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The uptake of air-borne substances in plants
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CONTENTS

SUMMARY

The Uniform System for the Evaluation of Substances (USES) contains a steady state model by which the total daily intake of humans during long-term exposure is estimated and subsequently compared to a suitable toxicity parameter. In this exposure estimation, concentrations of organic substances in water, soil and air are calculated on the basis of estimated emissions to water and air. Subsequently a daily intake for humans is calculated through exposure to organics via food, drinking water and air. An estimate for the concentration of a substance in crops following uptake from soil and air is required. The transfer of substances from air to plants has not been described so far.

In this report several models will be discussed which describe the deposition of aerosols and gases and the subsequent uptake into plants. In most models the description of deposition and uptake is combined. The models can be divided in time- dependant and time-independent models. In the former the rate of uptake can be calculated. USES, however, is only interested in the amount of substance in the plant after harvest. Therefore, it is not necessary to know the rate of uptake. Models assuming equilibrium between air and plants will suffice (time-independent models).

Two types of time-independent models will be distinguished: models for aerosols and models for gaseous substances. The model of McKone and Ryan (1989) seems to be the most appropriate one for implementation in USES with respect to aerosols. This model estimates a partition coefficient for all aerosols with a particle size below $< 5\ \mu$m. For gaseous substances the model of Riederer (1990) seems most appropriate: this model combines physico-chemical properties of the substance and the fugacity principles of Mackay and coworkers.

SAMENVATTING

Het Uniform Beoordelingssysteem Stoffen (UBS) bevat een module waarin de dagelijkse inname van de mens op de lange termijn als gevolg van blootstelling via het milieu wordt geschat en vervolgens vergeleken met een geschikt toxiciteitscriterium. Hiervoor is een steady state model ontwikkeld. In deze blootstellingsschatting worden, uitgaande van geschatte emissies van stoffen naar water en lucht, concentraties van deze stoffen berekend in bodem, water en lucht. Vervolgens wordt voor de mens een dagelijkse inname berekend via voeding, drinkwater en lucht. Voor de berekening van de inname via voeding is een schatting nodig van de concentratie van een stof in voedingsgewassen na opname vanuit de bodem en vanuit de lucht. De overdracht van stoffen vanuit de lucht naar planten was tot nu toe nog niet beschreven.

In dit rapport komen verscheidene modellen aan de orde die de depositie van aerosolen en gassen op en vervolgens de opname in planten beschrijven. In de meeste van deze modellen worden depositie en opname gecombineerd. Er zijn tijdsafhanke-lijke en tijdsonafhankelijke modellen beschreven. In het eerste type model kan de snelheid van opname in een plant bepaald worden. UBS is echter alleen geïnteres-seerd in de hoeveel-heid van een stof in de plant na de oogst. Hierdoor is de snelheid van opname niet van belang. Modellen die evenwicht veronderstellen tussen plant en lucht volstaan (tijdsonaf-hankelijke modellen).

Twee typen tijdsonafhankelijke modellen worden onderscheiden: modellen voor aerosolen en modellen voor gassen. Voor aerosolen lijkt het model van McKone en Ryan (1989) het meest geschikt voor implementatie in UBS. Dit model geeft een partitiecoëfficiënt voor alle aerosolen met een partikelgrootte van < 5 μm. Voor gassen lijkt het model van Riederer (1990) het meest voor de hand liggend. Dit model combineert de fysisch-chemische eigenschappen van de stof met de fugaciteitsprincipes van Mackay en medewer-kers.

1. INTRODUCTION

The fate of a chemical substance is governed by its equilibrium distribution
between environmental media such as soil, water, air and biota and the
concentration of the substance and its altered forms existing over time in media.
A substance may be concentrated from air by plants, then passed up the food
chain via herbivores, omnivores, and carnivores to finally man. In order to assess
the lifetime hazard of indirect exposure of man and top predators a steady state
model has been constructed, called the Uniform System for the Evaluation of
Substances (USES, 1992). In this risk assessment system emission concentrations
of organic substances in water and soil are linked to exposure concentrations for
humans and predators by applying transfer factors. Several routes of human
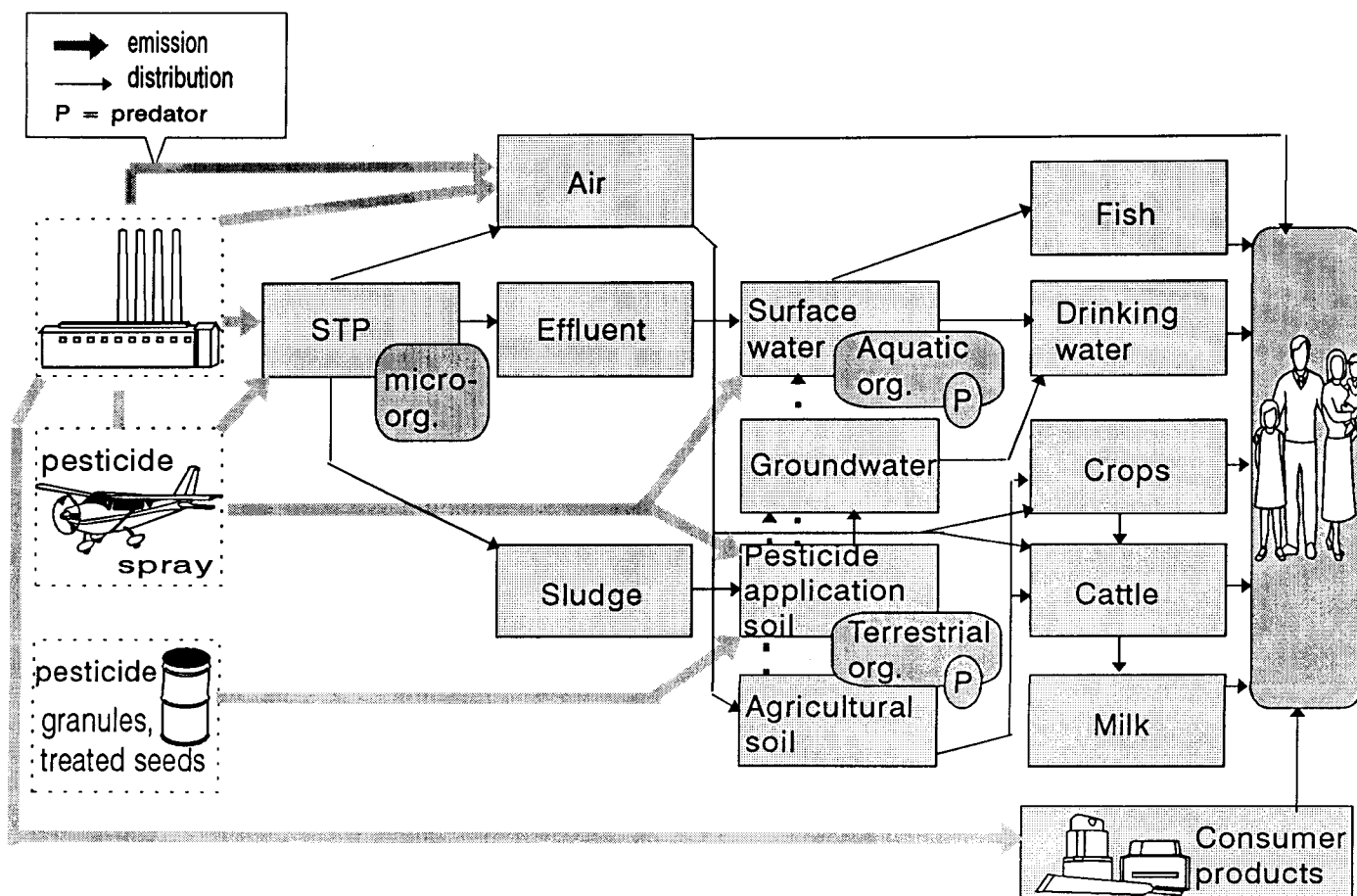exposure have been described (see fig. 1).

Fig. 1: Exposure routes in the prototype of the Uniform System for the
Evaluation of Substances

In the prototype of this model the route of the compound from the air into the plants has not been included. The contribution of aerial contamination to accumulation of compounds might be substantial. Barrows, et al.(1969), conducted greenhouse and field experiments in which corn was grown on silt loam containing added amounts of dieldrin. The plants grown in the greenhouse were protected from aerial contamination, but not in the field. Corn was harvested at maturity and dieldrin contents of the above ground parts was established. The leaves in the field-grown plants contained much higher concentration than those grown in the greenhouse. This difference was attributed to the aerial contamination of the foliage.

Nash and Beall (1970) and Beall and Nash (1971), used a special laboratory setting in which soil was contaminated with several insecticides on which soybean plants were grown. The soil in the pots were divided by a layer of paraffin. Distinction was possible between treatment of the subsurface and the lower soil layer. In this way also a distinction could be made between contamination of the above ground plant parts by vapour, if the subsurface was treated and by translocation, if only the lower soil layer was treated. They found that insecticides (even with low vapour pressure) vaporized from the soil and contaminated the leaves via vapour. Frank and Frank (1989), compared concentrations of tetrachloroethene in "uncontaminated" spruce needles and laboratory exposed needles and found that the concentration in needles are correlated to atmospheric levels. Gaggi and Bacci (1985) analysed different ages of pine needles in the boundaries of Milan for HCB, HCH and DDT derivatives and correlated the concentration in the pine needles with concentration of these chemicals in the surrounding air.

For certain compounds the accumulation from the air into the plant might be important. This route might be substantial for human exposure.

This report discusses the experimental and theoretical research on the uptake of air-borne organic compounds in plants described in literature. Further to the study the route of a substance from air to plants will be incorporated in (Jager and Visser, 1993). Therefore only those routes and studies will be described, which are useful in the USES model.

1.1 Exposure of plants to chemicals

The exposure of air-borne compounds to plants depends on (Chamberlain 1970):
- concentration in the air
- deposition
- interception by the crop
- amount of crop/m^2
- time of exposure
- removal processes

In the USES model the concentration in the air is determined by the emission from the manufacturing place and/or emmission from the STP (Sewage Treatment Plant). Therefore other emission routes will not be considered in this report.

1.1.1 Deposition
Deposition can be devided in dry and wet deposition. Deposition of gases and dry aerosols on the earth surface is called dry deposition.

Wet deposition is the total deposition of wet aerosols and the substances which are dissolved in the several forms of precipitation (rain, snow, hail) (Straalen en Verkley, 1991).

The deposition flux of dry aerosols is described as $g/m^2/s$. It is the product of deposition velocity (m/s) and immission concentration (=air concentration g/m^3). For the deposition of aerosols the physical properties of the aerosol are important.

The deposition flux of gases is principally the same ($g/m^2/s$) as described for aerosols. However, the concentration in the receptor should be taken into consideration; this should be substracted from the concentration in the air. As the deposition of gases is proportional to the dry deposition velocity (Toet en de Leeuw, 1992) the concentration of gases in the air and in the receptor can be neglected. For the deposition of gases the chemical properties of the substance are important.

Deposition rate is described as g/m^2.day and used by McKone and Ryan (1989)

Wet deposition flux ($g/m^2/s$) is the product of the rain rate (m/s), the concentration of the aerosol in rain and the scavenging ratio. The scavenging ration (SCAV-ratio) or washout ratio is the ratio between concentration in the rain water and the concentration in air. The SCAV-ratio is the partition of the substance between total rainwater (g/m^3) and total air (g/m^3).

$$SCAV\text{-}ratio = \frac{1-F_{ab}}{K_{aw}} + F_{ab}.2.10^5 \qquad \text{eq. 1}$$

F_{ab} = aerosol washout, in which Mackay (1991) estimated that every raindrop washes out 2.10^5 its volume of air.

K_{aw} = air/water partition coefficient (dimensionless), also called Henry coefficient.

The Henry coefficient can be described in two ways:

$$H = \frac{VP \times M}{S} \ [Pa.m^3/Mol] \qquad\qquad K_{aw} = \frac{VP \times M}{S \times R \times T} \qquad \text{eq. 2 and 3}$$

H   = Henry coefficient ($Pa.m^3/Mol$)
P   = saturated vapour pressure (Pa)
M   = molecular weight of a substance (kg/Mol)
S   = solubility in water (kg/m^3)
K_{aw} = air/water partition coefficient (dimensionless)
R   = gas constante = 8.3144 ($J/Mol.°K$)
T   = temperature in °K

1.1.2 Interception
After transport to the earth of the aerosols, part of the subtance will remain on the vegetation and part of it will fall on the earth. Interception is the part of the deposition which remains on the vegetation but might be washed off. After interception part of the substance will be absorbed onto the vegetation and cannot be

washed off by rain or washing. Interception and absorption (as is dry deposition) are functions of concentration, surface properties and atmospheric turbulence in the boundary layer (layer between leaf and air). After absorption by the leaf the subtance can move into the plant and might distribute over the various plant compartments water, air and lipid-phases, such as cuticula.

The relation between absorption and interception has been described by Chamberlain (1970) as follows:

$$1-p=\exp^{-\mu w}$$ <div style="text-align:right">eq. 4</div>

μ =   absorption coefficient in m^2/kg

p =   initial interception retained in the foliage described as a fraction of the total deposition

w =   vegetation density (kg/m^2)

Chamberlain (1970) sprayed radioactive aerosols of 1 μm and 30 μm diameters with water on vegetation of varying density. He found a linear relationship between interception, absorption and vegetation density if w < 0.3 kg dry weight/m^2. At these vegetation densities an absorption coefficient of circa 3 m^2/kg for these radioactive aerosols was determined. So the absorption coefficient μ was strikingly independant on the physical form of these compounds.

$$\mu = \frac{p}{w}$$ <div style="text-align:right">eq. 5</div>

μ =   absorption coefficient in m^2/kg

p =   initial interception retained in the foliage, described as a fraction of the total deposition

w =   vegetation density (kg/m^2)

At higher densities of 0.4-0.8 kg/m^2, the interception will increase and p becomes 0.7-0.95; the absorption coefficient will then be circa 1 m^2/kg.

1.1.3 Removal processes
There are at least five ways in which a compound may be lost from the aboveground parts of plants in the field.

After interception:
a)   leaching by rain (i.e. removal in solution)
b)   removal of compound in particulate form, from plant surfaces, by wind, rain or other disturbance.
After absorption:
c)   translocation to the roots
d)   volatilization
e)   dying back or weathering of leaves or their surface layers.
The removal processes will be described in chapter 5.

1.2 Modelling

Deposition and uptake of aerosol bound chemicals and gaseous substances can be calculated with time dependent and time independent models (steady state models). The former are the deposition models. The latter are steady state models, in which equilibrium between compartments is assumed.

A time independent model based on fugacity developed by Paterson and coworkers (1991) (described in chapter 4) is used mainly for gaseous substances but has also been extended for deposition of aerosols.

Time-dependent models
The air-borne compounds will reach the plant by deposition. As long as the plant can absorb the compounds the concentration in the plant will be a function of deposition, interception, kg biomass/m^2 and removal rate. The models of Chamberlain (1970) and McKone and Ryan (1989) and McKone and Daniels (1991) are based on this and will be described in Chapter 2. Most of these models are applied for aerosols. The model of McKone and Daniels (1991) was extended to gaseous substances, but then they assumed equilibrium between plant and air, as described below.

Time independent models
In these models the plant is assumed not to be a sink, but that equilibrium has been established between plant and air. For aerosols the concentration in the plant depends on the size of the aerosol (chapter 2). For gases the concentration in the plant depends on the partition coefficients of the compound and the properties of the leaf (chapter 3).

Fugacity model
The theoretical basis of this model is the fugacity concept developed for large scale modelling by Mackay/Paterson and coworkers (1979, 1981, 1982). This steady state model was applied for the air/leaf partition by Riederer (1990). Paterson et al. (1991) extended the model, so that it also can be used for deposition of gaseous substances and aerosols. Deinum (1992) combined the deposition model of Baldocci (1988) with the air/leaf partion fugacity-model of Riederer (1990). These models will be described in Chapter 4.

2 UPTAKE OF AEROSOLS INTO PLANTS

The amount of deposition of gaseous substances and aerosols will be determined by the USES model. In this report, deposition is only discussed if it is related to absorption or uptake into plants. Two main studies have been found relating deposition and absorption to plants: Chamberlain (1970) and McKone and Ryan (1989).

2.1 Chamberlain (1970)

Chamberlain (1970) experimentally determined the efficiency of vegetation as a filter for nuclides deposited on the earth's surface after application. With 3 different experiments he described the interception and absorption of the nuclides in grassland. The relation between interception, vegetation density and absorption has already been described in the introduction.
Thereafter the rate loss of activity by weathering from foliage was determined. With these measurements, he developed a model in which he assumed a constant rate of fallout onto the forage crop, which is in a state of linear growth rate.

$$A = \int_0^T a\mu f t \exp^{[-\lambda(T_0 - t)]} dt \qquad \text{eq. 6}$$

$$A = \frac{a\mu f T_0}{\lambda_b}[1 - \frac{1 - \exp^{(-\lambda_b \cdot T_0)}}{\lambda_b T_0}] \qquad \text{eq. 7}$$

$$A = a\mu f(\frac{T_0}{\lambda_b} - \frac{1}{\lambda_b^2} + \frac{\exp^{-\lambda_b T_0}}{\lambda_b^2}) \qquad \text{eq. 8}$$

A	=	radio activity in the crop (μCi/m^2/day)
a	=	radio activity deposited per unit area of ground per day (μCi/m^2/day)
f	=	daily increment in yield of vegetation (kg/m^2/day)
T_0	=	period of growth between successive days (kg/m^2)
fT_0	=	yield at harvest (kg/m^2)
μ	=	absorption coefficient of fallout in vegetation (kg/m^2) (see for relation with interception: introduction)
λ_b	=	field loss coefficient (days^{-1})

In his study values of 0.054 and 0.037 have been taken for λ_b. For μ 3 m^2/kg has been taken.

The yield at harvest is considered not to be larger than 0.3 kg dry weight/m², With this yield a linear relation between interception and absorption is established.
The method described above can be used with experimental data. The method described below is a more theoretical model.

2.2 McKone and Ryan (1989)

McKone and Ryan (1989) have described a model to convert environmental concentration to human exposure for the air/plant/food and soil/plant/food ingestion. They describe four ingestion routes: 1) fruits and vegetables, 2) grains, 3) meat and 4) dairy products. They calculate the transfer of atmospheric particles from atmosphere to vegetation. Thereafter they take the balance between material that deposits on the exposed and edible portion of the crops and is removed by weathering and senescence.

The steady state concentration in vegetation is approximated based on a mass-balance:

$$C_{vp} = \frac{V_{dp} \times C_{pf}}{M_f \times R_v} \qquad \text{eq. 9}$$

V_{dp} = the total deposition velocity (dry and wet) of atmospheric particles on food crops (m/day), which is the ratio of deposition rate on vegetation in mg/m². day to the air concentration in mg/m³

C_{pf} = the concentration in air, particle fraction (mg/m³)

C_{vp} = the concentration in fresh vegetation (mg/kg **fresh** weight)

M_f = the annual average inventory of food crops per unit area (kg fresh weight/m²), ranging from 1.0 up to 9.0 kg/m² (median, 3.0, log-uniform distribution)

R_v = the removal rate constant of chemicals from vegetation surfaces, ranging from 0.1 to 0.01 (day⁻¹) (median 0.03, log-uniform distribution).

In view of the high variety of the deposition velocities of aerosols McKone and Ryan (1989) use the deposition velocities of the particles less < 5 μm, which are estimated to be 2.6-860 m/day. In their simulation they use a log-normal distribution with a geometric mean of 300 m/day and a geometric standard deviation of 3.0 for particles < 5 μm.

McKone and Ryan (1989) calculate the fraction of deposited dry particles intercepted by vegetation (V_g) as follows:

$$V_g = V_t \, [1\text{-exp}^{(-\alpha Mv)}] \qquad \text{eq. 10}$$

where V_t is the total dry deposition velocity (m/s) and α is the foliar interception constant, estimated to be 2.8 (m²/kg dry weight) and M_v the dry mass inventory of vegetation per unit area, estimated to be 0.6 (kg dry weight/m²/year).

McKone and Ryan (1989) show that in general the dry deposition velocity exceeds by far the wet deposition velocity. They estimate the following relation:

$$V_{dp} = 0.8 \cdot V_g(dry) + V(wet). \qquad \text{eq. 11}$$

V_{dp}	=	Total deposition velocity (wet and dry) m/day.
$V_g(dry)$	=	Total dry deposition velocity onto vegetation (m/day)
$V(wet)$	=	$b \cdot R \cdot W_p$ (b is the fraction of material retained on vegetation from wet deposition, estimated to be 0.1-0.3; R is the annual average rainfall rate (m/day) estimated to be 1 m/year; W_p is the volumetric washout ratio estimated to be 2×10^5).

McKone and Ryan (1989) selected a dry deposition velocity of 500 m/day (V_{dp}) for particles < 5 μm, a removal rate of 0.039 and an annual inventory of 3.9 (kg fresh weight/m²/year). If these values are filled in, in the formula at page 7 (eq. 9), a partition coefficient ($K_{l/p}$) between leaf and particles of 3287 can be estimated.

This model is a one compartment model, which means that the compartment (the vegetation) will be filled up until the amount received will be the same as the amount removed.
The deposition velocity will be calculated with USES. As fixed values can be used for M_f and R_v, the concentration in the crop can be calculated.

Example:
The crop receives 80 mg/kg crop. Taking a removal rate of 0.03; than a steady state will be reached after the crop has received 80/0.03 is 2666 mg/kg crop.

2.3 Comparison between these two models

These two models have the same basic assumptions, deposition velocities and absorption determine the concentration in the plants, which has to be corrected for the yield and removal processes of the compounds. Chamberlain (1970) assumes a maximum yield of 0.3 kg dry weight/m² at harvest, while McKone and Ryan (1989) estimate yields (circa 0.1-0.9 kg dry weight/m²) on an annual base. McKone and Ryan (1989) assume an absorption rate of 3 m²/kg as did Chamberlain (1970). The removal rate constants used are comparable. In Chamberlain's study 0.054 and 0.037 days are used and 0.01 to 0.1 in the study of McKone and Ryan (1989).
So the results of both models should be comparable too.

3 UPTAKE OF GASEOUS SUSTANCES INTO PLANTS

3.1 Deposition of gaseous substances

According Thompson (1983) the rate of uptake of vapour is often expressed by the product of deposition velocity and immission concentration. He determined the uptake of sprayed pesticides in vegetation circa 100 m from the sprayed area. The uptake depends on atmospheric diffusion, which controls vapour concentration at the site of uptake, and absorption, which is a function of concentration, surface properties and atmospheric turbulance above the surface (resistance of the boundary layer). The problem was simplified by Thompson (1983) by considering only mechanisms which lead to the maximum uptake. He calculated the maximal vapour flux considering the cuticle as a perfect sink. In his case the maximal deposition velocity will then be 0.005 cm/s for a vapour with a molecular weight of 300. In the article of McKone and Daniels (1991) a summary is given of deposition velocities of gaseous substances of 0.002 cm/s - 26 cm/s.

The total amount in the crop depends on the time which is necessary for reaching equilibrium between air and leaf. In Reischl et al., (1989) equilibrium was established circa 5 days for dichlorobiphenyl and heptachlorobiphenyl in *Picea* leaves. In Bacci et al., (1990) the uptake of gaseous substances seemed to continue for a longer period circa 8 to 16 days (200 to 400 h) in *Azalea* leaves.

Example with the calculations of Thompson:
air conc. is 1 mol/m^3
concentration in vegetation is 1 (mol/m^3) x 5x10^{-3} (m/s) = 0.005 mol/m^2/s
Assuming equilibrium after circa 10 days (Reischl et al.,1989), the total amount will be:
0.005 x 864000 sec = 4320 mol/m^2.

3.2 Partitioning of gaseous substances between leaf and air

The leaf is not a perfect sink. After some time an equilibrium might be established between leaf and surrounding air.

The concentration in the leaf can then be expressed with an air/leaf partition coefficient. In different studies the concentration in the air and concentration in the leaf has been related to the physical chemical properties of the substance.

Travis and Hattemer (1988) proposed the relation between the bioconcentration factor (BCF) of the leaf and the log K_{ow} and Henry coefficients of the substance. Paterson et al. (1990) derived the following relation between BCF values and the Henry coefficient (Pa.m^3/Mol) for PCB's, α-HCH, gamma-HCH, p,p'DDE (high and low charge) and p,p'DDT) (based on the work of (Bacci en coworkers (1987)).

$$\log BCF = 1.25 \log H + 4.06 \qquad \text{eq. 12}$$

Bacci et al. (1990) determined the uptake and release kinetics for 5 compounds (trifluralin, HCB, mirex, thionazin, and sulfotep). They derived bioconcentration factors from these data. They found the following relation with the physico-chemical

properties of the substances, including the BCF values derived by Bacci et al. (1987).

$$\log (BCF_m H) = -0.92 + 1.14 \log K_{ow} \quad r=0.96 \qquad \text{eq. 13}$$

BCF_m is based on a mass/mass ratio (ng/g dw leaf/ng/g air)

The log K_{ow} values of these compounds varied from 1.2 for thionazin to 6.9 for mirex. The Henry coefficient in Pa m³/mol varied from 0.087 for thionazin to 839 for mirex.

Considering that both K_{aw} and K_{ow} are volume/volume partition coefficients and the BCF in the next chapters is also expressed in these units, these BCFs'should also be expressed as a dimensionless volume/volume partition partition coefficient. Bacci et al. (1990) consider the water content of the leaves as 70% of the wet weight, the leaf density at 890 g/l and the air density as 1.19 g/L. The BCF on a volume base can be calculated from the equation above:

$$(890 \times 0.3/1.19)BCF_m = 224.37 BCF_m = BCF \quad \text{(on a volume base) and}$$
$$H/RT = K_{aw}$$

The above described relation then becomes:

$$\log (BCF.K_{aw}) = 1.14 \log K_{ow} - 1.95$$
$$\log BCF = - \log K_{aw} + 1.14 \log K_{ow} - 1.95 \qquad \text{eq. 14}$$

Reischl et al. (1989) determined BCFs', for 9 substances, among which three chlorobenzenes, HCH and DDT, and 5 chlorobiphenyls. The best fits were obtained using either vapour-pressure or log K_{ow} and Henry coefficient.

$$\log BCF_m = -0.2946 \log P_s + 3.3917, \text{ or} \qquad \text{eq. 15}$$

$$\log BCF_m = -0.4244 \log H + 0.4254 \log K_{ow} + 2.2951 \qquad \text{eq. 16}$$

BCF_m is based on mass/mass ratio (ng/g dw leaf/ng/g air)
P_s = solid substance vapour pressure (Pa)
H = Henry coefficient (Pa.m³/Mol)

The above described regression lines have been fit for a limited number of data. These data could possibly be combined and an overall regression line with the Henry coefficient and the log K_{ow} be established.

The concentration of gaseous substances in plants can also be calculated with the fugacity model described in chapter 4.

3.3 Uptake of gaseous substances via the stomata

For gaseous substances it is also possible to move into the plant via the stomata. Little is known about uptake of organic substances via the stomata. So far there is not even conclusive evidence for stomatal uptake of organic compounds (Bukovac,

1976). If stomatal uptake is taken into consideration (Thompson, 1983, Deinum 1992) it is assumed that compounds are transported through the stomata by molecular diffusion ($g/m^2/s$) in the gas phase similarly as water vapour, but whith the influence of the molecular mass on the diffusion coefficient (m^2/s) taken into account.

$$g = g_W (\frac{M_W}{M_m})^{0.5}$$

<div align="right">eq. 17</div>

g   = the deposition velocity of the compound (m/s)
g_W = the deposition velocity of water (m/s)
M_W = Molar mass of water (g/mol)
M_M = Molar mass of the compound (g/mol)

The stomatal resistance, which is of the order of 20 - 10^3 s/m depending on the type of vegetation (stomata fully open), does not vary very much between compounds if their molecular masses are between 50 and 500.
Deinum (1992) includes in his model the stomatal pathway for three substances: HCB, 2,4-D and phenol. For 2,4-D the uptake of compounds in the leaf is much faster with open than with closed stomata in his model. For HCB and phenol there was not much difference. The velocity of uptake depends on the cuticular and stomatal resistance of the substance. If the resistances of these two are similar, open or closed stomata will not make a lot of difference. If the stomatal resistance is much lower than the cuticular resistance, the maximal uptake of the substance into the leaf will be reached much faster. However, in the end the concentration in the leaf will be the same. The velocity of uptake with open stomata might be overestimated in the model of Deinum (1992), because stomata are seldom fully open in the whole plant and the mesophyll resistance was stated to be zero. However, this resistance is probably not negligible (Deinum, 1992).
Thompson (1983) also calculated stomatal uptake of vapours of sprayed pesticides. He assumes a typical bulk stomatal resistance for water vapour transfer from a dense canopy with open stomata around 40 s/m. (This is 2.5-25 times less than assumed by Deinum, 1992). For a vapour of 300 g/mol he finds a deposition velocity of 3 x 10^3 m/s. For cuticular uptake he finds for the same substance 5 x 10^3 m/s and shows that the uptake via cuticula is substantially more rapid than through the stomatal pathway. This difference increases to almost 8 times, when the vegetation density is low.
Stomata are usually only open during the day, which make this pathway even less important.
In conclusion the stomatal pathway for organic substances might only fasten the uptake of gaseous substances, but does not influence the equilibrium between leaf and air.

4 FUGACITY-MODEL FOR UPTAKE OF COMPOUNDS INTO PLANTS

4.1 Gaseous substances

In this chapter the fugacity-model will be described. With this model total concentrations of gaseous substances in plants can be calculated and also the partitioning of the substance in the different leaf compartments: air, water and octanol-phases. The model described here, was first described by Riederer (1990) and was used by Paterson et al. (1991), Trapp et al. (1990) and Deinum (1992). In the fugacity models it is assumed that equilibrium has been reached between plants and air and between the different plant compartments. It is also assumed that the partitioning of the compound among these compartments can be described with partition coefficients.

The model has 3 outputs
1) prediction of equilibrium concentration in different leaf tissues of compounds occurring in the environment
2) estimates of air-to-vegetation bioconcentration equilibria
3) identification of the compartments of preferential accumulation within leaves

4.1.1 Leaf parameters
Fugacity is expressed in Pa and the amount of substance in a compartment is expressed in mol/m^3. Therefore it is also necessary to express the amount of plant or a leaf on a volume base. Riederer (1990) used the following leaf volumes:
The model leaf has a projected surface area of 50 cm^2 and a thickness of 0.3 mm. So the leaf volume is 1.5×10^{-6} m^3 based on *Brassica oleracea*. This model was also used by Deinum (1992). An overall fresh weight density of 715 kg/m^3 and a dry weight content of 70 kg/m^3 was estimated.
Bacci et al. (1990) used 890 kg/m^3 and a dry weight content of 30% for azalea leaves.
In the model of Paterson (1991) the foliage is considered to consist 20 leaves with each individual leaf having a total area and thickness of 25 cm^2 and 0.5 mm, respectively. This results in a total leaf volume of approximately 25 cm^3, and a density of 820 kg/m^3.

The relative volumes of the leaf compartments differ depending on the plant used. Riederer (1990) used the following relative leaf volumes for *Brassica oleracea*: air: 0.3, water: 0.645, polar constituents 0.047, cuticula: 0.007, and the the amount of glycerol lipids: 0.001. In Trapp et al. (1990) the relative water volume of the leaf used was 0.875 for barley (*Hordeum vulgare*). Paterson et al. (1991) used the following volume fractions: air: 0.18, water: 0.8, non-polar organic matter: 0.02. In the fugacity-based model the following partition coefficients are used.

4.1.2 Partitioning
Partitioning between air and water can be described with the dimensionless Henry coefficient (K_{aw}). The cuticle/air partition coefficient can be estimated by the cuticle/water partition coefficient divided by the air/water partition coefficient:

K_{cw}/K_{aw}. Kerler and Schonherr (1988) determined the uptake from substances by the cuticula experimentally by solving the substance in water first, after which the cuticula was exposed to the solved substance. Sablic et al. (1990) determined for partitioning between water and cuticle a formula slightly deviating from the partitioning between water and octanol:

Log K_{cw} = 0.970logK_{ow} + 0.057

Using this equation the difference in partitioning of the compound between cuticle/water or octanol/water is not big (K_{cw} is almost equal to K_{ow}). For average K_{ow} values between -1 and 5 the K_{cw} is almost the same as the K_{ow}. For the glycerol lipids in the leaves the partitioning is directly related to the octanol phase by Riederer (1990) followed by Deinum (1992), which means that $K_{gl/w}$ = K_{ow} . If this is also done for the cuticle, the relative volumes of cuticle and glycerol lipids can be added.

4.1.3 Fugacity-based model
The theoretical base of this model is the fugacity concept developed for large scale modelling by Mackay and co-worker (1979, 1985). The concept is based on the fact that at equilibrium equal fugacities are established in all compartments of a system regardless of the nature or the physical state of a compartment. The advantage of the fugacity based model is that if a concentration in one compartment is known, the concentration in other compartments can be calculated.

It has been shown that at low concentrations fugacity is linearly related to concentration by:

$C_i = Z_i f$

C_i representing the concentration in mol/m^3 (the absolute amount of a compound in a compartment). And f (in Pa) is the overall fugacity, which is the driving force behind the partitioning of the compounds into the compartments. The proportionality factor Z is called the fugacity capacity for a compartment (mol/m^3.Pa). Z determines the relative amounts of a substance in a compartment and can be compared with a partition coefficient (the latter, however, has no units, while Z has). Z is a volume based property depending on temperature, pressure, the nature of the substance and most importantly, on the properties of the medium.

The values of Z for the compartments included in the atmosphere/foliage model can be estimated from the aqueous solubilities, saturation vapour pressures and octanol/water partition coefficients (Mackay and Paterson, 1982).

$Z_a = 1/RT$

$Z_w = C_{ws}/P_s = 1/H$

$Z_{c+gl} = Z_w \cdot K_{ow}$

R = 8.314 Pa.m³/Mol.K,

T = absolute temperature K,

C_{ws} = mol/m³,

P_s = Pa

Z = mol.m³/Pa

H = Pa.m³/Mol

The subscripts denote the atmospheric and intercellular gas phase (a), the aqueous (w), the cuticula (c) and the glycerol lipids (gl) compartments, respectively. The polar constituents are ignored above, since they only form a small fraction of the leaf and are not important for lipophilic compounds.

The overall fugacity capacity (Z) for the whole leaf (Z_L) is the sum of the compartmental fugacity capacities (Z_i) weighted by the volume fractions of the compartments (v_i) according to

$Z_L = \Sigma v_i Z_i$

When the overall fugacity of a system in equilibrium is known, the concentrations in the different compartments or in the whole leaf can be estimated as follows.

$Z_L = v_a/H + v_w/H + v_{c+g} \cdot K_{ow}/H =$

$Z_L = 0.18 \cdot Z_a + 0.8 \cdot Z_w + 0.02 \cdot Z_{c+g}$ (Paterson et al., 1991)   eq. 18

H = Pa.m³/Mol

Z = Mol.m³/Pa

Z_L = relative amount of substance in the leaf (mol.m³/Pa)

In the above equation the Henry coefficient is used, below the dimensionless air/water partition coefficient, which is a more realistic description of the atmosphere surrounding the vegetation (Deinum 1992):

$K_{l/a} = v_a + v_w/K_{aw} + v_{c+g} \cdot K_{ow}/K_{aw}$ (Riederer, 1990)   eq. 19

$v_{a,w,c,gl}$ = the relative air, water, cuticula and glycerol lipid volumes in the leaf.

$K_{l/a}$ = representing the leaf/air partition coefficient.

The amount of material M_i (mol) in each compartment i is $f(V_iC_i)$ with V_i (m³) expressing the absolute volume of a compartments.

$$f = \frac{M_L}{\Sigma(Z_i \times V_i)} =$$

$$M_L = f\Sigma(Z_iV_i)$$

4.1.4 Examples

The air concentration is known. HCB is used as an example for calculating the leaf/air partition coefficient. The concentration in air is 1 mol/m^3.
Properties of HCB are: $\log K_{aw} = -2.54$ ($H = 7.1$) and $K_{ow} = 5.47$ (from Riederer, 1990).

The fugacity can be calculated from reported air concentrations as $f = C_i/Z_i$ (Paterson et al., 1991). The concentrations of gaseous substances in air C_i (mol/m^3) will only depend on the gas constant and temperature (in °K).

$$Z_{air} = 1/RT = 1/2436 \ (mol/m^3.Pa)$$

$$f = 1 \ (mol/m^3) \ / \ (1/2436) \ (mol/m^3.Pa) \ = 2436 \ (Pa)$$

Example following Paterson et al. (1991) using

$$Z_L = 0.18(=v_a)/RT + 0.8(=v_w)/H + 0.02(=v_{c+g})K_{ow}/H$$

$$\begin{aligned} Z_L &= 0.18/2436 + 0.8/7.1 + 0.02 \times 2.95.10^5/7.1 \\ &= 7.4 \times 10^{-5} + 0.11 + 831 \\ &= 831 \end{aligned}$$

$M_L = f\Sigma(Z_LV_L)$
M_L = the total amount available in the leaf, 1.5×10^{-6} = volume of a leaf

$$M_L = 2436(831 \times 1.5 \times 10^{-6}) = 3.07 \ mol/leaf$$

If the relative volumes of Riederer (1990) are taken then the amount in the leaf will be:

$$\begin{aligned} K_{l/a} &= 0.3 + 0.645/(2.88.10^{-3}) + 0.008 \times 2.95.10^5/(2.88.10^{-3}) \\ &= 8.2.10^5 \end{aligned}$$

$M_L = f\Sigma(Z_LV_L)$
M_L = the total amount available in the leaf, 1.5×10^{-6} = volume of a leaf

$$M_L = 2436(8.2.10^5 \times 1.5 \times 10^{-6}) = 2996.3 \ mol/leaf$$

In the above two examples it is shown that the air and water fraction in the leaf hardly influence leaf/air partition coefficient. $K_{l/a}$ is mainly determined by the cuticle and glycerol lipid phases. The differences between Paterson et al. (1991) and Riederer (1990) is caused by the use of the Henry coefficient and the K_{aw}, respectively.

An estimation of total amounts of substance in the leaf according to Thompson (1983) is highly depending on duration of the establishing of the equilibrium.

- Concentration in air is 1 mol/m^3, maximum vapour flux into cuticle is 0.005 m/s
- In chapter 2 the concentration in the vegetation would be 0.005 mol/m^2/s
- According to McKone and Ryan (1990) a m^2 crop is circa 3 kg fresh weight.
- According to Riederer (1990) m^3 contains 715 kg crop.

3 kg = 3/715 = 0.0042 m^3

0.005 mol/m^2/s = 0.005/0042 m^3/s

The amount in 1 m^3 foliage will be 1.19 mol/s

in 1.5x10^{-6} m^3 = 0.005/0.0042 x 1.5x10^{-6} = 1.79x10^{-6} mol/leaf/s

(It should be noted that deposition velocity of Thompson was calculated for a substance with a mol weight of 300.)

From this result it seems that equilibrium has been established between 0 and 2 hour comparing this result with the fugacity based model of Paterson (1991) and 8 days using the result of Riederer (1990).

4.2 Model of McKone and Daniels (1991)

McKone and Daniels (1991) extended the formula described in chapter 2 for aerosols also for gaseous substances. The formula in chapter 2 (eq. 9) can also be described as a partition coefficient and is given again for convenient reasons:

$$\frac{C_{vp}}{C_{pf}} = \frac{V_{dp}}{M_f \times R_v} \qquad \text{eq. 9}$$

V_{dp} = the deposition factor of atmospheric particles on food crops (m/day), which is the ratio of deposition rate on vegetation in mg/m^2. day to the air concentration in mg/m^3

C_{pf} = the concentration in air, particle fraction (mg/m3)

C_{vp} = the concentration in fresh vegetation (mg/kg **fresh** weight)

M_f = the annual average inventory of food crops per unit area (kg **fresh** weight/m^2), ranging from 1.0 up to 9.0 kg/m^2 (median, 3.0, log-uniform distribution)

R_v = the removal rate constant of chemicals from vegetation surfaces, ranging from 0.1 to 0.01/day (median 0.03, log-uniform distribution).

For gaseous substances the same formula can be used, except for the removal rate constant (R_v). This factor for gaseous substances is more difficult to estimate, because gaseous substances are not only removed by senescence and weathering but also by evaporation. McKone and Daniels (1991) suggest equilibrium between vegetation and surrounding air for gaseous substances and so they include the following partitioning between leaf and air:

$$\frac{C_{vg}}{C_a} = \frac{RT}{H} \times (0.9 + 0.1 K_{ow}) \times 10^{-3}$$

eq. 20

C_{vg} = concentration in vegetables and grains (mg/kg)
C_a = concentration in air
RT/H = $1/K_{aw}$
0.9 = water fraction of the plant
0.1 = lipid-phase fraction.
$10^{-3} m^3/L$ adjust kg vegetation in m^3 vegetation, estimating 1000 kg in 1 m^3.

(This formula is principally the same as used by Riederer (1990).
It is assumed that the gas components of the air and plant tissues have the same contaminant fugacity. Fugacity is estimated by assuming that plant tissues contain 90% water and 10% organic material. Also the following relationships are included:
1) the ratio of the concentration of a substance in the water component of vegetation $C_{w/vg}$, to the concentration of the substance in the gas component air C_a, is equal to RT/H.
2) the concentration of the compound in the organic component of vegetation $C_{o/vg}$, is equal to the product of $C_{w/vg}$ and K_{ow}.
3 the total concentration of the compound in the vegetation is equal to the sum of 0.9 x $C_{w/vg}$ and 0.1 x $C_{o/vg}$.

The formula for gaseous substances now becomes:

$$\frac{C_{vg}}{C_a} = \frac{RT}{H} \times (0.9 + 0.1 K_{ow}) \times 10^{-3} = \frac{V_{da}}{M_f \times R_v}$$

eq. 21

and the removal rate constant for gaseous substance is calculated as:

$$R_v = \frac{V_{da}}{M_f} \times \frac{H}{RT} \times \frac{10^3}{(0.9 + 0.1 K_{ow})}$$

eq. 22

This R_v can be incorporated in the formula described for aerosols and in this way the concentration of gaseous substances in plants can be described in a comparable way as for aerosols.

4.3 Model of Deinum (1992)

Deinum (1992) combined the fugacity model of Riederer (1990) with the deposition model of Baldocci (1988). This deposition model of Baldocci (1988) was used to determine SO2 deposition on a deciduous forest. He preferred to use this model, because it contains a more realistic approach of the atmosphere surrounding the vegetation, compared to the deposition model of Paterson (1991). These deposition models of Baldocci (1988) and of Paterson (1991) will not be discussed further, because we will use the USES deposition model.
He expressed movements of compounds from the air to the boundary layer of the leaf with this Baldocci (1988) model. The diffusion from the boundary layer into the

leaf and within the leaf was described in terms of resistances. The latter are related with physico-chemical properties of the compounds in the same way as Riederer (1990) did. Deinum (1992) included the possibility of the phloem transport of substance in his model, which will be described in chapter 4. The model was run with 3 substances: 2,4-D, phenol and HCB.

The uptake of the three test compounds was first computer simulated by placing the leaf inside a box in an air flow with a velocity of 0.05 m/s. The concentration in air of the compound was kept constant at 1 mol/m³, and it was assumed that the initial concentration in the leaf is zero. First the resistance of the boundary layer was calculated as well as the stomatal resistance. Both were derived from the resistance of water and converted to other compounds taking their molecular weight into account.

With these simulations a time dependant uptake can be determined untill a maximal concentration in the leaf is established. The maximum concentration for HCB was 2.1 mol/m³, for phenol and 2,4-D these values were 0.0043, and 0.012 mol/m³, respectively.

This maximum concentration can also be determined by the leaf/air partition coefficient. This model shows that some substances will reach their maximum concentration soon, while for other substances it may take weeks. This depends on the stomatal and cuticle resistance for the substance, but also on the translocatable part of the substance (the latter will be described in chapter 5).

It can be seen that the value for HCB is much lower than found in the previous examples, even though the same fugacity model is used. It is unclear if this difference is caused by the use of the deposition model of Deinum.

4.4 Case study

In the study of Trapp et al. 1991 barley (*Hordeum vulgare*) was exposed in soil to different pesticides (DDT, dieldrin, PCB, HCB, atrazine, trichlorobenzene and tetrachlorobenzene). The uptake of in soil-corporated compounds in plants was determined. The uptake via air was determined by measuring the uptake in barley plant which were grown in the same room but in uncontaminated soil. These compounds could only reach the plants by volatilizating from the contaminated soil. The uptake of the compound in the untreated plants were compared with the total uptake in the treated plants and in this way an estimation can be made which percentage was taken up via the air. With the fugacity model this route was calculated and compared to the concentration measured in the plants. For dieldrin, tri- and tetrachlorobenzene the measured values were circa twice as high as the calculated values. A portion of the compound might also transfer from the air into the uncontaminated soil and then into the roots. This route was not taken into account in the model. Thus the experimental determination of gas-phase uptake might led to an overestimation. For DDT, HCB and PCB the measured values were only slightly higher than the calculated ones. According to the authors the route: treated soil - air - untreated soil - roots and transport to the upper plant parts might be a cause for the differences found between the measured and the calculated values for dieldrin and the chlorobenzenes.

5 REMOVAL PROCESSES

After absorption of the compound into the plant, there are several dissipation routes. Dissipation of the compound either by degradation or translocation will lower the concentration in the leaf and the air-leaf equilibrium takes more time being established, because the whole plant has to be saturated first.

Translocation of the compound also means that plant parts (i.e. roots) might be exposed to the compound. The transport of pesticides from leaf to the roots has been studied extensively, but also from root to the leaf via the xylem transport.
For transport only the water soluble part is important. Soluble substances can be transported both via the phloem as via the xylem. The transpiration stream (xyleem) is going 50 to 100 times faster than the phloeem transport. Soluble compounds will therefore accumulate in the aboveground plant parts.
According to Bromilow (1990) less then 1% of the best transported pesticides will reach the roots and remain there. This probably applies to other organic compounds as well. For the human exposure uptake of compounds via the roots and/or tubers will not be important.

6 DISCUSSION

Several models describing deposition and uptake of aerosols and gaseous substances into plants have been described in this report. In most models described here deposition and uptake are combined. Aerosols and gases reach the earth by deposition. The deposition rates of both can be calculated from deposition velocities multiplied by the immission concentration. According to Toet and de Leeuw (1992) the deposition of gases is mainly dependant on the deposition velocity of the gases. At high deposition velocities the dry deposition exceeds the wet deposition (Toet en de Leeuw, 1992). For substances with H > 100, the deposition flux is proportional with the dry depostion velocity (Toet en de Leeuw, 1992).
In USES the deposition part has already been described and for implementation in the USES model the deposition part of these models can be left out.

The models described in this report can be divided in time dependant and time independant models. In the former the rate of uptake can be calculated (Chamberlain, 1970, Deinum, 1992). In the USES model, however, we are interested in the amount of substance in the plant after harvest. Therefore it is not necessary to know the rate of uptake and models assuming equilibrium between air and plants will suffice (time independant models). In this report two type of time-independant models can be distinguished, models developed for aerosols and models developed for gaseous substances.

Aerosols
The leaf/aerosol partition of McKone and Ryan (1989) is calculated by the deposition rate, divided by the annual inventory of the crop and the removal rate constant. They estimated fixed values for several parameters in their aerosol model. They have selected deposition rates of circa 500 m/day (for aerosols < 5 μm), removal rates of 0.039 and a mean average annual inventory of 3.9 kg fresh weight/m^2. The leaf/aerosol partition coefficient can then be calculated as 3287. This partition coefficient is independant on the physical-chemical properties of the substance. Toet and de Leeuw (1992) concluded also that the deposition of aerosols is independant of substance characteristics.
Depending on the deposition rates calculated by USES and the estimated annual inventory for the different types of crop, a partition coefficient can be calculated.

Gaseous substances
For gaseous substances equilibrium will be reached after a certain period of time. Bacci et al. (1990) and Reischl et al. (1989) experimentally determined uptake and dissipation rates. From these experiments they determined BCF factors and showed that K_{ow} and K_{aw} are the main properties for estimating BCFs'. These partition coefficients and uptake and release kinetics were also used in the fugacity-based model for leaf/air partition by Riederer (1990) and Paterson et al. (1991). Riederer (1990) used different volume fractions in the leaf for air, water and the lipid-phase than Paterson et al. (1991). The main difference between these two, is the use of K_{aw} (dimensionless, including the R, the gas constant and °K, the absolute temperature) and the Henry coefficient (Pa.m^3/Mol, excluding R and °K). As the K_{aw} seems more

appropriate describing the surroundings of the leaf the model of Riederer (1990) is preferred. McKone and Daniels (1991) include the model of Riederer (1990) in their deposition model, however with slightly deviating volume fraction of the plant and using 1000 kg fresh weight of vegetation/m^3 (McKone and Daniels, 1991), instead of 715 kg/m^3 (Riederer, 1990). It should be noted that the fugacity model described here is assuming equilibrium between all compartments. For some comounds this equilibrium might be established in a few days. For others however this might take years for instance compounds wich are higly soluble in water and are hardly volatile (low K_{aw} values).

The relative volume fraction of the leaf in the model of Riederer (1990) have been based on *Brassica*, a cabbage species. For green vegetables this seems appropriate. For seeds of grains other relative values might be used as they contain higher amounts of fat (circa 1%). For fruits lower values might be used.
For grass the values found by Trapp et al. (1989) can be used.

Removal processes
In the aerosol models described here the amount of substance lost by wind or washed off by rain is already included in the interception factor for dry deposition and in the retention factor for wet deposition. The remaining part of the substance will be retained in the crop, either by absorption in the cuticula or by uptake and afterwards distribution over the plant compartments. The amount of uptake will mainly depend on the possibility of the substance to move through the cuticula. After uptake distribution will take place over the air, water and lipid-fraction in the leaf. Only the water soluble fraction can be removed by translocation. Water soluble substances will hardly move through the cuticula. For these substances translocation will not be an important process. For non-dissociating, lipid soluble substances soon an equilibrium will be reached between the transportation stream and other the plant parts. As a "reasonable" worst-case it could be estimated that the total amount remains in the foliage. For dissociating compounds translocation might remove the compound from the leaf and equilibrium between air and leaf might be established after a longer period of time. In this case the uptake of the compound will continue and a higher accumulation will take place. However, according to Bromilow (1990) less than 1% of the best transported pesticides will reach the roots and remain there. This is caused by the much faster transpiration stream compared to the phloem stream. Therefore the main part of the substance will remain in the above-ground part of the leaf.

For using the USES model it should be calculated for which kind of subtances the route via the air will mean a substantial contribution to the concentration in the plant compared to the soil route.

CONCLUSION

The aerosol deposition model of McKone and Ryan (1989) seems appropriate for use in the USES-model as it is simple, transparant and seems plausible as they use experimental data for selecting fixed values for several parameters. In this model other fixed values can easily be incorporated. Removal processes such as removal by

rain and wind and also senescence and weathering are taken into account.
For gaseous substances the fugacity model of Riederer (1990) or the model of
McKone and Daniels (1991) can both be used as these are both based on the K_{aw} and
K_{ow} partition coefficient of the substance. The fugacity approach of Riederer (1990)
is preferred. These partition coefficients are also the main characteristics of
substances for which Bacci et al. (1991) and Reischl et al. (1989) determined
regression lines using experimental data.

RECOMMENDATIONS FOR FURTHER STUDIES

Aerosols:
With the model of McKone and Ryan (1989) a partition coefficient between air and
aerosols was estimated for particles $< 5 \mu$m. It should be validated if a partition
coefficient can be used for aerosols.
What is the main fraction of aerosols deposited onto plants in the vicinity of the
emission source?. McKone and Ryan (1990) used the fraction of $< 5 \mu$m as an
average for the total environment. In the USES model deposition is calculated in the
vicinity of the emission source. Particle size might be larger there. Other
assumptions, such as annual inventory of food crops and removal rate constant of
chemicals from vegetation surfaces should be validated too.

Gaseous substances:
The uptake of gases in plants is described with several models. The validation of the
fugacity based model should have the first priority, especially the model described
by Riederer (1990).

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