time in days* (the period over which the volatilization has to be measured)

* It can be useful to calculate with a default value for the time period.

6.1.2 Formulas

To calculate K_v:

$$K_v = \frac{Q * P}{K_{om} * S}$$

where:
K_v = volatilization rate constant in day^{-1}
P = vapour pressure in Pa
K_{om} = soil adsorption coefficient in dm^3/kg (organic matter basis)
S = solubility in mg/l
Q = coefficient which equals $5.6 * 10^5$ (assuming 1 mm Hg = 133 Pa and $K_{om} = 1.7\ K_{oc}$)

To calculate c_x:

$$c_x = c_o * e^{-K_v * t}$$

where:
c_x = concentration at the soil surface at $t = x$ days
c_o = concentration at the soil surface at $t = 0$ days
K_v = volatilization rate constant (day^{-1})
t = time (days)

To calculate the percentage volatilized:

$$\% \ volatilized = 100 - \frac{c_x}{c_o} * 100$$

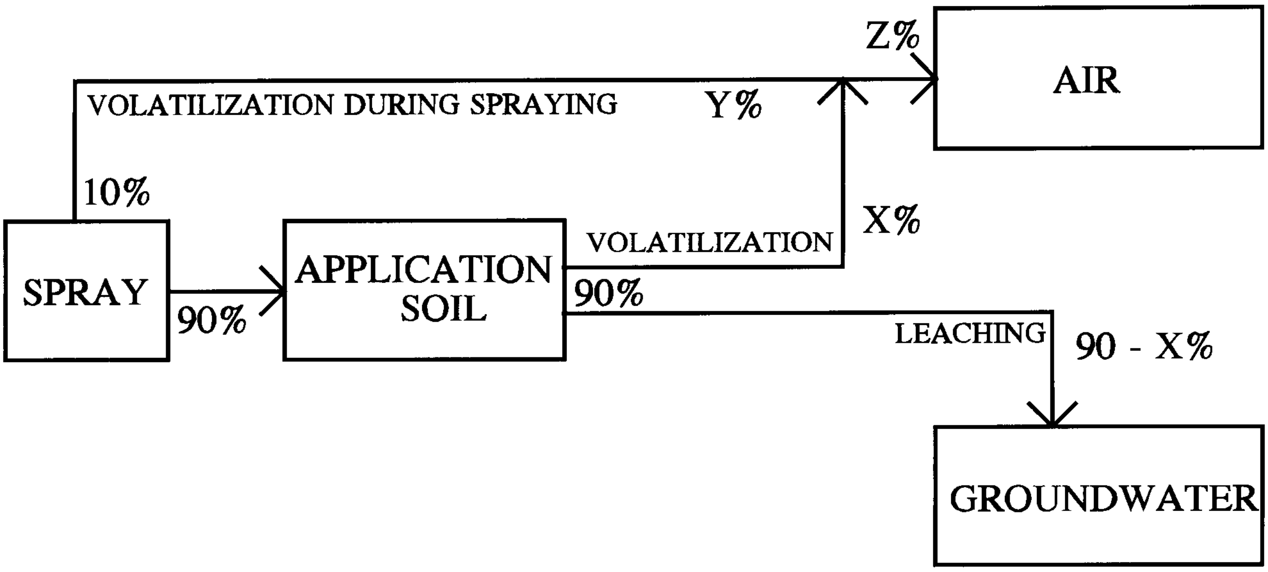
c_x = concentration at the soil surface at t = x days
c_o = concentration at the soil surface at t = 0 days

6.1.3 Output

The output file of USES should contain all input parameters and all calculated values (also intermediates like K_v and c_x. As a final result it should give the calculated percentage volatilized. This percentage should be directly connected with the time period over which it was calculated (e.g. 27% in 5 days).

The result of the calculation with this volatilization model will influence the amount of pesticide available for leaching to groundwater (see Figure 12 in USES). The concerning process is presented in figure 6.1.3.1.

Figure 6.1.3.1 Concerning routes and processes.



In USES the input into the air is calculated on long-term basis (input per year). Therefore, the percentages Y (10%) and X can be added.

The input dose for the PESTLA model (Boesten and v.d. Linden, 1991) which, among other things, predicts the extent of leaching to the groundwater, is 90 - X%. X not only depends on the volatility of the substance but also on the time the proces is running. A default value for the length of this time period is difficult to give as it depends on soil texture, water content, adsorption to soil, wind speed, temperature and so on. In literature (see Table 3.1 and 3.2) at most two measuring points are available per substance under the same conditions. As this is not enough to get a good impression of the volatilization rate curve, practical work is necessary to estimate a default value for the time the proces of volatilization from the soil surface is running.

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