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PESTICIDES IN AIR: CONSIDERATIONS FOR **EXPOSURE ASSESSMENT**

Report prepared by the FOCUS Working Group
On Pesticides in Air (FOCUS Air Group)

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FOREWORD

This Foreword is written on behalf of the FOCUS steering committee in support of the FOCUS Working Group on Pesticides in Air (FOCUS Air Group). The work presented here is in support of the European review of active substances of plant protection products under Council Directive 91/414 of July 15 1991.

FOCUS (FORum for the Coordination of pesticide fate models and their USe) is an organisation established under DG SANCO to develop approaches to environmental exposure assessment issues under 91/414. The aim of FOCUS is to provide guidance for notifiers and Member States concerning appropriate methods for calculating exposure concentrations for EU dossiers on plant protection products. While not specifically targeted toward Member State procedures, the approaches developed by FOCUS may also have applications at Member State level.

Directive 91/414 requires the generation of a PEC in air, but gives no guidance on how this should be calculated and how to identify problematic substances. Considerable uncertainty therefore surrounds how exposure from the aerial transport of pesticides should be calculated. Consequently, The FOCUS Steering Committee in its meeting in December 2001 proposed to establish a working group to review the available information and regulatory approaches in this area. The aim was to develop recommendations how to handle this potential route of exposure in the risk assessments required for Annex I inclusion of active substances under Council Directive 91/414. Such an activity was previously identified as a priority by the working group pesticides legislation of the Standing Committee for Plant Health in February and June 2001. It was suggested to exploit work done in this area by the European and Mediterranean Plant Protection Organisation (EPPO) and the proceedings of a workshop organised by the Health Council in The Netherlands (van Dijk *et al.*, 1999).

The FOCUS Air Group was established in June 2002 and delivered their report (version 1.0) in August 2006. The establishment and the main work of the Group therefore preceeded the formal splitting of responsibility for risk assessment and risk management between the European Food Safety Authority (EFSA) and the European Commission, respectively. In response to a request from EFSA, the Scientific Panel on Plant Protection products and their Residues issued an opinion on version 1.0 of the report in July 2007. Version 2.0 has been revised to take account of the Panel's opinion. The full text of the EFSA opinion is included as Appendix 11 to this report, the FOCUS Air Group's response to those comments, and details of changes made in the light of the EFSA opinion, appear in Appendix 12.

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EXECUTIVE SUMMARY

The FOCUS Air Group was established in June 2002 with the following remit:

1. Review the current level of knowledge of pesticides in air
2. Develop a list of suitable mathematical models for exposure calculation
3. Define criteria to identify chemicals of potential concern for medium- and long-range aerial transport and to indicate tools, in principle, appropriate to address these issues
4. Collect factors necessary to address the issue of the effect of pesticides on air quality
5. Propose a tiered risk assessment scheme for short-range aerial transport.

Residues arising from deposition following volatilisation are a new exposure term under Directive 91/414 and are distinct from spray drift. The group considered that the contribution from the deposition of volatilised residues was quantitatively less important than spray drift at the edge of field (defined as 1m for arable crops and 3m for vines and tree crops). However, the relative importance of deposition after volatilisation increases if spray drift mitigation is required (e.g. drift buffers, drift reducing nozzles etc).

The short-range exposure assessment scheme uses a vapour pressure trigger to identify substances of potential concern. The trigger is 10^{-5} Pa (at 20° C) if a substance is applied to plants and 10^{-4} Pa (at 20° C) if the substance is applied to soil. Substances that exceed these triggers, and require drift mitigation in order to pass the terrestrial or aquatic risk assessment, need to have deposition following volatilisation quantified and added to deposition from spray drift. Quantification is firstly done by modelling, if safety cannot be demonstrated by this means then further experimental data are required.

The group recommend a trigger of a DT_{50} in air of 2 days to identify substances of potential concern for long-range transport. Substances having a longer DT_{50} require further evaluation to assess their potential impact upon the environment; recommendations on how such an evaluation may be made appear in the FOCUS Air Group Report.

Whilst recognising the importance of medium-range transport, the group have not reported on this topic. In view of the limited time available, the FOCUS Air Group decided to provide recommendations on how to assess transport at the extremes of the range.

In addition to establishing the basis for the short- and long- range triggers, the FOCUS Air Group Report contains a comprehensive review of the state of knowledge of pesticides in air

and an evaluation of exposure models that can be used for exposure assessment. Criteria for assessing the risk to air quality are also discussed.

1. INTRODUCTION

1.1. Background

Concern over the transport of pesticides in air started in the 1960s with the detection of persistent and volatile substances such as DDT, dieldrin and aldrin far from their source of application. The USA clean air act of 1971 was perhaps the first legislation to consider air as an exposure route. Since then the issue of pesticides in air has been subject to intermittent regulatory concern, especially in Europe.

Landmark legislation regarding pesticides in air occurred in 1996 with the Stockholm convention on Persistent Organic Pollutants (POPs). This legislation covers all chemicals, including pesticides, and lays down criteria to identify substances for which aerial transport may be significant. If these criteria are met, then expert judgement is used to determine whether a substance may present a problem to the environment. Classification as a POP may lead to a worldwide ban of a chemical.

Within Europe, Directive 91/414, of July 15 1991, governs how pesticides should be evaluated for their potential effects on the environment. This Directive includes air as an environmental compartment and mandates that a PEC_{air} is calculated; however there is no guidance on how this should be done, or how problematic substances can thereby be identified. This has led to considerable uncertainty on behalf of Member States and registrants on how pesticides in air should be evaluated.

Member States differ in the amount of importance they attach to pesticides in air. For some, short-range transport of volatile pesticides is a significant concern, and estimates of volatilised residues are routinely added to residues arising from spray drift in the aquatic exposure assessment. Other Member States consider long-range transport to be significant, particularly when it involves deposition of pesticides for which there is no authorisation within the Member State concerned. Alternatively, some Member States do not consider pesticides in air to be significant compared to residues arising from spray drift, drainage and run-off.

1.2. Working Group Remit, Organisation and Outputs

The FOCUS Air Group was given the following remit:

1. Review the current level of knowledge of pesticides in air
2. Develop a list of suitable mathematical models for exposure calculation
3. Define criteria to identify chemicals of potential concern for medium- and long-range aerial transport and to indicate tools, in principle, appropriate to address these issues
4. Collect factors necessary to address the issue of the effect of pesticides on air quality
5. Propose a tiered risk assessment scheme for short range aerial transport

The Group took the proceedings of a workshop held in the Netherlands in 1998 (van Dijk *et al.*, 1999) as the state of knowledge on pesticides in air up to that date and reviewed literature starting from the date of this workshop. Initially, three subject areas were investigated: emissions of pesticides to the atmosphere; transport, transformation and deposition of pesticides; and modelling of pesticide residues. Separate subgroups were set up to report on these areas. Once these subgroups had reported, new subgroups were established on short-range risk assessment, air quality, and long-range exposure assessment. The work of these subgroups forms the bulk of the work in this Report.

The Group decided that it was beyond its remit to change how existing exposure estimates under 91/414 are calculated, because these have been commented upon by other expert (FOCUS) groups. Spray drift during application was therefore specifically excluded. Exposure of organisms to residues deposited after volatilisation from plants and soil is an exposure route not explicitly considered under 91/414. The Group therefore considered how this (short-range) exposure might be added to the existing exposure framework under 91/414.

The output of the Group may be summarised as follows:

- A review of the current state of knowledge and regulatory approaches to pesticides in air
- A Tiered risk assessment scheme for the deposition of volatilised residues at a distance <1km from the source of application (short-range). Guidance is given on how this exposure scheme fits into the existing schemes for exposure assessment under 91/414.

- A trigger to identify substances that are unlikely to show significant long-range transport (defined as >1000km from the source) behaviour and guidance on how to evaluate substances that are identified as being of potential concern.
- An inventory of suitable models to estimate exposure from long- and short-range transport of pesticides in air.
- Recommendations on how to assess whether a pesticide presents a risk to air quality.

2. CURRENT LEVEL OF KNOWLEDGE ABOUT EMISSION

Pesticides are applied to plants, soil, and water surfaces they are also used indoors. During and after the application of a pesticide, a substantial fraction of the dosage applied may enter the atmosphere and may be transported over shorter and longer distances (Gath *et al.*, 1993). This Chapter summarises the existing knowledge of the emission of pesticides to the air and discusses approaches to identify volatile substances.

Spray drift is defined in this report as losses during application measurable near the sprayed area (as downwind ground deposit) after sedimentation up to a few minutes after application. This phenomenon is already well understood and can be calculated using drift tables (Rautmann *et al.*, 2001); it is therefore not covered in this Chapter. The method proposed by FOCUS is described in the report of the FOCUS working group on Surface Water Scenarios (FOCUS, 2002). Similarly, the effect of the application technique (boom height, kind of nozzles, working pressure) on spray drift losses has been described elsewhere (e.g. Maybank *et al.*, 1974, Nordby and Skuterud 1975) and is not dealt with here.

2.1. Introduction

During spray application of a pesticide, a proportion of the spray will exist as pesticide in the gas phase and as small droplets or particles (aerosols). These particles are so small that they do not reach the target area and cannot be effectively captured by drift collectors. The proportion of a pesticide spray application that exists in the gas phase and as aerosol is therefore a loss that should be considered in addition to drift.

Volatilisation is the transfer of pesticide residues into the gas phase after application. Once present in the gas phase, these residues can be transported in air. The rate and the extent of the emission after application depend on the physical and chemical properties of the pesticide; the application parameters; the meteorological conditions during and after application; and the characteristics of the target. The chemical properties that most affect volatilisation are vapour pressure and Henry's law constant. The most important application parameters are: the kind of formulation used (Wienhold and Gish 1994), the droplet size and the water volume. Emission from green houses is governed by the indoor climatic conditions and the air exchange rate per hour.

It is well known that volatilisation processes may be influenced by relative humidity (Harper *et al.*, 1976), air temperature (Guenzi and Beard 1970), atmospheric pressure, and wind velocity (Grass *et al.*, 1994). Furthermore, irradiation may influence the metabolism of

compounds via direct or indirect photolysis (Hock *et al.*, 1995). Pesticide residues may be made unavailable for volatilisation from soil by sorption processes, by transport to deeper soil layers, and by chemical and biological degradation. These processes in turn may depend on soil characteristics such as structure, humus content and biological activity as well as soil temperature, soil moisture and pH-value (Van den Berg *et al.*, 1999). Volatilisation from plants is normally greater than from soils because plants have fewer sorption sites than soils. However, the potential amount of volatilisation may be reduced by uptake into the leaves or by degradation processes on the plant surface (Breeze and Fowler 1992).

Vapour pressure is a key factor involved in volatilisation because substances that have a high vapour pressure show a high volatilisation that is more or less independent of other influencing factors. In contrast, the volatility of compounds with a medium vapour pressure is significantly dependent on environmental and application factors. Compounds with very low vapour pressures are not volatile. The Henry's law constant is relevant to substances applied to water (rice fields) because it considers solubility as well as vapour pressure, but literature is scarce concerning the relation between the volatility of compounds applied to water and their Henry's Law constants.

It is widely agreed in the literature that vapour pressure can be used to identify substances with a very high or with no volatilisation potential. In order to establish a vapour pressure classification for risk assessment purposes, therefore, it is important to define high and low vapour pressure. Several authors have attempted to do this; their definitions are outlined in Section 2.7.

2.2. Emission During Application

The amount of a pesticide applied can be proportioned among the following routes: the proportion of the pesticide deposited onto the target area; the proportion deposited onto the adjacent non-target area; and the proportion lost to the atmosphere during application. The loss to the atmosphere can be caused either by volatilisation of small droplets on their way from the nozzle to the target area, or by transport of small droplets (<100 µm) over longer distances (not detectable by drift collectors). Volatilisation of the compound deposited during application is the dominant process from a few minutes after application, when all other processes can be regarded as having effectively ceased. Since drift can be calculated using drift tables, this part of emission loss is out of the scope of this Report. Further losses, not detectable by drift collectors and excluding volatilisation, should be determined exactly, which can be done by isokinetic air sampling from the start of application up to 5 minutes after application. These further losses should not be confused with drift.

Glotfelty *et al.* (1990) examined the distribution, drift and volatilisation of diazinon during and after application in a peach orchard. The authors measured air concentrations at different heights, calculated a flux rate, and expressed the result as loss in g/ha. Fifty minutes after application, they determined a loss of 2 % of the applied diazinon (Vapour pressure: 1.2×10^{-2} Pa at 25 °C; Tomlin, 1994). Since volatilisation starts immediately after application, this must have been a mixture of loss during application and volatilisation. Nevertheless, the amount determined was quite small, even though a tree crop was sprayed. The authors concluded that spray drift and losses during application are smaller than volatilisation after application.

Other papers report measured air concentrations during and after aerial application using either low-flight (2 – 3 m), fixed-wing spray application, or high-flight (8 m) application. Both applications used an ultra low volume application technique (ULV: droplets < 200 µm) (Bird *et al.*, 1996). They assumed that under these conditions the drift potential may be 5 to 10 fold higher than by conventional application technique, but they did not distinguish between drift and loss during application. Symons (1977) reported an extreme 60 % loss of fenitrothion during application and concluded that this portion must remain in the atmosphere. This was confirmed by monitoring in blueberry fields located in the neighbourhood of the application area (Wood and Stewart 1976). Concerning this work, it must be pointed out that Symons carried out aerial spraying to forests, which is an application scenario very different to normal agricultural practice. Nevertheless, these papers show that the emission during application (either drift or the airborne residues) is strongly dependent on the application technique and independent of the chemical and physical parameters of the compounds applied. Application techniques can therefore be used to minimise this emission. Another option is to use a recycling technique; which significantly reduces spray drift losses, and was developed especially for tree crops.

Holterman (2001) carried out a preliminary simulation study using the IDEFICS spray drift model (Holterman, 1997) to investigate the emitted pesticide fraction during application, not covered by the drift tables. In his model calculations he varied the parameters sprayer boom height, spray cone angle, relative humidity and temperature, and nozzle orientation. The Table below lists the major results of this study (Holterman, pers.comm. 2003). In each run only one parameter was changed to the value listed in the table, all other parameters were set to the same values as taken for the reference run.

Table 2.2–1: Simulations to investigate the evaporated fraction of a spray

Simulation setting	Emitted fraction (%output)	Relative increase (%)
Reference ¹	3.9	(0)
Lowered boom (0.3 m)	3.1	-21
Raised boom (0.7 m)	4.7	21
Top angle 90°	4.0	3
Top angle 130°	4.0	3
T=10 °C, RH=40%	4.8	23
T=10 °C, RH=80%	1.9	-51
T=20 °C, RH=40%	5.8	49
T=20 °C, RH=80%	2.3	-41
Nozzle orientation horizontal (averaged)	5.4	38
Nozzle orientation vertically upward	6.1	56
Nozzle orientation 45° upward (averaged)	6.9	77

¹ reference: crop height 0.5 m; BCPC fine/medium threshold nozzles; wind speed 3 m/s; boom height 0.5 m; top angle 110°; temperature 15°C; relative humidity 60%; nozzle orientation vertically downward; neutral atmospheric conditions.

The emitted fraction represents the *total volume fraction of nozzle output that loses its solvent by evaporation before depositing* onto the ground (or crop). ‘Evaporation’ in this context refers to evaporation of the *solvent only* (usually water); the remaining ‘dry’ particles (whether solid or liquid) are essentially non-volatile on the time scale involved. Note that the above definition of the evaporated fraction does not say that this fraction remains airborne permanently; it just states that *before* reaching the surface, the particle has completely lost its solvent by evaporation.

For BCPC fine/medium nozzles these calculations show that, depending on the spraying conditions, the losses during application (beside drift) may be between 1.9 and 6.9 % and confirm that this kind of loss can be significantly reduced by application technique. Nevertheless, more work and experiments are necessary in future to investigate influences not considered up to now i.e. the effect on crop structure as well as the atmospheric conditions during spraying.

The effect of nozzle type on emitted fraction has been investigated as well (Holterman, 2001). Simulation results indicate that the emitted fraction ranges from 0.7% of nozzle output for very coarse nozzles (BCPC threshold nozzle ‘very-coarse/extra-coarse’) up to 10.8% for very fine nozzles (BCPC threshold ‘very fine/fine’), under moderate environmental conditions (15°C, 60% RH).

2.3. Emission From Soil

The emission of pesticides from soil involves volatilisation from the soil surface and wind erosion of soil particles containing sorbed pesticides. These processes are investigated separately in the following Section. In particular, the driving forces and influencing parameters of the emission processes are scrutinised in this review of the current scientific literature.

Volatilisation of pesticides from soil is governed by a combination of several factors (van den Berg *et al.*, 1999):

- physico-chemical properties of the compounds (vapour pressure, solubility, adsorption coefficient, molecular mass, chemical nature and reactivity);
- soil properties (water content, soil temperature, soil density, organic matter content, clay content/texture, pH);
- meteorological conditions (air temperature, solar radiation, rain/dew, air humidity, wind/turbulences);
- agricultural practices (application rate, application date, ploughing/incorporation, type of formulation).

Most of these parameters are closely linked and interact with each other. Their combined effects on the volatilisation process are therefore far from linear (Bedos *et al.*, 2002).

Volatilisation is dependent upon vapour pressure. Bedos *et al.* (2002) mentioned in an overview report that the kinetics of volatilisation from soil is similar for different pesticides having the highest volatilisation fluxes just after application, and that the flux halved after 8 hours (Nash 1983). Compounds with higher vapour pressures (e.g. heptachlor, trifluralin, lindane) have initially high volatilisation fluxes ($> 30 \text{ g ha}^{-1} \text{ d}^{-1}$) followed by a rapid decrease. In contrast, the volatilisation of pesticides with lower vapour pressures (e.g. dieldrin, endrin, DDT) is initially lower ($< 10 \text{ g ha}^{-1} \text{ d}^{-1}$) but decreases more slowly. Although these fluxes were measured following soil application at different rates (0.87 – 4.2 kg/ha) the difference

between fluxes for compounds with high and low vapour pressure remains after normalisation to a rate of 1kg/ha.

Vapour pressure also governs the partitioning of a semi-volatile substance between the gas and the air-borne particle phases. According to Bidleman (1988) substances with a vapour pressure $> 10^{-2}$ Pa are predominantly observed in the vapour phase whereas those with a vapour pressure $< 10^{-5}$ Pa are almost exclusively present in the particle adsorbed phase. The majority of pesticides have a vapour pressure in-between these values and partition between these phases.

Cousins *et al.* (1999) summarised the basic principles of the exchange of semi-volatile organic compounds across the soil-air interface. For a soil-sorbed compound to volatilise, it must first desorb from the soil solids to the interstitial soil water from which it may be exchanged to the soil-air. Subsequent transport to the atmosphere can occur either with the soil-air, or with the soil-water.

A first approach to describe these processes is to assume equilibrium between the corresponding phases. The interchange from solid to the solution has frequently been represented by the Freundlich isotherm ($S = K_f * C^{1/n}$ with S : solid concentration (mol kg⁻¹), K_f : Freundlich coefficient, C : equilibrium concentration in the liquid phase (mol l⁻¹) and $1/n$: index of Linearity), which relates the solid concentration to the equilibrium solution concentration. The partitioning between soil-water and soil-air can, in principle, be characterised by the Henry's law constant if soil volumetric air and water contents, bulk density and porosity are known. Finally, the gaseous transport in soil to the atmosphere can be described by diffusion coefficients (Cousins *et al.*, 1999). However, ideal equilibrium conditions scarcely describe the reality. For example, desorption can be biphasic with a rapid initial phase followed by a much slower rate. In addition, diffusion processes in an open system are dynamic rather than equilibrium processes and are significantly influenced by the concentration gradient.

Cousins *et al.* (1999) noted that volatilisation from soil to the air refers to a sum of processes consisting of, among others, the migration of soil-incorporated compounds to the soil surface. This migration may occur

- (1) Through mass transfer with evaporating water
- (2) By upward gas and/or liquid phase diffusion in response to a concentration gradient
- (3) Through soil disturbance – either man-made or by invertebrates.

For most of the semi-volatile compounds mechanism (1) is the main transport route. Mechanism (2) becomes significant for volatile compounds and under very dry conditions. For the upward transport of a compound with evapotranspiring water (1) is a significant process, even for less water-soluble substances like Dieldrin (Spencer and Cliath, 1973). This phenomenon is known as ‘*wick effect*’. The soil column acts as a wick; the water in the soil moves up the capillaries of the wick dragging along dissolved compounds, as in thin-layer chromatography, to replenish the lost water at the soil surface by evaporation.

Once transported to the soil surface, a compound is vaporised to the stagnant air boundary layer by molecular diffusion. The existence and thickness of this boundary layer varies depending on micrometeorological conditions (air velocity and turbulence) and surface geometry. Jury *et al.* (1983) suggested a typical layer thickness of approximately 5 mm.

Wang and Jones (1994) suggested that volatilisation of organic compounds from soil is governed by the ratio of the Henry’s law constant (H) and the octanol-water partition coefficient (K_{OW}). Using the semi-empirical correlation between K_{OW} and the soil organic carbon-water distribution coefficient K_{OC} (Karickhoff, 1981), i.e. $K_{OC} = 0.411 \times K_{OW}$, the soil-air partition K_{SA} can be expressed as

$$K_{SA} = K_d/H = 0.411 f_{OC} \rho (K_{OW}/H)$$

where K_d is the soil-water distribution coefficient, f_{OC} is the fraction of organic carbon and ρ the bulk density of the soil (Mackay, 1991). The higher the value of K_{OW}/H the greater the susceptibility of a compound to partition from air to soil.

Temperature has a major influence on the volatilisation rate, mainly through its effect on the vapour pressure. According to Jury *et al.* (1987) and Spencer and Cliath (1970), the vapour pressure of the most intermediate molecular weight organic compounds increases three to four times for each 10°C increase in temperature. As a consequence, an increase of 10°C in soil temperature increased the volatilisation of halogenated pesticides applied to moist soil by a factor of 1.8 (Nash and Gish 1989). To a lesser extent, an increase in temperature may also increase volatility through its effect on: the soil-water desorption; the diffusion of a chemical in soil-water; and the mass flow of evapotranspiring water (Cousins *et al.*, 1999). Typical patterns of volatilisation flux from moist soil in the field show an increase after sunrise to a maximum in the early afternoon, followed by a decline until sunset (Rice *et al.*, 2002). However, increasing temperature also increases the drying rate of the soil, thereby decreasing the vapour density by stronger adsorption to soil, resulting in turn in less volatilisation (Rice *et al.*, 2002).

An increase of the wind speed and atmospheric instability generally reduces the thickness of the stagnant boundary air layer on the top of a solid surface. Consequently, both volatilisation and the opposite process, the dry gaseous deposition flux to the soil, are increased (Cousins *et al.*, 1999). High wind speed and high temperature also increase the water evaporation rate, causing partial drying out of the top soil layer, and this can lead to a decrease in the volatilisation rate (Grass *et al.*, 1994).

The humidity of soil and air has an indirect influence on the volatilisation rate of a semi-volatile organic substance. Drying of the soil (decreasing soil humidity) can result in a reduced vapour pressure as a consequence of increased sorption (Cousins *et al.*, 1999). This can cause accumulation of a chemical at the soil surface. Re-moistening of the soil surface by exposure to higher air humidity can result in rapid volatilisation (Spencer and Cliath 1973). A similar result was observed by Stork *et al.* (1998); in a field study with an initial soil moisture content of only 3 % within the first millimetres of soil, the initial volatilisation rate of parathion-methyl and terbuthylazine was very low due to strong adsorption, but increased considerably with re-moistening of soil after rainfall events. However, the volatilisation flux in the field was abruptly stopped due to an intensive rainfall on the day following application as a result of leaching into the soil (Rice *et al.*, 2002). Volatilisation flux increased again when the rain came to an end as a result of back-migration due to the 'wick effect'. Soil moisture can also explain a surprising flux pattern with highest volatilisation rates in the morning and evening. Taylor (1995) explained that the increase of flux in the evening is due to moistening of the soil surface by dew formation (thus blocking the adsorption sites by water molecules), which persists through the night until it is evaporated after sunrise with increasing temperature.

Naturally, the top few millimetres of soil can dry and cut off volatility in the field. However, higher soil moistures deeper in the soil profile (typically > 15 %) may slowly rewet the surface and prevent complete cessation of volatile release (Rice *et al.*, 2002). The moisture content of the soil can greatly affect the soil-air partition coefficient K_{sa} , if the moisture is low (0.3 to 0.8 %). In contrast, higher soil moisture (1.9 – 12 %) did not affect K_{sa} (Hippelein 1997). This phenomenon may be explained by a water layer on the surface of the soil pores. At higher soil moisture the complete soil surface is saturated by at least a monomolecular water layer. The vapour density of a weakly polar compound in the soil-air is then greatly increased. Additional soil water does not influence further the tendency of a compound to leave its sorbed site. Conversely, if the air humidity was reduced from 100 % (no net loss of water from soil to air) to 50 %, the volatilisation flux of dieldrin from the soil was increased

due to a more effective transport from deeper layers to the soil surface ('*wick effect*'), followed by volatilisation (Spencer and Cliath 1973).

Another influencing factor is soil pH for those compounds having pKa-values within the range of soil pH. Volatilisation of amines is expected to increase with higher soil pH (van den Berg *et al.*, 1999). Müller *et al.*, (1998) studied the influence of soil pH on the volatilisation of [¹⁴C] fenpropimorph after application to bare soil (loamy sand with different pH) and found a strong increase in volatilisation with increasing pH.

The soil organic matter content influences the soil adsorption coefficient K_{oc}, which is inversely related to the vapour density of both wet and dry soil, and consequently to volatilisation. Clay content has only a minor effect (Spencer and Cliath 1970). Soil texture has an indirect influence on volatilisation; sandy soils will dry more quickly than silt loam soils, resulting in increased sorption and reduced volatilisation with decreasing soil moisture (Glotfelty *et al.*, 1984b).

The duration of volatilisation for volatile substances is short. Measurement of volatilisation losses from fields treated with metolachlor revealed that 95 % of the cumulated flux occurred during the first 12 hours after application (Prueger *et al.*, 1999). Rice *et al.* (2002) showed that volatilisation of different pesticides from the soil of a freshly tilled field occurs mainly on the day of application and following day, though some minor volatilisation flux could be measured up to 21 days after application. Emission of lindane from a field, into which canola seed treated with lindane was planted at a depth of 3 cm, began immediately after planting and reached a maximum rate during the second week (Waite *et al.*, 2001).

Barometric pressure was observed to influence the volatilisation rates of the very volatile soil fumigant methyl bromide (Yates *et al.*, 1997); increasing barometric pressure slightly decreased the volatilisation.

Volatilisation can be reduced using special application techniques, e.g. incorporation into the soil and covering the soil surface. Volatilisation is minimised if the substance is applied under a tarpaulin in cool temperatures and is deeply injected in moist soil. The use of '*virtually impermeable films (VIF)*' could effectively reduce atmospheric emission of methyl bromide and alternative fumigants (Wang *et al.*, 1999). Dissolving the fumigant 1,3-dichloropropene in irrigation water and '*subsurface drip irrigation*' also can reduce emission into the atmosphere, compared to standard shank injection (Wang *et al.*, 2001).

2.3.1. Wind Erosion of Soil Particles with Adsorbed Pesticides

Glottfelty *et al.*, (1984a) reported another emission pathway for pesticides in the atmosphere, i.e. when pesticides are sorbed to soil particles and entrained into the atmosphere on wind-blown particles. There are few data on the significance of this pathway, and on the quantitative effects of soil and environmental factors that influence this process (van den Berg *et al.*, 1999). This process is most important for herbicides as they are applied either at pre-emergence or post-emergence at an early growth stage of the crops (e.g. summer cereals, maize) when there is low soil coverage (Fritz, 1993). Fritz estimated the frequency and intensity of soil erosion events on light sandy soils in north-western Germany.

Table 2.3–1: Soil erosion classes (Fritz, 1993)

	Low	Medium	High	Very high
Soil erosion (t/ha)	< 1	1-15	15-100	>100
Frequency of erosion events per 10 years on highly erodable soils	10	5-10	3-5	1-2

Wind erosion events shortly after application of a pesticide with high initial residues on the topsoil can therefore result in significant emission rates.

The emission of pesticides adsorbed to soil was concluded by Scharf and Baechmann (1993) from the presence of low volatile pesticides in the air. Further evidence was drawn from the temporal deposition behaviour of fenpropimorph. Fenpropimorph reached peak levels in precipitation during three distinct periods: April/May, July, and October. The pesticide's presence during the first period was explained by its application, the second peak was caused by harvesting and the third by sowing of the succeeding crop (winter cereals). These agricultural activities cause soil and plant particles with old residues of the pesticide to enter the atmosphere. The second and the third peak cannot be explained by volatilisation of unbound residues.

If non-sealed agricultural roads are oversprayed during aerial application in Australia some residues of a pesticide are also adsorbed to the dust of the road. This contaminated dust can be whirled up by vehicular traffic and deposited to a distance of up to 1000 m from the site of emission, depending on the wind direction and velocity at the time of vehicle passage (Larney *et al.*, 1999).

2.4. Emission From Plants

Recently, it has been clearly shown that the volatilisation of pesticides after application to plant surfaces may be significant. For example, results from laboratory chamber experiments show significant volatilisation for parathion-methyl (50 – 80 %), parathion – ethyl (40 %),

endosulfan (60 %) fenpropimorph (40 – 70 %), lindane (55 %), trifluraline (79 – 99 %), mecoprop-P, mecoprop-methylester, bromoxynil (33 %), fluoxypyr (12 – 88%), vinclozolin (34 – 38 %), penconazole (37 – 55 %) (Stork *et al.*, 1998, Rüdel 1997, Maurer 1995, Müller 1997, Staimer 1997, Larsen 2001).

It is well known that organophosphates and carbamates can be categorised as volatile according to the classification of Seiber and Woodrow (1983) and Unsworth *et al.* (1999), whereas triazines, DDT, aldrin or the pyrethroids are categorised as non-volatile. It is difficult to assess the importance of volatilisation processes for medium volatile active ingredients, which comprise most of the registered compounds, because the significance of the volatilisation process is extremely dependent on the environmental and spraying conditions for these compounds. The resulting complex interaction between influencing factors is important for plants for the following reasons:

- Most insecticides and fungicides as well as the contact-herbicides are sprayed on crops.
- Leaves are the main surface for plant-applied pesticides. They have a wide range of surface topologies ranging from an uneven rough or hairy surface to a smooth surface that is frequently coated with epicuticular wax layers. These waxes consist of a mixture of long-chain carbon-hydrates (C21 – C35), oxidized derivatives of these, short-chain saturated and unsaturated as well as long-chain fatty acids and alcohols, aldehydes and esters from mostly aliphatic acids (Müller 1986). Because of this, leaf surfaces provide limited sorption sites for both lipophilic and hydrophilic compounds, and the resulting sorption capacity is significantly lower than that of soil. The interaction between more or less lipophilic active substances, their kind of formulation, and the wax layer is also important. The possibilities for leaf-sorption on the surface as well as further transport within the matrix are limited compared to soils.
- The wax layers of different crops are more or less structured or plain (Barthlott 1990). These structures affect the turbulence within the canopy and influence the convection exchange rates between leaves and air.
- Water evaporation may also be different between plant surfaces and soil.

It has been shown by many authors (e.g. Maurer, 1995, Müller, 1997, Stork, 1995) that volatilisation from plants may be significantly higher than from soil, especially because of the limited sorption sites and uptake rates. Therefore further influences are important:

1. Compound characteristics
Vapour pressure, water solubility (and hence Henry's law constant), and K_{oc} (coefficient for the adsorption on organic carbon) are important parameters governing volatilisation. Additionally, the degradation rate on plant surfaces (photolytical stability) and the possibility for uptake into leaves influence volatilisation. Formulation may play an important role because it influences sorption and uptake.
2. Application characteristics
The kind of nozzle used, the resulting droplet sizes and the formulation determines the distribution of the compound on the plant surface. The droplet diameter determines the duration of the drying process. As long as the compound is available in the liquid phase, Henry's law can describe the volatilisation process. Volatilisation from the solid phase (sublimation) is of lesser importance.
3. Meteorological conditions
Rainfall after application leads to wash off of applied substances from plant surfaces. In general, temperature enhances volatilisation as does low air humidity. Wind speed and turbulence are important because air exchange rates prevent the building up of rising compound concentrations in the air, which would prevent further volatilisation according to 1st order kinetics and also influences the thickness of the stagnant boundary layer.

Vapour pressure is a key factor driving volatilisation and is therefore a good trigger for screening compounds in a tiered risk assessment scheme. However, for medium volatile substances and their volatilisation from plants, the mentioned influences are important because vapour pressures in the literature are measured under controlled conditions at constant temperature. In the environment, actual vapour pressure is influenced by the dilution of the substance, by other substances, and by temperature. Therefore, actual vapour pressures under field conditions may vary over a wide range, but are not normally determined. This has important consequences, especially for the pesticide residues on plants, because residues on plants are more available to volatilisation than soil residues.

Another important factor is Henry's law coefficient (H), mostly given as the result of $(V_p \times M)/S$ where V_p is the vapour pressure, M the molecular weight and S is the water solubility. Under liquid conditions, H may also be used as a trigger and is therefore only effective directly after spraying, when the spraying solution has not yet dried. After that, sublimation or re-wetting processes caused by rain, air humidity, or the release of water by the plant itself lead to further volatilisation. Chamber experiments by Staimer (1997), Müller (1997), and

Stork (1995), for example, show that this is a measurable effect. In consequence, volatilisation data for certain compounds may differ over a wide range. For example, chamber experiments with parathion-methyl in EC and WP-formulation showed volatilisation rates between 40 and 80% 24 h after application to different plants under standardized conditions of 20° C, 50 % air humidity and a wind speed of 1 m/sec (Kubiak 1999). Under field conditions, with varying climatic influences and in comparison with other chamber types, even higher differences are possible (Walter *et al.*, 1996).

Proceedings of a workshop held in Driebergen 1998 (Van Dijk *et al.*, 1999) review the state of knowledge about volatilisation from plants up to 1998. The following key sentences can be extracted from this review.

- Different types of experimental approaches to investigate volatilisation from plants are described in literature. Chamber experiments provide well-described environmental conditions and enable mass balances when ^{14}C -labelled compounds are used. Therefore their uncertainty level is low (around 10 %). Their reproducibility is high but the transferability of the results to actual field situations is limited because of the use of constant conditions and possible artefacts of the experimental system itself (limited size, wind flow conditions etc.).
- For a screening-level judgement a good correlation was observed by Woodrow *et al.* (1997) between the logarithm of the volatilisation rate and the logarithm of the vapour pressure ($n = 12$, $r^2 = 0.989$). This relation was confirmed by Smit *et al.* (1998) using literature data on volatilisation rates from plant surfaces either measured under field conditions or in chambers ($n = 19$; $r^2 = 0.78$).
- No models are available to describe the volatilisation from plants. Consequently more research is needed to describe the influence plant developmental stage, leaf surface characteristics, photo-degradation, uptake and wash off. A plant growth model would be a useful way to describe the processes on the leaf surfaces.

Bidleman (1999), in a review, stressed the importance of the exchange of vapour-phase compounds between vegetation and air. In addition to the approach of Woodrow *et al.* (1997), Thomas *et al.*, (1998), introduced the concept of a plant/air partition coefficient $K_{\text{pa}} = K_{\text{ow}}/H$. Both K_{ow} and H can quite easily be measured or calculated.

The knowledge about volatilisation from plants can be summarised as follows:

- Plant volatilisation is up to three times as high as soil volatilisation under similar meteorological conditions.
- Because of a relatively high availability of compound residues on plant surfaces, complex interactions between actual vapour pressure, surface and climatic conditions, Henry's law constant, and formulation dominate the further fate of the compound and are highly variable.
- This interaction is not fully understood and cannot be described mathematically.

Nevertheless, comparing data from literature with given vapour pressures valuable co-relations to the volatilisation could be determined with V_p and K_{pa} . These rather simple relations and the resulting empirical approach should be investigated in more detail to judge their ability for a first tier risk assessment. Further scientific work is needed to understand and model in more detail the volatilisation from plants under different conditions.

2.5. Emission From Water

The volatilisation of pesticides from water is influenced by their physicochemical properties such as vapour pressure, water solubility, and Henry's law constant as well as fugacity. Temperature effects on physico-chemical properties, vertical transport in the water column, the influence of the sea-surface microlayer and the climatic conditions are also important (Bidleman 1999). However the exchange of pesticides between air and water has not been as extensively studied compared to other stationary phases.

Maguire (1991) showed that volatilisation from the water surface microlayer is the major dissipation process for low water-soluble pesticides sprayed on water. He found that volatilisation of the insecticides fenitrothion and deltamethrin was significantly higher than for soluble compounds that are well mixed with water. This phenomenon can be explained by the formation of a surface film that can either volatilise or penetrate into the water body. If the water solubility is low, evaporation dominates, even if the substances proved non-volatile during wind tunnel experiments.

There are some papers reporting data about re-emission from oceans, lakes and snow after introduction via re-deposition of volatilised compounds or from other sources. These data are reported in Chapter 3. In Europe, pesticide application to water is predominantly carried out in rice ecosystems.

In the late 80s the California Department of Pesticide Regulation studied the emission to air of pesticides used in the cultivation of rice in flooded fields. Seiber and McChesney (1988) measured and modelled the volatilisation rate (flux) of molinate and methyl parathion from paddy water. They concluded that only 5-10% of the initial water content of molinate was lost in the first 72 hours by volatilisation and an even smaller amount of methyl parathion (1/10th of that of molinate) was lost. This flux significantly decreased over the next few days. They correlated flux to Henry's law constant, which for methyl parathion is approximately 1/10th of that of molinate. Emission from rice paddies becomes important when it is considered that rice is the main nourishment for a very important percentage of the global population. Brown (1989) also studied the loss to air of pesticides used in rice production and stated that the fact that volatilisation of rice pesticides accounts for a small part of their dissipation accounts for the lack of literature on this subject.

2.6. Emission From Indoor Uses

The indoor uses of crop protection products may lead under certain circumstances to emission of trace amounts of pesticides into the environment. In the following, it is understood that indoor uses cover greenhouses, glasshouses, plastic tunnels, and warehouses.

This emission is governed primarily by:

- The characteristics of the applied compound (physicochemical parameters like vapour pressure, stability, water solubility),
- The characteristics of the greenhouse (dimension, shape, air tightness),
- The greenhouse management including for instance application techniques, ventilation frequency and techniques (height of grown plants, humidity in the shelter), and the outside climatic conditions (temperature, humidity, wind speed).

The total area of greenhouses needs to be known in order to assess the relative importance of emissions from this source compared to emissions from normal agriculture. The following Table shows the total land area of greenhouses worldwide.

Table 2.6–1: Greenhouse area in the EU and Mediterranean (data from Wacquant, 2000)

Region	Glasshouse area (ha)	Other shelters (ha)
EU (north west)	22000	1200
EU (south)	7000	59500
EU (central)	5000	22000
Other Mediterranean countries	1500	28950

EU represents about 45 % of the greenhouse area in the world, but this is a small fraction of the amount of the cultivated land. However, it does not mean that the emission of pesticides from greenhouses into the atmosphere may be neglected.

2.6.1. Factors Influencing the Gaseous Emission of Pesticides from Greenhouses

2.6.1.1. Dutch studies on pesticide emission from greenhouses and calculation models to evaluate outside air transfer

In the following two studies Heidema *et al.* 1992, and Baas and Bakker 1996, considered that the following factors influence the emission potential of pesticides from greenhouses: the characteristics of the compound and of the greenhouse; the greenhouse management techniques; and the impact of outdoor climatic conditions. Heidema *et al.* (1992) have shown that chemicals applied in a closed shelter may be found in the environment. Their concentration in the outdoor air depended upon chemical vapour pressure, application techniques and ventilation of the shelter. Emission is also possible through volatilisation of the compound during and after application and through leakage of particles, mainly during air renewal phases. Smaller droplets remain longer in the air and consequently have a greater potential for leakage than large droplets (200 to 500 μm), which deposit rapidly onto leaves, stems or ground.

Emission from a standard greenhouse

A typical greenhouse (256 m^2 , 901 m^3) was treated using 3 different techniques and 3 chemicals having different vapour pressures (Tomlin 1994).

Table 2.6–2: Characteristics of applications and vapour pressures

Application type	Spray volume (l/ha)	Droplet size (µm)	Chemicals	V _p (Pa)
Ultra low volume (ULV)	5 – 10	< 20	dichlorvos,	2.1 *
			parathion ethyl,	8.9 x 10 ⁻⁴ *
			fenbutatinoxide	8.5 x 10 ⁻⁸ *
Low Volume (LV)	50 – 100	about 50	parathion ethyl	8.9 x 10 ⁻⁴ *
High volume (HV)	700 – 2000	200-500	parathion ethyl	8.9 x 10 ⁻⁴ *

* Tomlin (1994)

From this experiment, calculations of active ingredient concentrations in the lee eddy (downwind concentration) have been made using a ‘lee eddy model’; the following results for the first hour after application were found.

Table 2.6–3: Calculated concentrations in the lee eddy

V _p (Pa)	Spray techniques	Concentrations in the eddy (µg/m ³)
dichlorvos	ULV, LV, HV	7.0 - 7.6
parathion ethyl	ULV	4.8 - 4.7
	LV	0.50 - 0.55
	HV	0.09
fenbutatinoxide	ULV	0.86 - 1.4
	LV	< 0.1 - < 0.2
	HV	-

This Table shows the influence of the high vapour pressure of a chemical like dichlorvos, even during HV application. In contrast, low vapour pressure of fenbutatinoxide leads to its absence in the eddy.

The influence of ventilation was also measured. The following Table summarizes the total amount of chemical emitted from the greenhouse at four different times expressed as a percentage of the application rate. The four times were: first hour after application (P1), second hour before ventilation (P2), during the ventilation period (P3) (rate of 33% per hour, wind speed of 4 m/s) and after the ventilation period (P4).

Table 2.6–4: Calculated percentage of applied dose emitted in air according to vapour pressure and application technique

V _p (Pa)	Spray techniques	P1	P2	P3	P4	% Total emission
> 10 ⁻²	ULV, LV, HV	17	13	5	4	39
10 ⁻² – 10 ⁻⁵	ULV	19	2	1	1	23
	LV	2	2	2	3	9
	HV	1	2	2	3	8
< 10 ⁻⁵	ULV	3	1	<1	-	<5
	LV	<1	-	<1	-	<1
	HV	-	-	-	-	-

It can be concluded from this study that ULV applications (droplet size < 20 µm) have the greatest potential for emission from a treated greenhouse; for the other application systems (LV, HV), this potential is weaker. Note that the calculation was run according to the following equation:

$$C = Q / K \cdot A \cdot u$$

C = concentration in the lee eddy (g/m³)

Q = emission source (g/s)

K = constant depending on greenhouse shape and wind direction

A = area of front shelter (m²)

u = wind speed at roof height (m/s)

The concentration in the eddy may reach 8 µg/m³ for compounds with a high vapour pressure like dichlorvos in a ULV application system. Nevertheless, authors stress that uncertainties due to the calculation system do exist in estimating K (variation between 0.2 and 1.2) and u (greater the speed, smaller the concentration in the eddy); therefore, the maximum downwind concentration can vary from 3 to 25 µg/m³ for a highly volatile compound like dichlorvos.

Emission from a greenhouse area

Baas and Bakker (1996) have considered the emission of crop protection products applied in a greenhouse area to the outdoor air from pesticides applied to plants, soil and water. From this study, only the emission into the air from greenhouse horticulture will be considered. The following tables summarize the characteristics of the pesticides, greenhouse parameters and area used during the study.

Table 2.6–5: Pesticide properties

	Dichlorvos	Bupirimate	Methomyl
DT ₅₀ soil (days)	2	79	8
Rate (g/ha) a.i.	850	500	250
Application frequency	Some weeks / year	Once / 2 weeks	Once / 3-4 weeks

Table 2.6–6: Standard greenhouse parameters

Area	Height	Air exchange rate	Air tightness
1 ha (100x100 m)	3.5 m	33 % / hour	50 %

For calculation purposes, it was assumed that the greenhouse area was 1, 3 or 10 km² and that there were 50 greenhouses per square kilometre (greenhouse density of 50 %). The calculated emission to the outdoor atmosphere right after the application was made according to 2 models ('lee eddy model' and the so-called 'National Model' or Gaussian plume type). The latter is used in the Netherlands to assess emission concentrations for air pollution beyond 100 m. Within a greenhouse area, the greatest aerial concentrations of dichlorvos were calculated in the air behind treated shelters and are shown in Table 2.6-7.

Table 2.6–7: Calculated dichlorvos concentrations

Distance to greenhouses (m)	Concentration (µg/m ³)
0	50 (lee eddy model)
25	50 (lee eddy model)
50	36 (linear extrapolation from lee eddy model)
100	10 (linear extrapolation from lee eddy model)
500	0.9 (national model)
1000	0.3 (national model)

(Worst case' calculation parameters: 5 'emitting' greenhouses out of a greenhouse area of 1 km² (worst case scenario as 3 shelters are usually sprayed at the same time), wind speed of 2 m/s, emitting source of 34 mg/s of dichlorvos, first hour after application, downwind.)

Out of the greenhouse area and at its borderline, the following dichlorvos concentrations were calculated from a theoretical point source application located in the middle of 1 km².

Table 2.6–8: Calculated dichlorvos concentration ($\mu\text{g}/\text{m}^3$) as a function of the size and of the distance to the greenhouse area

GH area (km*km)	0km	1km	2km	4km	8km	16km	32km
10 x 10	3.5	2.1	1.6	1.2	0.80	0.40	0.17
3 x 3	1.7	0.98	0.65	0.33	0.15	0.06	0.02
1 x 1	0.76	0.27	0.14	0.06	0.02	0.006	0.002

In the same simulation, bupirimate and methomyl yearly average concentrations were found to reach about 200 times less than that of dichlorvos, due to their significantly lower vapour pressure and application systems. The yearly average concentration of bupirimate and methomyl at the borderline of the greenhouse area was about $10 \text{ ng}/\text{m}^3$, decreasing to $0.05 \text{ ng}/\text{m}^3$ at 32 km from the source. Here again, the authors stressed the level of uncertainty, which remained high mainly due to the poor knowledge of pesticide behaviour in air and the absence of real concentration measurements in the atmosphere.

2.6.1.2. German studies on aerial concentration and deposition measurements after emission from indoor uses

In the framework of a recent research project of the German Environmental Protection Agency (UBA), several experiments were done to determine the emission of pesticides from buildings. In these studies, measurements of emission and deposition were performed. The project was divided in two parts – glasshouses (Schmidt *et al.*, 2002) and warehouses (Klementz *et al.*, 2002).

i) Glasshouses

The dispersion behaviour of pesticides with different vapour pressures was measured at two locations (Berlin-Dahlem and Braunschweig) outside the glasshouse after application to tomatoes. Air concentrations were measured inside the greenhouse, at the ventilation flaps, and up to 50 m from the glasshouse in the wind direction. Windows were opened immediately after application. Deposition in standard model waters was measured at different distances from the greenhouse. The substances tested were lindane, parathion, procymidon and tebufenpyrad in different combinations. Lindane was used in all cases. The application rate was $750 \text{ g}/\text{ha}$ active substance using a high volume technique. Air sampling started in two-hour cycles (except at night) after application.

RESULTS

At the Braunschweig trial site, average atmospheric concentrations measured in the middle of the greenhouse 24 hours after application were $6.3 \mu\text{g}/\text{m}^3$ (lindane), $1.2 \mu\text{g}/\text{m}^3$ (parathion), $0.64 \mu\text{g}/\text{m}^3$ (pirimicarb), $0.28 \mu\text{g}/\text{m}^3$ (procymidone) and $0.026 \mu\text{g}/\text{m}^3$ (tebufenpyrad). At Berlin-Dahlem, concentrations were $6.4 \mu\text{g}/\text{m}^3$ (lindane), $1.2 \mu\text{g}/\text{m}^3$ (parathion), $0.75 \mu\text{g}/\text{m}^3$ (pirimicarb), $0.46 \mu\text{g}/\text{m}^3$ (procymidone) and $0.19 \mu\text{g}/\text{m}^3$ (tebufenpyrad). There was correspondence between source emissions and greenhouse emissions at both sites. The outdoor emissions were different at the two sites however, because of different environmental conditions.

On average, at both trial sites, and all times of measurement, concentrations measured in the main wind direction 5 m away from the greenhouse were lower by more than one order of magnitude compared to those inside the greenhouse, with $0.39 \mu\text{g}/\text{m}^3$ for lindane and $0.043 \mu\text{g}/\text{m}^3$ for parathion outside the greenhouse. Averaged measurements were mostly below or around the limit of quantification (LOQ) for all other substances.

Average concentrations in a model surface water (depth of 6 cm) were $0.68 \mu\text{g}/\text{L}$ (lindane), $0.15 \mu\text{g}/\text{L}$ (parathion), and $0.072 \mu\text{g}/\text{L}$ (pirimicarb) after a 24-hour period of exposure at 20 m distance. Procymidone and tebufenpyrad were hardly found above the limit of quantification. Average concentrations of lindane were found reduced to $0.29 \mu\text{g}/\text{L}$ at 20 m distance and $0.1 \mu\text{g}/\text{L}$ at 50 m distance, while all other substances were below or around the limit of quantification. If concentrations found in water are converted into area-related depositions, the following amounts are calculated at 5 and 20m distances in main wind direction (cumulative deposition within 24 hours after the application):

Table 2.6–9: Area-related depositions ($\mu\text{g}/\text{m}^2$)

	5m distance	20m distance
Lindane	37	14.5
Pirimicarb	4.3	1.5
Parathion	5.9	2.5
Procymidone	<1	<1
Tebufenpyrad	<1	<1

ii) Warehouses

The transport of chemicals up to 200 m from warehouses has not yet been investigated in detail. The experiments of Klementz *et al.*, 2002 serve for determination of potential air contamination by contact insecticides during and after warehouse fogging. For the volatile insecticide dichlorvos, indoor concentrations in six warehouses, their outlets, and outdoor concentrations at distances of 5, 10, 20 and 50 m on three divergent lines in wind direction were measured. The following parameters varied within the following ranges:

- Warehouse volume (between 400 m³ and 2200 m³),
- Application dose (6 l preparation /1000m³),
- Exposition time (4 or 6 hours),
- Climatic conditions (temperature, wind direction, wind speed).

The German warehouse experiments are only based on one substance with a high vapour pressure applied in two warehouses with different application techniques. More experimental data are not available. As the outdoor exposure after warehouse use depends on parameters that have not been quantified it is scientifically not justified to derive a general conclusion from these experiments. Therefore, no general recommendation on emissions from warehouses can be given here.

RESULTS

From six applications, the maximal concentration amounted to 95 µg/m³ inside the warehouses. At the windows and doors, the maximal concentration was reached four to six hours after fogging. Depending on wind speed and temperature, the maximal concentrations ranged from 100 µg/m³ to 550 µg/m³. On non-target areas, deposition was measured in water-filled bathtubs as well as on filter papers. The concentrations in water decreased with time as well as with distance from warehouses. At distances of 5, 10, 20 and 50 m maximum values of all experiments were 123 µg/m³, 16 µg/m³, 6 µg/m³ and 0.6 µg/m³. These values diminished within 12 hours by a factor of 10. Maximum concentrations (5-50 µg/l) in water of depth 6cm were found at a distance of 5 m for all experiments.

2.6.2. Outdoor Exposure from Indoor use

Two sources of information relating to exposure from indoor uses were identified: data from the Netherlands on human exposure, and data from Germany on environmental exposure.

2.6.2.1. Dutch modelling of the inhalative human exposure after uses of pesticides in greenhouses

An attempt was made to assess the exposure of population living in the vicinity of greenhouse areas (Leistra *et al.*, 2001). The concentration of a pesticide was calculated in the lee eddy of a glasshouse at about 20-30 meters distance according to the calculation model of Baas and Huygen (1992) within the first hour after application. Dose rate, vapour pressure, deposition rate, emission flow from the source, air exchange rate in the greenhouse and wind direction are considered as well as two application techniques (ULV and HV); the concentration was calculated for 24 pesticides (insecticides, acaricides and fungicides) used in NL greenhouse treatments.

In the study, ADI was considered as a kind of “toxicological credit” and converted in $\mu\text{g}/\text{m}^3$ considering a human being of 70 kg breathing $23 \text{ m}^3/\text{day}$ which can vary between $11 \text{ m}^3/\text{day}$ for a sedentary human (CRC Handbook of Radiation Measurement and Protection, 1989, ISBN 0-8493-3757-7, p. 136) and $60 \text{ m}^3/\text{day}$ for a hard-working human (Wissenschaftliche Tabellen, Geigy). The concentration calculated in air is then compared to this credit and a safety margin extrapolated. If the credit is greater than the calculated concentration in air, a risk for human health is not expected.

It was demonstrated that inhalation via air did not result in health concern for 21 compounds out of 24 whatever the application technique was. Two old compounds of concern (dienochlor, heptenophos) were withdrawn from the market; for dodemorph, the assessment was not possible due to the lack of toxicological information.

2.6.2.2. Studies assessing the environmental exposure of pesticides used in greenhouses

BBA greenhouse studies

The percentage deposition 24 hours after application in greenhouses can be derived from the previously mentioned studies; the applied rate in the greenhouse, expressed in $\mu\text{g}/\text{m}^2$, was compared to the pesticide concentration in water converted in area related depositions (in this case the applied rate was $750 \text{ g}/\text{ha}$ for each pesticide using a high volume application technique).

Table 2.6–10: Calculated deposition percentage referred to the applied rate from BBA concentration measurements

	Deposition at 5m distance		Deposition at 20m distance	
	µg/m ²	% of applied rate	µg/m ²	% of applied rate
Lindane	37	0.05	14.5	0.02
Pirimicarb	4.3	0.006	1.5	0.002
Parathion	5.9	0.006	2.5	0.003
Procymidone	<1	<0.001	<1	<0.001
Tebufenpyrad	<1	<0.001	<1	<0.001

The highest percentage of deposition is 0.05% for lindane. This can be considered as a worst case as this compound is known to deposit at a higher level than expected from its vapour pressure and as greenhouse windows were open immediately after the application. Moreover, the percentage of deposition decreases to 0.02% at 20m distance from the greenhouse. These deposits look negligible when compared to spray drift deposits and should not result in unacceptable risk to non-target organisms.

From this overview of pesticide emission after greenhouse application, it can be concluded that:

- The deposition after volatilisation from greenhouses is in general less than in the field
- The deposition percentage of 0.05% based on BBA lindane emission measurements should be used for compounds where the application technique is by high or low volume,
- A conservative estimate of a four-fold increase in deposition percentage i.e. 0.2%, based on the emission percentage from Dutch calculations, should be used in the case of an ultra low volume application technique.

2.7. Considerations for Vapour Pressure Classes

A tiered risk assessment scheme for the entry of pesticides into the atmosphere requires the definition of triggers that identify whether further studies are required. Vapour pressure (V_p at 20 °C) is an important indicator of volatilisation potential that has already been used for

classification purposes. Seiber and Woodrow (1983) and Unsworth *et al.* (1999) proposed schemes that categorised substances into high, medium and low volatility classes. A more conservative, according to the authors ‘arbitrary’, classification was published by Kördel *et al.* (1999) - note that the authors acknowledged that there was no scientific justification for their classification. The European Plant Protection Organisation (EPPO) proposes different vapour pressure classes for soil and for plants.

Table 2.7–1: Vapour pressure classifications

	Vapour Pressure in Pa		
Volatility of compounds	Seiber, Woodrow, 1983 Unsworth <i>et al.</i>, 1999	Koerdel <i>et al.</i>, 1999	EPPO
Volatile	$> 10^{-1}$	$> 10^{-3}$	Soil : $> 10^{-1}$ Plants : 10^{-3}
Medium volatile	between 10^{-1} and 10^{-5}	between 5×10^{-3} and 10^{-6}	Soil : between 10^{-1} and 10^{-3} Plants : between 10^{-3} and 10^{-5}
Low or non volatile	$< 10^{-5}$	$< 10^{-6}$	Soil : $< 10^{-3}$ Plants : $< 10^{-5}$

Smit *et al.* (1997, 1998) correlated measured data from volatilisation experiments with vapour pressure (see Figure 2.7 – 2). For volatilisation from bare soil, they distinguished between dry and normal moist soil; for plants, they distinguished between field and chamber experiments with direct measurement of volatilised compounds (see Figure 2.7 – 3). No clear correlation was found in the soil experiments. In the plant experiments, many substances with relatively high vapour pressures ($> 5 \times 10^{-3}$ Pa) were used.

Figure 2.7–2: Relation between cumulative volatilisation from soil at 21 days after application and fraction of compound in gas phase under various field conditions (From: Smit *et al.*, 1997)

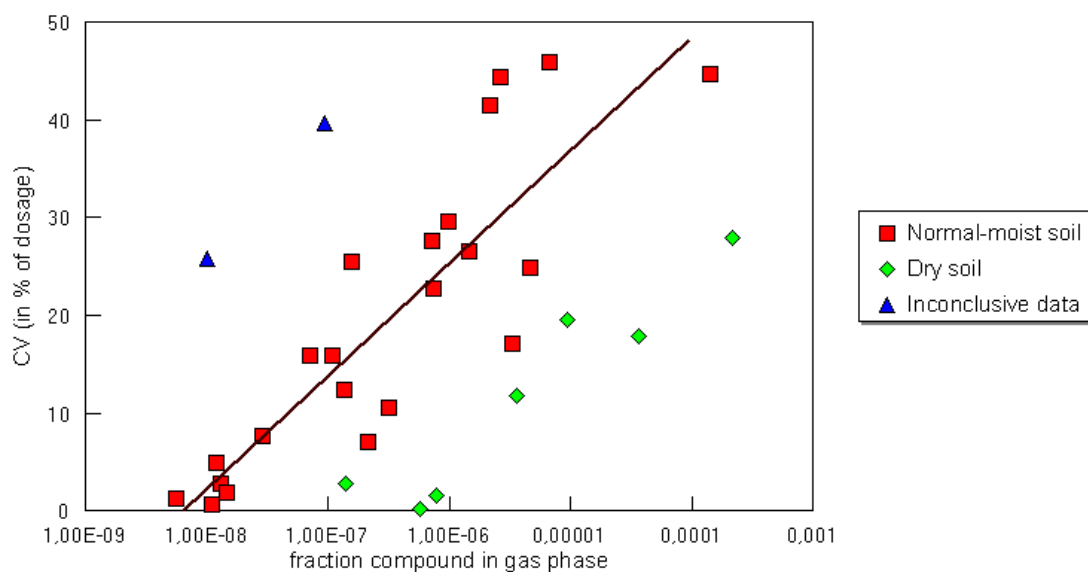
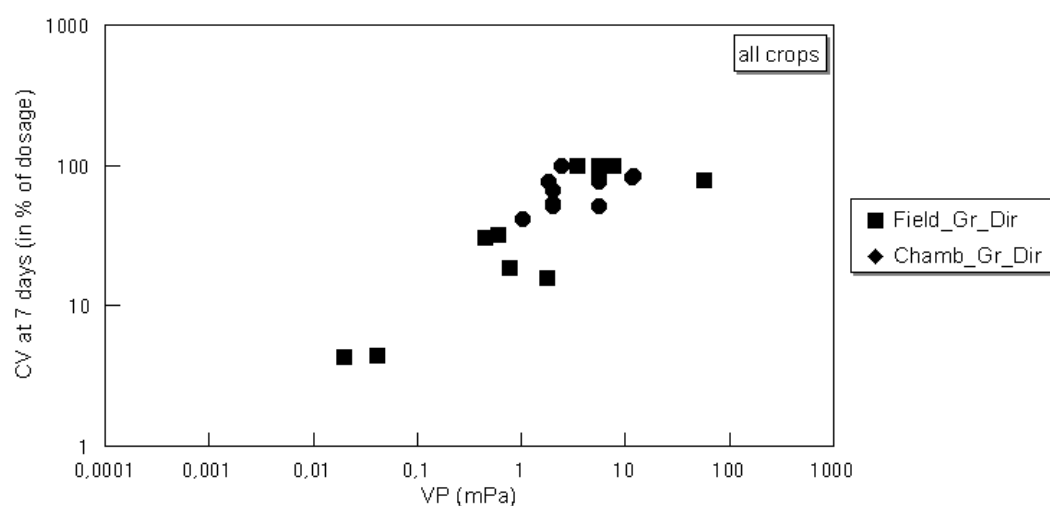


Figure 2.7–3: Cumulative volatilisation from plants at 7 days after application against vapour pressure (without redundant data). Field=field measurement, Chamb=climate chamber measurement, Dir=direct measurement of pesticide concentration in air (From: Smit *et al.*, 1998)



In order to establish a vapour pressure trigger as part of a tiered risk assessment scheme a comparison between vapour pressure and measured volatilisation data (expressed as a percentage of the applied amount) needs to be made. Such results can be obtained using several scientific approaches:

- Closed chambers in the laboratory allow for the direct measurement of volatile active ingredients as well as volatile metabolites. When ^{14}C -labeled compounds are used full mass balances are possible since the detection of non-extracted residues as well as the formation of $^{14}\text{CO}_2$ after degradation of the labelling position is possible.
- In open systems, either in the laboratory or in the field, only the indirect determination of volatiles is possible on the basis of a percentage value. The time-dependent residues are determined in soil and/or plants and the results are compared with the residues directly after application. When ^{14}C -labeled compounds are used the chance for a misinterpretation of the results can be reduced by determination of the non-extractable residues in soil and/or plants.
- Concentration measurements in the air in combination with meteorological models are also possible, but the results vary depending on the model used and the level of uncertainty is quite high.

From the analytical point of view, the most precise way to determine volatilisation is by direct measurement using ^{14}C -labelled compounds in wind channels. The resulting mass balances are a tool to quantify the uncertainties of the experiment. The combination of air measurements carried out in the field and meteorological dispersion models also enable mass balance. Indirect determination by residue analysis of the application target, and the resulting differences between the residues directly after application and hours or days after application, may include other processes like transformation, uptake by plants, transport to deeper soil layers, mixture into water bodies and the formation of bound residues.

Consequently, directly measured volatilisation rates (Müller 1997, Maurer 1995, Staimer 1997, Stork 1995) are often lower than those measured by indirect methods. A recently published paper by Hassink *et al.* (2003) compares the vapour pressure and volatilisation rates (% of applied) from soil and plants measured during 24 h at 20 °C. These results confirm the tendency of higher volatilisation determinations when indirect methods are used. The results from experiments using direct measurements indicate that volatilisation is significantly below 10% of applied for compounds with vapour pressures below 10^{-3} Pa after soil application (Fig. 2.7-4) or 10^{-4} Pa after plant application (Fig 2.7-5).

Figure 2.7–4: Volatilisation after soil application related to the vapour pressure

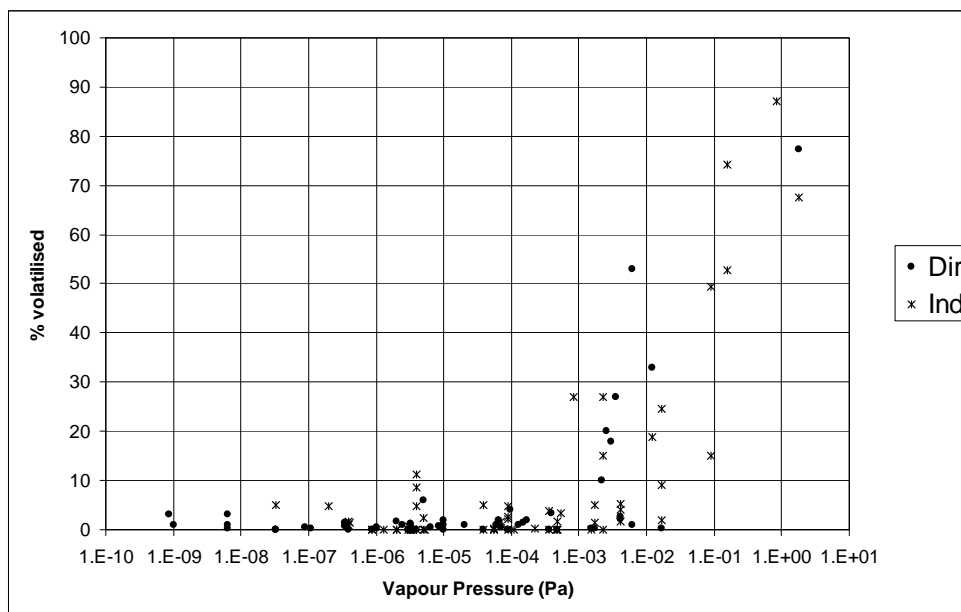
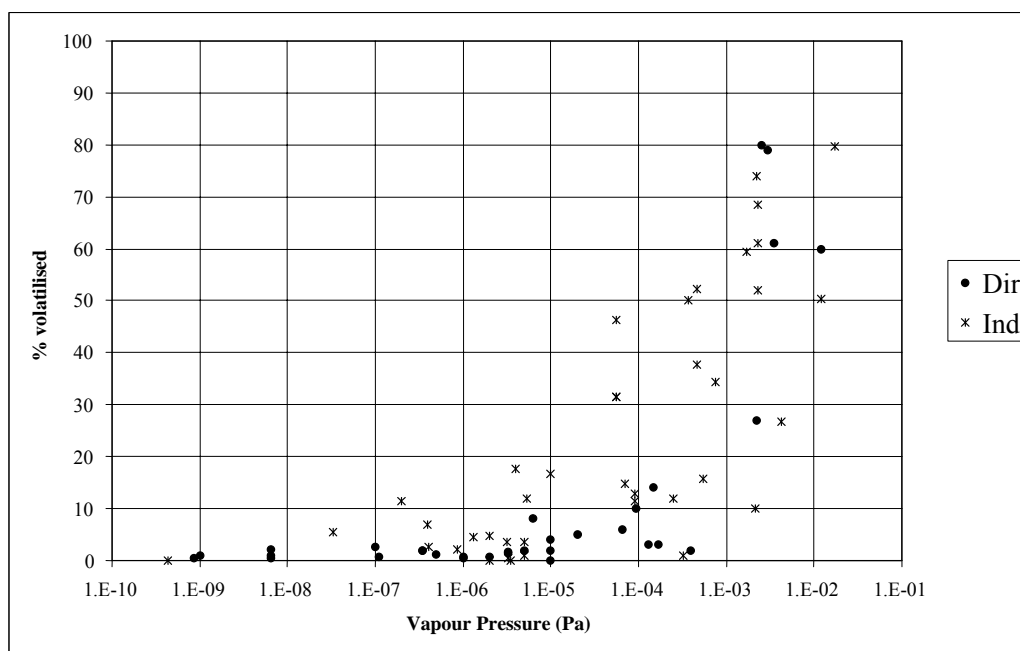


Figure 2.7–5: Volatilisation after plant application related to the vapour pressure



Although the number of experiments used for this comparison is limited, the results confirm the proposed EPPO classification and — with respect to the border between low and medium volatility — the classification proposed by Seiber and Woodrow (1983) and Unsworth *et al.* (1999). These results show that vapour pressure alone (rather than another measure such as Henry's constant) can be used to distinguish between substances having high and low

volatility. In order to distinguish between compounds for which volatilisation is relevant and those for which it is not, the following has to be taken into account:

- The determination of vapour pressures especially of older compounds may still have uncertainties today because of the method or the temperature used.
- The poor correlation above 10^{-4} Pa shows that, within a relevant vapour pressure range, other parameters like formulation type, kind of soil, soil pH or plant species may influence the volatilisation process.

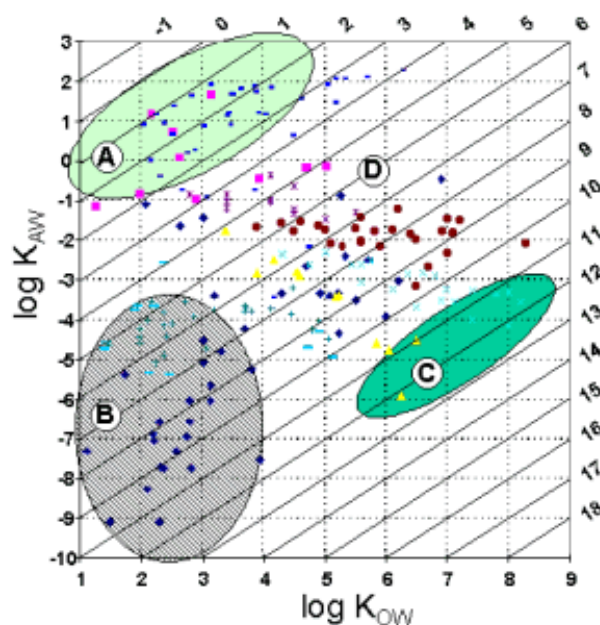
Using the above data, and taking into account the potential uncertainties of volatilisation and vapour pressure measurements, the following conservative values are proposed by the FOCUS Air group to establish whether a substance has the potential to reach the air:

$V_p \geq 10^{-4}$ Pa (20°C) for volatilisation from soil and

$V_p \geq 10^{-5}$ Pa (20°C) for volatilisation from plants

Only few experimental results are known concerning the volatilisation (% of applied) after application to water bodies. For water bodies, the Henry's law constant could potentially be used as a trigger because it also includes water solubility. A comparison between $\log K_{AW}$ and $\log K_{OW}$ from van de Meent *et al.* (1998) showed that compounds with a $\log K_{AW} > -1$ and a $\log K_{OW} < 5$ can be classified as predominantly available in air (see Figure 2.7–6). Further research is needed to identify a trigger for the relevance of volatilisation after application to water bodies.

Figure 2.7–6: Environmental distribution of chemicals $\log K_{OA}$



A: exists predominantly in air
 B: exists predominantly in water
 C: exists predominantly in soil
 Others: multiple media chemicals
 (van de Meent et al. 1998)

3. CURRENT LEVEL OF LEVEL OF KNOWLEDGE ABOUT ATMOSPHERIC TRANSPORT, TRANSFORMATION AND DEPOSITION

3.1. Introduction

The intention of this Chapter is to provide a clear, concise and up to date overview of the major processes relating to the fate of a pesticide once it reaches the atmosphere (either by losses at the time of application or by subsequent volatilisation losses from plant or soil surfaces). The processes are considered primarily from the standpoint of the effect of the physicochemical parameters of the compound on the fate. However, other important processes (e.g. meteorological) are also noted. The Chapter has been subdivided into sections on transport, transformation and deposition for ease of reading. For discussion on how these processes are addressed by simulation models, the reader is referred to Chapter 4.

In addition to the mechanistic description of the processes that govern pesticide fate in air, the Chapter also gathers together relevant experimental results and data on what has been observed in practice (i.e. monitoring data). True monitoring data (as opposed to experimental data) shows only the levels present and does not provide any direct information on the origin of the compounds – although such data is routinely interpreted to try and assess the source of the concentrations measured. Therefore it is particularly suited to long range transport (LRT) issues since for short range transport (SRT) experiments can be undertaken to relate the source of the compound (for instance spraying of pesticide onto a crop) to the levels of pesticide found a short distance outside the treated area. The monitoring data collected in the Chapter relate to wet deposition of pesticides in rainfall/fog and concentrations in air (Section 3.5) and to the levels of more general organic pollutants which can be found in waterbodies as a result of deposition from other sources (Section 3.6). These data also provide information on the phenomenon of re-volatilisation, which results in compounds being moved over even longer distances.

Before any detailed discussion of the relevant fate processes for pesticides in air it is necessary to address the question of scale. The ability of a pesticide to move short, intermediate or long distances in the atmosphere will clearly depend on a number of factors – some relating to pesticide properties and others to meteorological factors. From Chapter 2 it can also be seen that application techniques may additionally impact on the sort of distances travelled.

For further discussion it has been decided to define three distances for transport within the context of this report. These are short-range transport (SRT), medium range transport (MRT) and long-range transport (LRT). These terms may mean different things to different readers and so we have chosen to define them as follows:

- SRT is considered as 1-1000m (1 km) from the point of application
- MRT is considered as 1-1000 km from the point of application
- LRT is considered as >1000 km from the point of application

The basis for this classification is a pragmatic approach based on order of magnitude differences. SRT was considered to end at 1 km since this distance enables the area of deposition to be related to the source of emission and therefore to existing ecotoxicology risk assessment principles. LRT was considered to start at 1000 km since this is approximately the distance moved by a compound with a DT_{50} in air of 2 days (a DT_{50} in air of 2 days is often used as an alerting parameter in other sorts of chemical assessments e.g. POPs, Convention of Stockholm). MRT is simply the distances between those defined for the end of short range. It is, by definition, an area that falls between SRT and LRT and so is likely to be governed by processes intermediate to those governing SRT and LRT. The remainder of this Chapter concentrates on the extremes of the transport range (i.e. SRT and LRT) and does not provide specific detail on MRT. The Group acknowledges that MRT is important but has not reported further on this. The work on the long and short ranges has been prioritised in view of the limited time available.

3.2. Atmospheric Transport of Pesticides

Moving outwards from the earth's surface, the atmosphere can be divided into a surface boundary layer, the troposphere (ca 15km high), the stratosphere – includes the ozone layer (extends to 50 km above earth's surface) – and then the mesosphere (extends to 90 km above earth's surface) and finally the ionosphere (comprising the thermosphere and exosphere). Once a pesticide becomes airborne it enters into the surface boundary layer. This boundary layer forms over the surface of the earth and plays an important role in the vertical movement and horizontal distribution of airborne pollutants. The boundary layer shows fluctuations in height that are dependent on surface properties such as temperature, roughness and vegetation (type and quantity) (Majewski and Capel, 1995).

During daytime, this boundary layer is usually unstably stratified, generally well mixed in the vertical by mechanical and thermal turbulence, and typically extends 1-2 kilometres above the

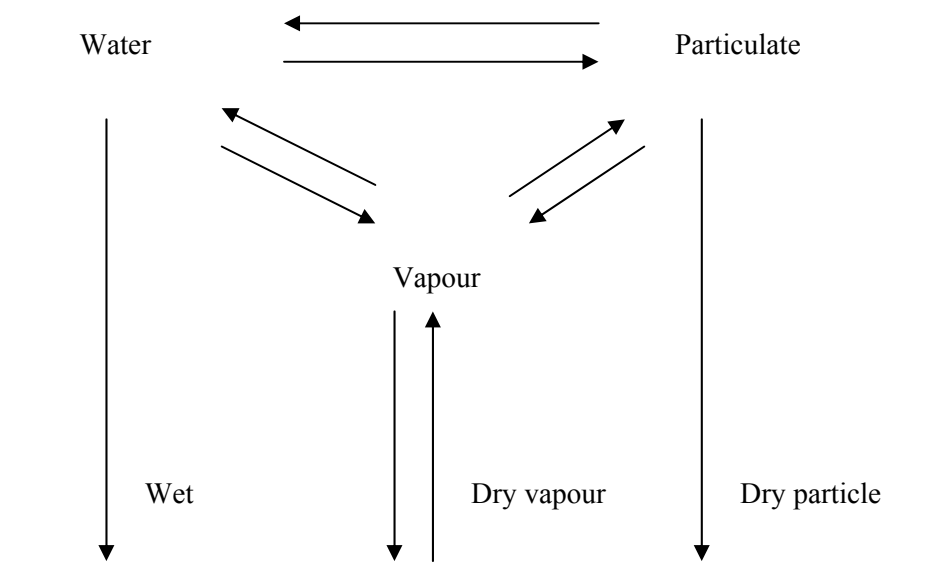
surface (Schroeder and Lane, 1988). Any chemical released into the atmosphere under these conditions will also tend to become well mixed and dispersed throughout the surface boundary layer (Majewski and Capel, 1995). At dawn and dusk there is often lower wind intensity, in which case relatively more stable conditions prevail. At night, because of surface cooling, the boundary layer depth typically decreases to a few hundred meters and is usually only slightly turbulent or even stable. Where chemicals are released into a stably stratified atmosphere, they can be transported horizontally for long distances and generally undergo little mixing or dilution (Majewski and Capel, 1995). In this case steep vertical gradients of pollutant concentrations can be found. The overall fluctuations between day and night result in emissions tending to be uniformly distributed throughout the surface boundary level after one diurnal cycle (Schroeder and Lane, 1988) due to daytime turbulence homogenising the concentrations.

Once a pesticide becomes suspended in the atmosphere, it will distribute itself between the vapour, aqueous and particle phases in order to reach an equilibrium state. This is shown schematically in Fig. 3.2–1. (however it should be noted that many authors combine the water phase with the particulate and refer to “particulates including aerosols”). The distribution of a pesticide between these phases is dependent on the physical and chemical properties of the compound, such as water solubility, vapour pressure and partition coefficients, as well as environmental factors such as temperature, humidity and the nature and concentration of suspended particulate matter (Majewski and Capel, 1995). The most frequently used approaches to estimate this distribution are the Junge-Pankow approach (Junge, 1975; Pankow, 1994; Liang *et al.*, 1997) and the octanol/air partition model (Finizio *et al.*, 1997). Using the Junge-Pankow approach it should be noted that the vapour pressure referred to should be that of the sub-cooled liquid in the case of solid compounds (see e.g. TGD, 1994). Most pesticides are likely to lie between the extremes of being either only in the vapour, or only in the particulate phase, and their distribution and atmospheric lifetimes depend largely on the particle concentration and composition (e.g. size, surface area and organic carbon content) in the atmosphere (Eisenreich *et al.*, 1981). Partitioning of pesticides to the particle phase in the atmosphere is favoured by lower temperatures (Atkinson *et al.*, 1992; Pankow, 1994).

Movement of pesticides in the atmosphere takes place through dispersion, which is a combination of eddy diffusion and convective transport processes that occur simultaneously (Schroeder and Lane, 1988). Diffusion, which promotes the dispersion of gases and atmospheric particles (aerosols), is caused by turbulent motions that develop in air that is unstable. Transport, on the other hand, results from air-mass circulation driven by local or

global forces. Certain meteorological conditions such as thunderstorms can move these airborne pesticide vapours and particles into the upper troposphere. Once there, they can be distributed regionally and even globally (Majewski and Capel, 1995). The actual distance travelled by pollutants strongly depends on the amount of time a specific pollutant resides in the atmosphere and is available for dispersion.

Figure 3.2–1: Possible atmospheric partitioning pathways (Majewski, 1991)



(It should also be noted that particulate matter in the atmosphere could result from erosive loss processes at the soil surface).

3.2.1. Short Range Transport

At the local scale (i.e. short range transport) the most important parameters influencing the dispersion of substances are: *i*) the effect of atmospheric stability and wind speed on emission rates, *ii*) lateral and vertical dispersion, *iii*) atmospheric boundary layer height and *iv*) wind speed (as a function of height) (Van Jaarsveld and Van Pul, 1999). Note that these factors are not independent. The time scale at which the dispersion takes place at the local scale is typically rather fast (a few minutes to an hour). Therefore compounds are mostly lost from the local area by transport processes since the transformation and deposition processes are generally of a longer timescale (Van Jaarsveld and Van Pul, 1999). However, some deposition does occur and this is rather more significant in terms of entry onto an uncontaminated surface (i.e. soil or water) than as a loss mechanism from the relatively higher amounts in the atmosphere.

3.2.2. Long range transport

At the regional scale (i.e. long-range transport) the most important parameters influencing the dispersion of substances are: *i*) emission characteristics (such as seasonal distribution), *ii*) vertical transport to higher layers, *iii*) removal and exchange processes and *iv*) land-sea differences (Van Jaarsveld and Van Pul, 1999). The time scale at which the dispersion takes place at the regional scale is typically from hours to several days. At these time scales the substance is mixed rather homogeneously over the atmospheric boundary layer.

Generally, pollutant time into the free-moving troposphere is on the order of a few weeks to months (Majewski and Capel, 1995). However, due to the diurnal cycle of the atmospheric boundary layer and large-scale weather systems (e.g. thunderstorm systems and convective instabilities such as upsliding at fronts) airborne pesticides can also move into the upper troposphere and stratosphere (Van Jaarsveld and Van Pul, 1999). The transport time of an air parcel during large-scale vertical perturbations from the surface to a height of 10 km is on the order of hours (Majewski and Capel, 1995). When in the upper atmosphere, the global wind circulation patterns control long-range transport of airborne pollutants.

3.3. Transformation

As noted in the previous section transformation is not usually a significant factor in SRT due to the relative time frames for moving out of the short range (1 km maximum as defined in this report) in comparison to the transformation rate. However, the capacity for pesticides to be transported over long distances is a function of their atmospheric lifetime, which is the result of emission and removal processes. In fact long-range transport of pesticides will occur when compounds have a significant lifetime (Atkinson *et al.*, 1999).

Photooxidative processes (indirect photolysis) and light-induced reactions (direct photolysis) are the main transformation pathways for pesticides in the atmosphere. According to Finlayson-Pitts and Pitts (1986) four processes can be considered (the first three being photooxidative processes and the fourth being direct photolysis):

- Reactions with OH-radicals which are considered to be the major sink for most air pollutants, including pesticides (Klöpffer *et al.*, 1985; 1988), due to the reaction with double bonds, the H abstractive power of hydroxyl and its high electrophilicity (Atkinson, 1986; Becker *et al.*, 1984; Atkinson *et al.*, 1979).
- Reactions with O₃ (ozone), which are only efficient with molecules with multiple bonds (Klöpffer *et al.*, 1988).

- Reactions with NO₃-radicals, which are potentially important for compounds containing double bonds (Atkinson *et al.*, 1999).
- Direct photolysis which acts only with molecules absorbing at $\lambda > ca\ 290\text{ nm}$ which corresponds to the cut-off region of sunlight UV radiation.

Most transformation occurs in the atmospheric boundary layer and troposphere. This is due to the length of time a chemical must persist in order to reach the higher levels of the atmosphere i.e. the stratosphere (see Section 3.2). In the troposphere OH radicals are formed by the reaction of water vapour with excited O(¹D) (activated oxygen), which is the result of the photolysis of tropospheric ozone in the wavelength region 290-330 nm (Atkinson *et al.*, 1999).



A diurnal, seasonally and annually averaged global troposphere OH radical concentration of $1 \times 10^6 \text{ molecules.cm}^{-3}$ has been estimated (Atkinson *et al.*, 1999).

In the troposphere, ozone is formed photochemically from the interactions of volatile organic carbon compounds (VOCs) and oxides of nitrogen (NO + NO₂) in the presence of sunlight.



where M represents N₂ or O₂ or another third compound that absorbs the excess vibrational energy and thereby stabilizes the O₃ molecule formed. There is also a net transport of ozone from the stratosphere (where the majority of the atmospheric ozone is present) into the troposphere (Roelofs and Lelieveld, 1997). Losses are by dry deposition processes and photochemical destruction. All these processes leads to the presence of ozone throughout the troposphere with mixing ratios at “clean” remote sites at ground level in the range of $1-4 \times 10^{-8}$ (*Mixing ratio in atmospheric chemistry is defined as the ratio of the amount (or mass) of a substance in a given volume to the total amount (or mass) of all constituents in that volume. In this definition, for a gaseous substance, the sum of all constituents includes all gaseous substances, including water vapour, but not including particulate matter or condensed phase water (Seinfeld and Pandis, 1997).*). The mixing ratio for O₃ in polluted areas can exceed 1×10^{-7} .

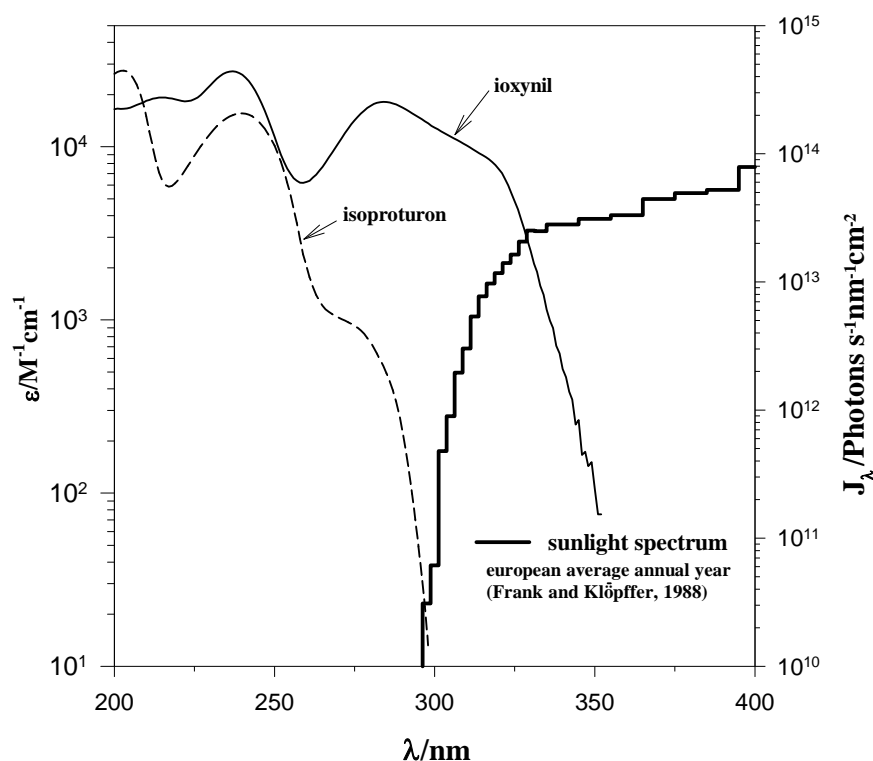
The presence of NO in the troposphere from natural and anthropogenic sources is followed by reaction with O₃:



leading to the formation of an NO₃ radical. This radical has a very short lifetime in the presence of sunlight; hence its levels remain low during the day but increase to measurable levels during night-time. Measurements made over the past 20 years show night-time levels of NO₃ radical at ground level over continental areas up to 1×10^{10} molecules.cm⁻³.

The transformation of pesticides by sunlight occurs when pesticides absorb in the relevant wavelength region leading to a chemical reaction (decomposition or isomerisation). Because of absorption of short wavelength solar radiation by O₂ and O₃ in the stratosphere, photolysis in the troposphere requires the pesticide to absorb radiation at wavelengths between 290 and ~800 nm, the latter wavelength is the longest one which can break a chemical bond. As an example, Figure 3.3–1 shows the UV-spectra of isoproturon and ioxynil; the first one is not degradable by photolysis in contrast to the second one, where an overlap with sunlight spectrum is important.

Figure 3.3–1: The UV-spectra of isoproturon and ioxynil (from Millet *et al.*, 1998a,b)



If reaction with OH-radicals and direct photolysis occur only during the day, reaction with NO₃-radicals can contribute to degradation and transformation of certain classes of compounds during night-time (Klöpffer *et al.*, 1988).

Pesticides are present in the atmosphere in the gas phase (from volatilisation processes) and in the particle phase (including aerosols). For pesticides in the gas phase, removal by chemical transformation processes involves photolysis, reactions with OH radicals, NO₃ radicals, O₃ and possibly with HNO₃ in polluted urban areas. In the particle phase, reactions with OH-radicals, O₃ and photolytic reactions are assumed to be the major chemical transformation processes based on information from the gas phase (Atkinson *et al.*, 1999).

Only a relatively small amount of experimental data concerning the atmospheric chemical transformation rates of pesticides in the gas or particle phase is available. This has recently been compiled by Atkinson *et al.* (1999) and is presented in Table 3.3–1. Reaction products observed from gaseous and particulate phases are available for some compounds and were also recently compiled by Atkinson *et al.* (1999). Transformation products available are summarised in Table 3.3–2 and are the combination of Atkinson *et al.* (1999) paper and other new experiments (Briand *et al.*, 2001). Transformation products have been found in field samples of rain, snow and fog (*in* Atkinson *et al.*, 1999) but no information is available concerning the origin of these transformation products (gas or particulate reactivity).

Table 3.3–1: Overview of published data on reaction rates of pesticides in the gaseous and particulate phases (Data obtained from Atkinson *et al.*, (1999), except isoproturon and bromoxynil obtained from Palm *et al.*, (1998) and alachlor obtained from Briand *et al.*, 2001).

Compounds	Type of pesticide	Phase	k _{OH} *	k _{NO₃} *	k _{O₃} *	Photolysis **
Methyl bromide	fungicide	Gas	2.9.10 ⁻¹⁴			
1,2 dibromo-3-chloropropane	nematicide	Gas	4.3.10 ⁻¹³		<3.10 ⁻²⁰	
cis-1,3-dichloropropene	nematicide	Gas	8.4.10 ⁻¹²		1.5.10 ⁻¹⁹	
trans-1,3-dichloropropene	nematicide	Gas	1.4.10 ⁻¹¹		6.7.10 ⁻¹⁹	
EPTC	herbicide	Gas	3.2.10 ⁻¹¹	9.2.10 ⁻¹⁵	<1.3.10 ⁻¹⁹	
Cycloate	herbicide	Gas	3.5.10 ⁻¹¹	3.3.10 ⁻¹⁴	<3.10 ⁻¹⁹	
α-hexachlorocyclohexane	insecticide	Gas	1.4.10 ⁻¹³			
γ-hexachlorocyclohexane	insecticide	Gas	1.9.10 ⁻¹⁴			

Compounds	Type of pesticide	Phase	k_{OH} *	k_{NO_3} *	k_{O_3} *	Photolysis **
Hexachlorobenzene	fungicide	Gas	$2.7 \cdot 10^{-14}$			
Trifluralin	herbicide	Gas				$\sim 3 \cdot 10^{-4}$ $/\sim 6 \cdot 10^{-4}$
Phorate	insecticide	Gas				$\sim 2 \cdot 10^{-3}$
Parathion	insecticide	Gas				$\sim 6 \cdot 10^{-3}$
Phosphine	insecticide	Gas	$1.6 \cdot 10^{-11}$			
Chloropicrin	insecticide	Gas				$5.7 \cdot 10^{-5}$
methyl isocyanate	All	Gas				$6.7 \cdot 10^{-6}$
Lindane	insecticide	Particulate	$6.0 \cdot 10^{-13}$			
Terbutylazine	herbicide	Particulate	$1.1 \cdot 10^{-11}$		$< 5 \cdot 10^{-19}$	
Pyrifeno	fungicide	Particulate	$1.8 \cdot 10^{-11}$		$< 2 \cdot 10^{-19}$	
Bomoxynil	herbicide	Particulate				not estimated
Isoproturon	herbicide	Particulate	$1.21 \cdot 10^{-11}$			
Alachlor	herbicide	Particulate				$4.2 \cdot 10^{-5}$

* : unit = $cm^3 molecules^{-1} s^{-1}$

** : unit = s^{-1}

Table 3.3–2: Reaction products observed in laboratory experiments (Data from Atkinson *et al.*, 1999).

Parent compound	Transformation product	Phase
Methylbromide	Formaldehyde	Gas
1,3-dichloropropene	formyl chloride, chloro-acetaldehyde	Gas
Molinate	keto-derivative	Gas
Trifluralin	N-dealkylation	Gas
Parathion	Oxones	Gas
Chloropicrin	Phosgene	Gas
Terbutylazine	N-dealkylation	Particulate
Pyrifeno	keto-derivative	Particulate

Reasons for the relative paucity of such experimental data for pesticides include practical constraints such as distinguishing the action of direct photolysis and the OH-radical reactivity in the case of photosensitive pesticide molecules in smog chamber experiments (Atkinson *et al.*, 1999). However, Palm *et al.* (1999) have recently solved this problem in the case of pyrifeno by conducting photolysis experiments using different optical filters. Also, data for particulate phase reactions are generally more difficult to obtain than for the gaseous phase (Atkinson *et al.*, 1999).

Generally, the monitoring of OH radical concentration in smog chambers is done after injection of OH radical precursors, or by using relative rate of disappearance of reference compounds of known k_{OH} . (Kwok *et al.*, 1999; Palm *et al.*, 1997, 1998). Decay of concentrations with time of these reference compounds is done by pumping air from the chamber and analysis by GC-FID (Palm *et al.*, 1997; 1998). This method induces a dilution effect that can be important when the volume of the chamber is small. Generally, chambers have a large volume and need expensive materials and human resources for experiments.

Currently the most often used technique for obtaining data on the transformation rates of pesticides is the use of Structure Activity Relationships (SAR). These allow programs such as the Atmospheric Oxidation Program (AOP; also known informally as “the Atkinson calculation” and available from the US EPA website as part of the EPI suite) to derive a calculated transformation rate for the compound in question. The Atkinson approach involves a standard group rate constant for a particular reaction, which is then adjusted depending on the relevant substituents (see e.g. Kwok and Atkinson, 1995). The Atkinson approach for the hydroxyl radical reactions further assumes that a number of different reaction pathways exist — H atom extraction from C-H and O-H bonds, OH radical addition to C=C and C≡C bonds, OH radical addition to aromatic rings, OH radical interaction with N-, P- and S- containing groups — and that the overall rate constant is equal to the sum of these interactions. The degradation rate constant can then be determined using a mean OH radical concentration in air. The AOP program assumes a mean diurnal concentration of 0.5×10^6 OH radicals cm^{-3} for a 24 hour day or a mean concentration of 1.5×10^6 OH radicals cm^{-3} for a 12 hour day (based on experimental data; OH radical concentrations are known to vary during the day since the action of light on ozone is a major formation pathway).

The overall derived OH radical degradation constants have been compared to 667 organic compounds whose rate constants were measured at room temperature in the gaseous phase. The results show a correlation coefficient (r^2) of 0.963 and a standard deviation of 0.218. Hence 90% of the calculated values are within a factor of 2 of the experimental ones and 95% are within a factor of 3 (AOPwin program, version 1.90). The derived ozone degradation rate constants have been compared to 112 organic compounds whose rate constants were measured at room temperature. The results show a correlation coefficient (r^2) of 0.88 and a standard deviation of 0.52. (AOPwin program, version 1.90).

For both sets of comparisons however, the compounds compared tend to be relatively simple low molecular weight organic compounds with a limited number of functional groups. The principle of the degradation rate estimation is that each individual hydroxyl radical (and ozone) reaction pathway rate can be summed to provide an overall rate constant (although

Sabljić and Peijnenburg (2001) have concluded that this has never been proven). Therefore for larger, more complex organic molecules (including most pesticides) the program generally estimates higher reaction rates (due to the larger number of possible reaction sites) although there is relatively little data available to confirm this to be correct. Nonetheless the use of established reaction pathways are sound and hence Sabljić and Peijnenburg (2001) have further concluded that this estimation is the best approach currently available for deriving degradation rates.

Further validation of the program with more complex organic molecules containing more functional groups would be helpful in increasing confidence in the accuracy of the estimations for pesticides. Also, the lack of accuracy in the predictions for haloalkanes, haloalkenes and halogenated ethers and some difficulties with ethers (Kwok and Atkinson, 1995) should be borne in mind when assessing pesticide degradation. There are also some caveats regarding the applicability of these predictions in subsequent assessments of the fate of the pesticide in actual outdoor conditions. The calculated rates in reality have been derived for “room temperatures” (up to 25°C) whilst temperatures in the troposphere may be significantly lower (particularly at more remote locations). Hence, if utilized in predictions of atmospheric concentrations the user should additionally consider the effect of temperature on reaction rates. Also, the program does not account for any effect of absorbance to particulates or water droplets on the calculated degradation rate of the compounds. In reality this process may enhance or inhibit degradation depending on compound properties and/or structure.

3.4. Deposition

“Deposition” is defined as the entry path for transport of airborne substances from the air as an environmental compartment to the earth’s surface, i.e. to an aquatic or terrestrial compartment. It is also a loss pathway for substances from the air. Dry and wet deposition should be considered separately because they are subject to different atmospheric physical processes. In essence, wet deposition is the removal of pesticides in precipitation, whilst dry deposition of particulates is due to a settling out effect (often referred to as the deposition velocity).

Dry deposition from the gaseous phase is due to the partitioning of pesticides to the soil or water phases, or uptake by plants (therefore dry deposition is influenced by the nature of the receiving body). The theoretical description of dry and wet deposition can be found in literature (see e.g. Trapp and Matthies (1998) and Asman *et al.* (2002)). Key input values for the dry deposition are the deposition velocity for the gaseous pesticide (see e.g. Thompson (1983) for a diffusion based approach) and the deposition velocity for aerosol particles.

Duyzer and Van Oss (1997) used a gas chamber to study the uptake of selected pesticides by water, soil and vegetation. The dry deposition velocity could be parameterised (most important parameters: Henry's law constant and other phase partition coefficients i.e. K_{ow} , K_{oc} , K_{oa} , and the organic carbon content of soils) within a factor of 3 for a range of 10^4 in the physicochemical properties. For agricultural soils, far away from air/soil equilibrium (oversaturation of pesticide in soil), it could be shown by Aigner *et al.* (1998) that there was no strong correlation between the organochlorine residues in those soils and their organic carbon content.

Wet deposition is determined by the precipitation rate, the air/water partition coefficient and the washout ratio for particles. The highest concentrations are observed in the beginning of a rainfall event, especially after extended dry periods. Higher pesticide concentrations can also be observed with smaller rainfall events for some pesticides. (Bucheli *et al.*, 1998, Goolsby *et al.*, 1997). Both the dry and wet deposition depends on the distribution of the pesticide in air, i.e. the fraction of substance adsorbed to aerosol. Table 3.4–1 provides an overview about the different main processes due to the initial occurrence of pesticides in the atmosphere.

Table 3.4–1: Definition of the different kinds of depositions

Initial state	Dry deposition	Wet deposition
Gaseous	Molecular, dispersive deposition	Via rainfall, substance is dissolved in rain drops
Adsorbed to particles (aerosols)	Deposition of dry aerosols, which contain adsorbed substance	Rain out of aerosols, which contains adsorbed substance

Compounds adsorbed to particulate matter are mostly found in wet deposition (Unsworth *et al.*, 1999). Compounds mostly in the vapour phase are likely to be more evenly divided between wet and dry deposition and the deposition.

The environmental compartment “air” represents a rather complex system based on its content and diversity of matter (natural and anthropogenic origin) and chemical microparticulate solid compounds (e.g. SiO_2 , Al_2O_3 , CaO , $(\text{NH}_4)_2\text{SO}_4$, metals and organic carbon). In addition atmospheric processes as well as the effect of industrial output etc cause a spatial and temporal inhomogeneity in aerosol concentration. Different types of aerosols can be identified according to their particle size:

- $< 0.1 \mu\text{m}$: Nucleus type, coagulation results to the accumulating type (see below)
- $\mu\text{m} - 1 \mu\text{m}$: accumulating in the atmospheric mixing layer, ability for long range transport (LRT)

- 1 μm : sedimentation of particles, ability for short range transport (SRT)

The size of aerosol particles determines their residence time in the atmosphere and thereby their potential for long- or short- range transport. This is also true of the particle size distribution of pesticide application sprays and hence these could be considered in the same manner as the existing aerosols in the atmosphere. Information on particle size distribution should be necessary for modelling therefore.

Van Pul *et al.* (1999) have provided an assessment of current knowledge about the atmospheric deposition of pesticides. The main conclusions related to deposition are:

- There is a shortage of measurement data to evaluate deposition processes
- The mechanisms for dispersion of pesticides can be described similarly to those for other organic pollutants
- Uncertainties are present in exchange processes at interface between air and soil/water/plants
- Uncertainties in physicochemical properties and their temperature dependency are obvious, e. g. for vapour pressure and Henry constant

3.4.1. Dry Deposition Measurements

Historically most published experiments on dry deposition have related to the terrestrial environment. Using the herbicide DCPA, Ross *et al.* (1990) studied its volatilisation, off-crop deposition and dissipation in the field (crop: onions, surrounded by parsley, wind: 1 m/s – 6.9 m/s, temperature: 9 °C - 29 °C). For the first 12 h after application (application rate: 7 kg/ha) a deposition rate of 0.02 mg m⁻² h⁻¹ was observed. The deposition rate was found to increase with increasing wind velocity and temperature. Under the specific conditions used in the volatilisation experiment, an off-crop deposition (onto foliage) could be confirmed even after 5 d – 10 d with a deposition rate of 3.9 g/ha up to 23 m distance from the target area.

Klöppel and Kördel (1997) performed field experiments in barley with a spring and summer application of bentazone/dichlorprop-p/chlorothalonil/fenpropimorph (application rates: 999, 699, 800 and 375 g/ha) and parathion-ethyl/chlorothalonil (100 and 800 g/ha), respectively. While the total amounts of herbicide and fungicide discharges were low during the treatment in spring, the downwind loss from the treated plot of the insecticide parathion-ethyl was 16-17 % of the applied amount in summer 1995, depending on meteorological parameters. For concentrations on off-crop plants (standardized grass cultures and of leaves of the natural

hedge situated downwind) it was demonstrated that both fenpropimorph uptake by plants after application in spring, and chlorothalonil uptake by plants after application in summer, resulted in high concentrations in non target plants. Fenpropimorph concentration reached its maximum about 25 h after the spray phase with 0.69 µg/g grass in a sampling height of 4 m in front of the hedge, whereas the respective concentration of 0.14 µg/g grass was found for chlorothalonil at a sampling height of 1 m.

Analysing chlorpyrifos concentration in pine needles in the Sequoia National Park (California) Aston and Seiber (1997) calculated a dry deposition rate of about 0.1 g ha⁻¹ for the period of May through October indicating that foliar uptake of pesticides might be substantial.

More recent studies have concentrated to a larger extent on the dry deposition into water bodies and also attempted to more closely attribute the relative importance of spray drift deposition and dry deposition. Siebers *et al.* (2003a) reported on measured concentrations in air (up to 250 m) and off-crop depositions (up to 50 m) after spray application of lindane, parathion and pirimicarb (application rate: 250 g/ha for each pesticide) (vapour pressure range of 10⁻⁴ Pa – 10⁻² Pa) under outdoor conditions (cereals in summer) at 20°C; the measurements included sedimentation via spray drift during application as well as dry deposition via volatilisation up to 24 h after application. To distinguish between sedimentation of spray drift and dry deposition via volatilisation, simultaneous measurement with covered (during and 10 min after application) and uncovered steel bowls filled with water have been performed.

For a distance of 10 m the highest deposition rate for lindane was determined to be 138.5 µg m⁻² during 24 h for a mean wind velocity of 3.4 m/s (50 m: 61.3 µg m⁻² during 24 h) while a second experiment with lower wind speeds and varying wind directions gave much lower deposition rates. The respective 2 h – values for a mean wind velocity of 4.7 m/s were 103.9 µg m⁻² for the 10 m distance and 42.4 µg m⁻² for 50 m, indicating that the volatilisation after application is most relevant during the first hours after application under the specific conditions. The deposition rates for parathion and pirimicarb were found to be one order of magnitude lower (Table 3.4–2). The data have also been transformed into the percentage of the applied dose and are shown in this format in Table 3.4–3.

The relative importance of dry deposition reflects the fact that drift reducing injector nozzles (Teejet AI 110025) have been used in the field experiment. However comparisons to the Rautmann *et al.* (2001) spray drift values that are used in the EU assessment procedure confirm that dry deposition would be less significant when spray reducing equipment is not

used (spray drift 0.29% at 10 m). Whereas it is possible to minimize spray drift emission to the off-crop area using appropriate application techniques (e. g. drift reducing nozzles) this does not apply to volatilisation, which is driven by mainly substance and crop specific data as well as meteorological conditions.

Table 3.4–2: Deposition ($\mu\text{g}/\text{m}^2$) in standard surface water downwind of a treated barley plot during 21 hours after application.

Distance (m)	Deposition ($\mu\text{g}/\text{m}^2$) during 21 hours after application					
	Lindane		Parathion		Pirimicarb	
	Open	Covered*	Open	Covered*	Open	Covered*
10	153	139	50	37	6.9	6.4
50	65	61	14	14	< 5	< 5

* surface water container was covered during the application

LOQ: $5 \mu\text{g}/\text{m}^2$

Covered = dry deposition only; open = spray drift deposition and dry deposition

Table 3.4–3: Percentage deposition in standard surface water downwind of a treated barley plot during 21 hours after application.

Distance (m)	% Deposition during 21 hours after application					
	Lindane		Parathion		Pirimicarb	
	Open	Covered*	Open	Covered*	Open	Covered*
10	0.61	0.56	0.20	0.15	0.03	0.03
50	0.26	0.24	0.06	0.06	<0.02	<0.02

* surface water container was covered during the application

LOQ: $5 \mu\text{g}/\text{m}^2$

Covered = dry deposition only; open = spray drift deposition and dry deposition

In an experiment by Gottesbueren *et al.* (2003), lindane (82.5 g/ha) and pendimethalin (1600 g/ha) were applied to winter barley on 11/12 Sept 2002 as a spray mixture and the dry deposition measured. The temperature during application was 19 °C (11:00h) and (on day 1) reached a maximum of 25 °C (19:00 h). The wind velocity was ca. 3.6 m/s (10:35 h – 19:00 h). Model surface waters were placed at different distances (0, 5, 20, 50 m) downwind from the edge of the field along three measurement lines (ML). The different angles of the measurement lines accounted for differences in the wind direction. During the application the waters were covered with a lid to prevent deposition from spray drift. The lids were removed 10 minutes after application. The surface waters were allowed to trap volatilised test compounds for an interval of 10 min to 24 h after the application. The water samples were then analysed for the collected compounds.

This study measured dry deposition only (see Table 3.4–4), but the authors also related the dry deposition after volatilisation to the standard spray drift predictions (2.77 % in 1 m, 0.57 % in 5 m, 0.15 % in 20 m and 0.06 % in 50 m distance (Rautmann *et al.*, 2001) that are currently used in the EU evaluation procedure. They concluded that the major contribution to surface water concentrations for pendimethalin is the drift pathway. For lindane, the measured deposition after volatilisation was similar to that from drift at short distances. However, the relevance of dry deposition as a proportion of the total exposure increased with increasing distance. In addition it should be taken into account that lindane has generally high deposition rates in experiments, which could not be explained with its relatively high vapour pressure alone.

Table 3.4–4: Residues of pendimethalin and lindane after volatilisation and dry deposition 24 hours after application in % of the application rate.

Distance (m)	Residues (% of applied)					
	ML I		ML II		ML III	
	Lindane	Pendimethalin	Lindane	Pendimethalin	Lindane	Pendimethalin
0-5	0.69	0.12	0.76	0.17	0.56	0.13
20	0.27	0.04	0.29	0.05	0.29	0.05
50	0.11	0.01	0.19	0.03	0.11	0.04

Extensive sets of experiments were undertaken in a wind tunnel to measure the dry deposition of pesticides to waterbodies (Fent, 2004). Wind tunnels have the advantage that experimental conditions (e.g. wind speed and direction, rainfall) can be controlled. However, they are a representation of the actual field behaviour and this should be recognised when extrapolating the results to field conditions.

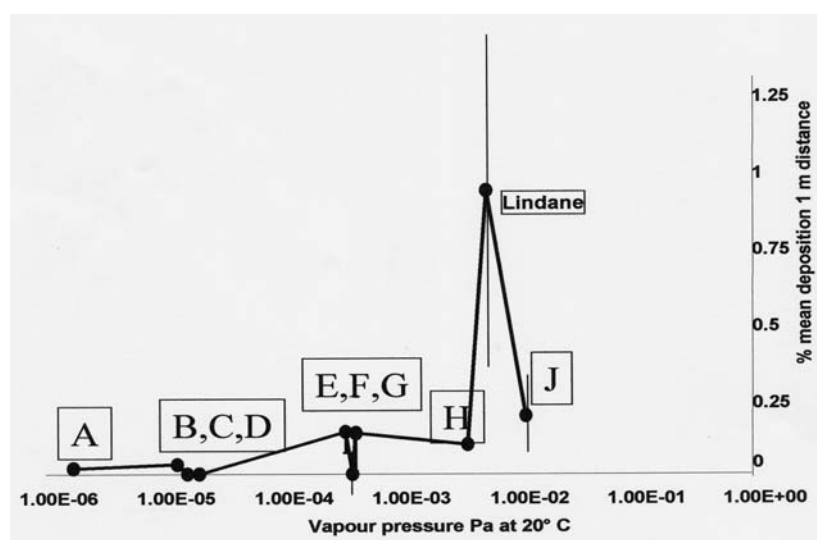
In total 15 experiments were carried out with sugar beets or barley using 10 compounds differing in vapour pressure and water solubility. The detailed important physical chemical data for the compounds are given in Table 3.4–5.

Table 3.4–5: Important Chemical and Physical Properties Of The Test Substances

	Molecular weight	Melting point	Water solubility at 20 °C ¹⁾	Vapour pressure at 20 °C ¹⁾	Henry coefficient
	Mol	°C	mg l ⁻¹	Pa	(Pa m ⁻³ mol ⁻¹)
A	307.8	105	36	1.70E-06	9.36E-07
B	342.2	-23	110	1.30E-05	7.62E-06
C	264.7	81	1.4	1.60E-05	1.45E-05
D	221.0	139	580	2.00E-05	3.31E-05
E	225.3	75.9	13	3.50E-04	4.04E-05
F	214.7	91	860	4.00E-04	9.98E-05
G	238.3	91.6	3100	4.30E-04	3.03E-03
H	246.3	-17.8	1000000	3.80E-03	6.07E-03
Lindane	290.8	113	7.3	5.60E-03	2.23E-01
J	273.5	-64.4	530	1.20E-02	6.19E-03

In total 105 datasets (1 dataset is defined as results from 1 compound, one treatment and measurements at distances between 1 and 20m from the treated field) were generated. Samples were analysed from the waterbody and the air phase. The deposition at 1 m distance from the treated field is shown in Figure 3.4–1:

Figure 3.4–1: Mean deposition for all experiments at 1 m distance as a function of vapour pressure



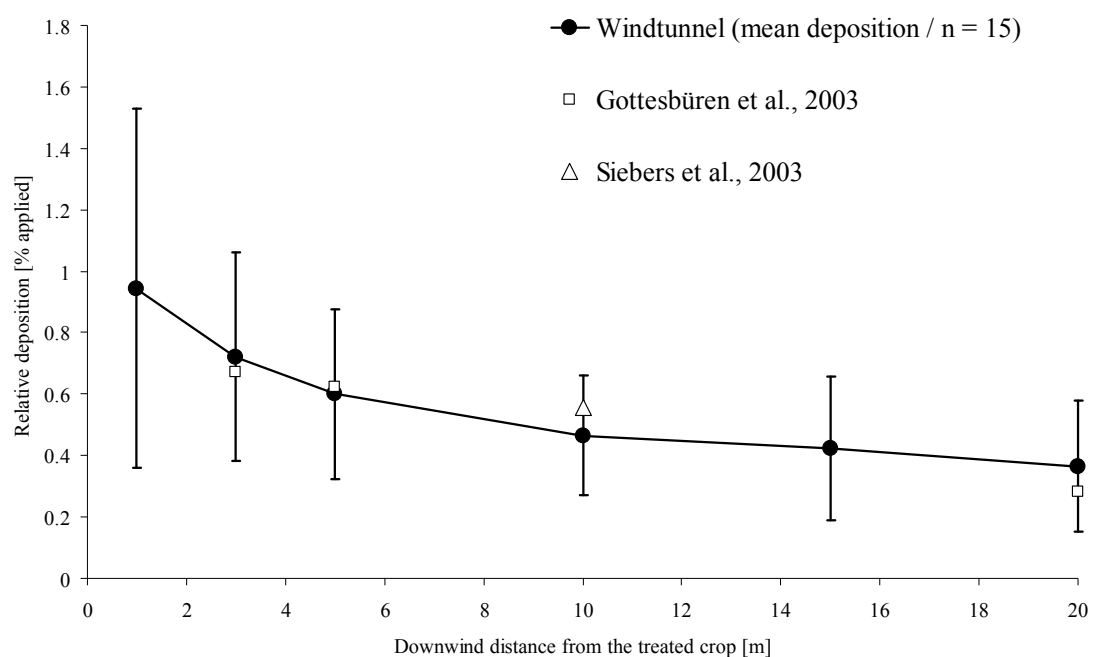
Error bars show the standard deviation of all measurements for each compound. Note: different numbers of datasets exist for each compound (3-15). Note also that the %mean deposition is calculated as the ratio between the applied dose (mass/unit area) and amount deposited (mass/unit area).

The major outcomes of all wind tunnel results can be summarized as follows:

- Despite differences in habit, morphology and LAI (4 versus 8) there was no significant effect of the volatilisation matrix (sugar beet or winter wheat)
- No consistent relationship between deposition and air temperature, air humidity or wind speed was observed. For example in comparable experiments done with wind speeds of 2m/s and 4m/s, mean deposition varied by a factor between 1.2 and 4.8 for winter wheat and 0.5 to 1.3 for sugar beet
- The deposition range of lindane observed in the wind tunnel match literature data for the deposition observed in the field
- Lindane concentrations in the air in the wind tunnel are higher than observed in the corresponding field experiment (Siebers *et. al.*, 2003a)
- Vapour pressure is the most relevant factor influencing deposition

These three experiments (Siebers *et al.*, 2003a, Gottesbeuren *et al.*, 2003, Fent, 2004) all show consistent results for lindane (see Figure 3.4–2) and therefore suggest that the different methodologies are valid and that the results are robust.

Figure 3.4–2: Lindane deposition: Comparison of field and wind tunnel experiments



Error bars show range of data

3.4.2. Wet deposition

Wet deposition of pesticides is most relevant for LRT issues since the principles of good agricultural practice prevent pesticide application when rainfall is imminent. Once rainfall occurs, pesticides will largely have moved out of the short range (1 km maximum as defined in this report) from their site of application. Due to this distance effect wet deposition is extremely difficult to correlate with particular pesticide applications at an experimental scale. Therefore it is more suited to general monitoring approaches and relevant data are provided in Section 3.5. The relative importance of dry and wet deposition to the total deposition loading appears to be still uncertain and recent information on this aspect is summarised below.

Van Dijk and Guicherit (1999) estimated depositions of pesticides (measured with bulk or wet-only samplers) of the order of a few $\text{mg ha}^{-1} \text{y}^{-1}$ up to more than $1 \text{ g ha}^{-1} \text{y}^{-1}$ for individual pesticides ($1 \text{ g ha}^{-1} \text{y}^{-1}$ equals $0.27 \mu\text{g m}^{-2} \text{d}^{-1}$). This is approximately less than one percent of the total amount applied of a pesticide. However, calculations demonstrate that this may represent many tons over larger areas for some high use pesticides. Based on results from different studies in adjacent regions, estimations of approximate amounts of atmospheric deposition over larger areas can be made. In Canada calculations estimate the deposition of individual pesticides to be in the range of 10 kg to 1 ton per million hectares during the summer season (Waite *et al.*, 1995). The variation for deposition related to different years is more than a factor of 10, which may be explained mainly by the timing of rainfall events relative to application dates. Comparing the results gathered with bulk and wet-only samplers it has been concluded by some authors (see e.g. Siebers *et al.*, 1994) that the dry deposition of pesticides is of minor importance compared to the total atmospheric deposition. However, it should be noted that funnel samplers are probably not representative for real non-target surfaces like water, soil and plants.

A new sampler with the ability to collect dry (particle deposition plus gas adsorption) and wet deposition separately has been used by Waite *et al.* (1999). The experimental results (average values) for a five weeks period in Regina (Saskatchewan) during mid-May until the end of June (most relevant for pesticide application in southern Saskatchewan) for three pesticides are given in Table 3.4–6. The sampling area was located in the south of Regina on farmland owned by the Agriculture and Agri-Food Canada Research Station.

Table 3.4–6: Average dry and wet deposition rates of Lindane, Dicamba and 2,4-D in southern Saskatchewan

	Dry deposition (mg ha⁻¹ d⁻¹)	Wet deposition (mg ha⁻¹ d⁻¹)
Lindane	3.27	< LOQ, max. 2.15
Dicamba	0.69	<LOQ, max. 1.07
2,4-D	2.76	1.89

LOQ = Limit of quantification

The construction of the sampler was designed to simulate a water surface for dry deposition; therefore measured dry deposition rates should not be considered to be representative for soil or vegetation. The results given above indicate that dry deposition, including gas exchange at the water surface, could not be neglected relative to wet deposition via precipitation. Since most semi-volatile pesticides reveal low water solubility, dry deposition to water surface is dominated by atmospheric turbulence and not by uptake or diffusion processes for these pesticides. As discussed by Van Pul *et al.* (1998) the resistance of the water surface (to air) is small compared to the transport resistance for the opposite direction from air to water. Nevertheless the initial pesticide concentration in water and the respective equilibrium concentration will determine the dry deposition rate which is the reason that even a reverse flux (volatilisation) has been reported e.g. by Bidleman *et al.* (1995). See also Section 3.6.

3.5. Monitoring Data for Wet Deposition and Atmospheric Concentrations

During the last decade a large number of field studies throughout Europe have investigated the occurrence of pesticides in the atmosphere and their subsequent deposition (most recently Duyzer and Vonk, (2003). Most studies have focused on concentration levels and deposited amounts in wet deposition, with only a limited number of studies on pesticide concentrations in air. Recently two review articles were published summarising results from pesticide monitoring studies within Europe: *i*) Van Dijk and Guicherit (1999) based on 14 air and 52 rainwater studies, and *ii*) Dubus *et al.* (2000) based on 28 rainwater studies. A comprehensive review of the occurrence and distribution of pesticides in the atmosphere within the US and Canada has also been published (Majewski and Capel, 1995). Together these compilations provide a thorough update on current knowledge on pesticide occurrence and distribution in the atmosphere.

It can be concluded that a large number of pesticides have been detected in atmospheric deposition. Today more than 80 different pesticides have been detected in precipitation in Europe and 30 in air (Van Dijk and Guicherit, 1999). A compilation of existing data by Dubus *et al.* (2000) is summarised in Table 3.5–1 and shows that pesticides have been detected in the atmosphere throughout Europe, from Italy in the south to Norway in the north. Approximately half of the compounds that were analysed for were detected. For those detected, most concentrations were below about 100 ng/L, but larger concentrations, up to a few thousand nanograms per litre, were detected occasionally at most monitoring sites. The most frequently detected compounds were lindane (γ -HCH) and its isomer (α -HCH), which were detected on 90-100% of sampling occasions at most of the sites where they were monitored. Also the herbicide atrazine was detected on a regular basis in most countries where it was monitored.

Table 3.5–1: Pesticide detections and concentrations measured in precipitation (total deposition) in a number of European studies (after Dubus *et al.*, 2000)

Pesticide	Max. conc. (ng/L)	Mean conc. of detections (ng/L)	n/N	Years	Country
Alachlor	810		5/49	88	Italy
Aldicarb	14000	1700	20/31	91-93	France*
Aldrin	310	50	10/31	91-93	France*
	180			91-92	UK
	3		8/12	90-92	Croatia
Atrazine	5000	220	7/31	91-93	France*
	1110		35/38	85-88	Germany
	650		26/42	85-88	Germany
	600		16/24	88-89	Switzerland
	430		29%	90-92	Germany
	430	105	6/21	90-91	Germany
	400		18/21	92-93	France
	380		19/21	92-93	France
	240		24%	90-92	Germany
	199		10/49	88	Italy
	160		30/54	90-92	Sweden
	140		8/21	90-91	Germany
	135	76	13/41	90-91	Germany
	135			91	France*

Pesticide	Max. conc. (ng/L)	Mean conc. of detections (ng/L)	n/N	Years	Country
	134	36	7/22	90-91	Germany
	130		6/21	90-91	Germany
	113	44	22%	90-92	Germany
	100			91	Germany
	86		1/28	92-93	Norway
	84		2/36	92-93	Norway
	80		3/16	90-91	Germany
	65			91-92	UK
	60		8/42	90-92	Sweden
	39	25	5/10	90-91	Germany
	10		3/22	91-92	Finland
Bentazone	32		21/79	90-92	Sweden
	20		14/56	90-92	Sweden
	5		5/22	91-92	Finland
Bitertanol	140	40	28/40	92	Germany
Carbaryl	110		4/26	88	Italy
Chloridazon	880	60	10/40	92	Germany
Chlorothalonil	1100	160	34/40	92	Germany
Cyanazine	120		14/21	92-93	France
	80		10/21	92-93	France
	23		3/54	90-92	Sweden
	4		1/42	90-92	Sweden
2,4-D	420			91	Germany
	70		31/56	90-92	Sweden
	48		56/79	90-92	Sweden
	8		11/22	91-92	Finland
DDD	3500	320	10/31	91-93	France*
	120	40	22/41	90-91	Germany
	84	44	4/10	90-91	Germany
	66	22	6/22	90-91	Germany
DDE	3400	350	12/31	91-93	France*
	96	49	6/22	90-91	Germany
	95	32	27/41	90-91	Germany
	18	18	1/10	90-91	Germany

Pesticide	Max. conc. (ng/L)	Mean conc. of detections (ng/L)	n/N	Years	Country
	11		9/15	92-93	France
	1.9		8/14	92-93	France
DDT	6000	500	5/31	91-93	France*
	87	40	14/41	90-91	Germany
	72	60	2/22	90-91	Germany
	17	17	1/10	90-91	Germany
	2		1/12	90-92	Croatia
Desethylatrazine	882	258	9/41	90-91	Germany
	244	111	7/22	90-91	Germany
	220		16/21	92-93	France
	170		9/38	85-88	Germany
	150		12/21	92-93	France
	113	113	1/10	90-91	Germany
	90		14/42	85-88	Germany
	70		22/54	90-92	Sweden
	17		4/42	90-92	Sweden
Desisopropylatrazine	232	103	3/22	90-91	Germany
	174	100	6/41	90-91	Germany
	133	111	3/10	90-91	Germany
Diazinon	322	82	11/41	90-91	Germany
	188	81	6/22	90-91	Germany
	117	63	4/10	90-91	Germany
	80		11/49	88	Italy
Dicamba	8		4/56	90-92	Sweden
	5		3/79	90-92	Sweden
Dichlobenil	3120		10/49	88	Italy
Dichlorprop	6200		15/40	85-88	Germany
	1810		1/49	88	Italy
	470			91	Germany
	440		16/38	85-88	Germany
	389		2/18	92-94	Denmark
	250		10/36	92-93	Norway
	190		9/22	91-92	Finland
	140		23/56	90-92	Sweden

Pesticide	Max. conc. (ng/L)	Mean conc. of detections (ng/L)	n/N	Years	Country
	129		1/16	92-94	Denmark
	92		44/79	90-92	Sweden
	40		2/28	92-93	Norway
Dieldrin	2400	500	20/31	91-93	France*
Dimethoate	20		1/25	90-92	Sweden
Etrimfos	1130		6/38	85-88	Germany
Fenporpimorph	5000	260	9/31	91-93	France*
	300	78	10/41	90-91	Germany
	69	47	5/22	90-91	Germany
	67	49	3/10	90-91	Germany
HCB	17		14/14	92-93	France
	4,5		15/15	92-93	France
	1		9/12	90-92	Croatia
HCH- α	350	70	28/31	91-93	France*
	280			91-92	UK
	230		22/35	85-88	Germany
	12	12	6%	90-92	Germany
	7		12/12	90-92	Croatia
	7		13/16	90-91	Germany
	7		20/21	90-92	Sweden
	6.9		14/14	92-93	France
	6.5		15/15	92-93	France
	6		22/22	91-92	Finland
	5		15/21	90-91	Germany
	5		12/21	90-91	Germany
	4		27/27	90-92	Sweden
		2		90-93	Denmark
HCH- γ (lindane)	833	208	39/41	90-91	Germany
	800	160	27/31	91-93	France*
	760	151	22/22	90-91	Germany
	710	171	77%	90-92	Germany
	560			91-92	UK
	550		35/40	85-88	Germany
	400	117	81%	90-92	Germany

Pesticide	Max. conc. (ng/L)	Mean conc. of detections (ng/L)	n/N	Years	Country
	360	130	15/15	91	Germany
	350			92-93	France
	310			90-92	Germany
	297			90-91	Germany
	270			90-91	Germany
	200	116	21/21	90-91	Germany
	183		9/10	90-91	Germany
	130		14/14	92-93	France
	120		16/16	90-91	Germany
	84		11/28	92-93	Norway
	73		27/27	90-92	Sweden
	43		14/36	92-93	Norway
	38		12/12	90-92	Croatia
	29		20/21	90-92	Sweden
	20		22/22	91-92	Finland
		15		90-93	Denmark
Isoproturon	6000	700	16/31	91-93	France*
	376	84	41%	90-92	Germany
	361		11/21	90-91	Germany
	230	56	31%	90-92	Germany
	168	35	41%	90-92	Germany
	136		6/21	90-91	Germany
	130		5/16	90-91	Germany
	125			91-92	UK
	62		7/21	90-91	Germany
MCPA	3190		4/49	88	Italy
	650			91	Germany
	377		1/18	92-94	Denmark
	320		10/36	92-93	Norway
	240		18/56	90-92	Sweden
	170		28/79	90-92	Sweden
	110		10/22	91-92	Finland
	89		1/16	92-94	Denmark
	48		3/28	92-93	Norway

Pesticide	Max. conc. (ng/L)	Mean conc. of detections (ng/L)	n/N	Years	Country
Mecoprop	60000	16	21/31	91-93	France*
	410		19/40	85-88	Germany
	150		13/38	85-88	Germany
	140			91	Germany
	119		1/18	92-94	Denmark
	46		42/79	90-92	Sweden
	32		7/22	91-92	Finland
	32		16/56	90-92	Sweden
Metalaxyl	480	100	19/40	92	Germany
	20		6/51	90-92	Sweden
	15		2/41	90-92	Sweden
Metazachlor	134	83	2/41	90-91	Germany
	35	29	3/22	90-91	Germany
	29	29	1/10	90-91	Germany
Methyl-parathion	3400	500	11/31	91-93	France*
Metolachlor	510	100	27/40	92	Germany
	330	215	5/41	90-91	Germany
	311	204	3/22	90-91	Germany
	212	212	1/10	90-91	Germany
Metribuzin	130	67	5/41	90-91	Germany
	60	57	2/10	90-91	Germany
	41	31	4/22	90-91	Germany
Parathion	569	254	17%	90-92	Germany
	320	122	15%	90-92	Germany
	190	117	14%	90-92	Germany
	170		11/49	88	Italy
Pendimethalin	260	165	10/41	90-91	Germany
Phorate	30		3/49	88	Italy
Pirimicarb	1300	125	11/21	90-91	Germany
	490		19%	90-92	Germany
	150		8%	90-92	Germany
	30		2/21	90-91	Germany
	<20		4/21	90-91	Germany
	14		1/42	90-92	Sweden

Pesticide	Max. conc. (ng/L)	Mean conc. of detections (ng/L)	n/N	Years	Country
	12	12	5%	90-92	Germany
	5		4/54	90-92	Sweden
Propazine	157	78	15/22	90-91	Germany
	126	50	3/10	90-91	Germany
	50	34	11/41	90-91	Germany
Propiconazole	1388	337	16/41	90-91	Germany
	295	295	1/22	90-91	Germany
	223	223	1/10	90-91	Germany
	150	50	17/40	92	Germany
	53	37	11%	90-92	Germany
	33	28	10%	90-92	Germany
Propoxur	31	31	5%	90-92	Germany
	27	23	10%	90-92	Germany
Simazine	8100			91	Germany
	680		14/21	92-93	France
	650		20/21	92-93	France
	220		17/38	85-88	Germany
	220			91-92	UK
	140	40	14/40	92	Germany
	140		18/54	90-92	Sweden
	121		17/24	88-89	Switzerland
	94	32	7/41	90-91	Germany
	70		10/42	85-88	Germany
	63	25	5/10	90-91	Germany
	44	28	2/22	90-91	Germany
	40		3/42	90-92	Sweden
Terbuconazole	320	100	15/40	92	Germany
Tebutam	92	30	10/40	92	Germany
Terbuthylazine	800		28/38	85-88	Germany
	520	100	29/40	92	Germany
	198		14/24	88-89	Switzerland
	120		14/21	92-93	France
	56		15/21	92-93	France
	50		19/54	90-92	Sweden

Pesticide	Max. conc. (ng/L)	Mean conc. of detections (ng/L)	n/N	Years	Country
	34	34	1/11	90-91	Germany
	34	24	6/11	90-91	Germany
	30		8/42	90-92	Sweden
	26	19	21%	90-92	Germany
	22	16	25%	90-92	Germany
	20	16	20%	90-92	Germany
Triadimenol	1740		6/21	90-91	Germany
	230		3/21	90-91	Germany
	60		8/21	90-91	Germany
	30		4/16	90-91	Germany
Tri-allate	2137	403	13/41	90-91	Germany
	340	176	2/10	90-91	Germany
	316	232	5/22	90-91	Germany
	200		14/41	90-92	Sweden
	9		2/53	90-92	Sweden
Trifluralin	3440		8/49	88	Italy
Vinclozolin	16	16	5%	90-92	Germany
	11	11	5%	90-92	Germany
	11	11	5%	90-92	Germany

* Measured as wet deposition.

n/N = frequency of detection – as a percentage or a fraction where n= positive results and N = number or analyses

Most of the compounds detected showed good correlation between their appearance in rainwater or peak in concentration and their local spraying season. Detection of some of these compounds can extend over a few months after the end of the local spraying season, probably because of volatilisation from treated soils and plants and long residence time in the atmosphere (Dubus *et al.*, 2000). There were also pesticide detections in rainwater at times that cannot be related to the local spraying seasons or at sites remote from application areas suggesting some form of long-range transport via the atmosphere (Dubus *et al.*, 2000).

Concentrations in precipitation depend not only upon the amount of pesticides present in the atmosphere, but also on the amounts, intensity and timing of rainfall (Van Dijk and Guicherit, 1999). The highest concentrations are observed in the beginning of a rainfall event, especially after extended dry periods.

In general, monitoring studies have been conducted under a variety of different conditions, with a lack of consistency in sampling methodologies, sampling site selection, collection time and duration, selected analytes, analytical methods and detection limits (Van Dijk and Guicherit, 1999). Study designs ranged from monitoring airborne concentrations of a single pesticide near its application site to studies that investigated concentrations of a wide variety of pesticides in areas away from agricultural areas. So far, all European studies have been short-term, lasting one to three years, and none has been on a multi-national scale, thus making it difficult to draw any general conclusions on long-term trends and large-scale atmospheric movements of pesticides. However, in an attempt to trace the origin of prohibited pesticides in precipitation in Sweden, back-trajectory analyses were performed using data based on event related sampling (Kreuger, 1995). The general conclusion was that the origin of air masses had an influence on the composition and concentration of pesticide levels in rainfall.

Most studies that have attempted to link pesticide wet deposition solely to their physico-chemical properties have failed (Dubus *et al.*, 2000). This is most likely due to the complicating effects of other factors such as amount and frequency of usage, potential for binding to dust particles etc.

3.6. Re-emission Issues Following Deposition

The majority of the literature involving air-water surface exchange of chemicals relates to persistent organic pollutants (POPs) rather than pesticides. The data comes from northern countries (North America, Scandinavia, etc), and deals with oceans, lakes, snow and ice. Even though such compounds are not used in those countries to the extent they are used in temperate or tropical regions of the globe, the so-called ‘global distillation’ (Goldberg 1975) or ‘global chromatography’ (Risebrough 1990) phenomenon or ‘grasshopper’ (Wania and Mackay 1996) or ‘cold-finger effect’ (Ottar 1981) is responsible for a significant concentration of POPs at those colder regions of the planet. In fact, northern countries receive tons of POPs per year via atmospheric transport. As is shown below, this is partially due to cycles of deposition and re-emission during transport from other regions. The same effect could potentially occur with pesticides, though there are much less data available on currently registered pesticides (as opposed to older, organo-chlorine pesticides). Also most currently registered pesticides are less volatile than POPs.

3.6.1. Re-Emission from Oceans

Duce *et al.* (1991) collected the results of two large-scale investigations of atmospheric transport, the International Decade of Ocean Exploration (IDOE) and the Sea-Air Exchange (SEAREX) program, that the U.S. National Science Foundation funded in early 1970s to mid 1980s. Measurements of organochlorine (OC) pesticides and polychlorinated biphenyls (PCBs) in marine air were carried out in the North Atlantic, North Pacific and South Pacific oceans and were used to estimate loadings into the world's oceans. It was concluded that atmospheric processes accounted for 80-99% of total loadings of the oceans while the contribution of rivers was minor on a global scale.

Chesapeake Bay in the U.S. has been the site for several gas exchange studies for PAHs (Gustafson and Dickhut, 1997, Nelson *et al.*, 1998), PCBs (Nelson *et al.*, 1998) and chlorpyrifos (McConnell *et al.*, 1997). The conclusion of the studies was, as far as emission to air is concerned, that volatilisation was taking place during March and April only. During those two months riverine inputs were the most important source of chlorpyrifos to the bay while during the rest of the year atmospheric deposition was dominant.

Iwata *et al.* (1993) estimated gas exchange fluxes of pesticides and PCBs in temperate and tropical oceans. They concluded that when the fugacity in surface water was taken into account chlordanes were near air-water equilibrium or volatilising in the temperate and tropical oceans and depositing only in the colder regions.

Several studies of HCH gas exchange in the Arctic Ocean and regional seas have been carried out since 1988 as cited by Bidleman (1999). It was concluded that atmospheric concentrations of HCHs have shown stepwise decreases over the last two decades, with a three-fold drop of since ~1990. This has brought about a change in the net exchange of α -HCH in the Bering-Chukchi seas and Canada basin from deposition in the 1980s to volatilisation in the 1990s (Falconer *et al.*, 1995, Jantunen and Bidleman 1995, Jantunen and Bidleman 1996). In the Resolute Bay in 1993 net volatilisation was found during the ice-free period for HCB, HCHs and dieldrin whereas the net flux direction was depositional for toxaphene and endosulfan (Hargrave *et al.*, 1997).

In a recent study carried out by Lakaschus *et al.* (2002) fugacity fractions were used to estimate the direction of air-sea gas exchange. These showed that α - and γ -HCH do volatilise at different latitudes, however each one to a different extent. Wiberg *et al.* (2001) collected paired boundary air and surface water samples to study the concentration and fluxes of HCH

in the Baltic Sea. They estimated the fraction of α -HCH in the boundary air-layer that had volatilised from the water.

3.6.2. Re-Emission from Lakes

A great deal of data is cited by Bidleman (1999) which shows that net deposition or volatilisation of organic compounds, including pesticides, in lakes tends to be variable. The Canada – U.S. IADN program on the Great Lakes found that gas exchange (dry deposition), rather than wet deposition or dry particulate deposition, dominated for PCBs, pesticides and 3-4 ring PAHs. However, for benzopyrenes and benzofluoranthenes wet deposition and dry deposition of particulates was most important. On an annual basis, volatilisation exceeded gas absorption by surface water for PCBs, HCB, DDE and dieldrin. Other investigations in the Great Lakes for PCBs and HCHs cited by Bidleman (1999) showed cycles of net deposition and net volatilisation, which were related to changes in atmospheric concentration and surface water temperature.

Investigations at Lake Ontario (Ridal *et al.*, 1997) indicated that volatilisation of α -HCH took place during summertime. In fact a mass balance indicated that up to 40% of the α -HCH in air over the lake in summertime was due to revolatilisation. A recent study (James *et al.*, 2001) of the volatilisation of toxaphene from Lakes Michigan and Superior provided the data to calculate the annual and seasonal fluxes of toxaphene from water to air and sediment. Lake Superior is 200-1000% saturated with toxaphene, and Lake Michigan is 200-500% saturated. It seems clear that both lakes will outgas toxaphene into the atmosphere for some considerable time in the future, and Lake Superior, because of its generally lower water temperatures and higher toxaphene concentration, will outgas toxaphene even longer than will Lake Michigan.

Two investigations (McConnell *et al.*, 1996, Iwata *et al.*, 1995) in lake Baikal in Siberia during June 1991 and May 1992 indicated volatilisation of light PCBs, chlordanes and HCB and deposition of HCHs, DDT and toxaphene.

Bow Lake is a high-altitude, glacier-fed, subalpine lake in the Canadian Rocky Mountains. A study by Blais *et al.*, 2001 showed that HCB, chlordane and most polychlorinated biphenyls volatilised to the air.

3.6.3. Re-Emission from Snow

Patton *et al.* (1988) investigated ice cores and found that freshly fallen snow had 2-6 times higher POP residues than subsurface snow. This suggests that during summertime POPs re-

volatilise from the snow as temperatures rise or may be released by changes in the physical structure of the older snow.

Atmospheric PCBs and OC pesticides have been routinely sampled (weekly) at three locations in the Canadian and Russian Arctic over several years. According to a study carried out by Halsall *et al.* (1997), re-volatilisation of PCBs off arctic surfaces plays a minor role driving the atmospheric concentrations.

3.7. Considerations for pesticide exposure

After defining distances to be used in this report for SRT, MRT and LRT and assessing the general processes that determine the fate of pesticides in air, it is then reasonable to look in more detail at the specific factors that affect SRT, MRT and LRT for pesticides. As has previously been mentioned, both meteorological factors and application practices will affect the extent of movement in the atmosphere. Meteorological factors are clearly independent of any pesticide and so are not useful for criteria to identify problematic substances. Application practices can and should be used to mitigate (where possible) the possible atmospheric exposure of a pesticide, but again are not appropriate as any sort of criteria for problematic substances. Deposition velocities for gaseous pesticides and particulates (including aerosols) are also important but these are not commonly measured properties for pesticides and it is uncertain how much the values themselves are pesticide-specific.

Once in the atmosphere, pesticides have been shown to exist in equilibrium between the vapour phase, particulate phase and a water droplet phase (which is also considered as an aerosol within the particulate phase by various authors). The amounts subsequently deposited back to soil or water by dry or wet deposition are partly dependent on which phase predominates in the atmosphere. In addition, for dry deposition, the partitioning properties between surface soil/water and air would also be broadly relevant. These partitioning characteristics can be assessed based on properties such as the Henry's law constant (air/water partition coefficient) and the soil sorption coefficients (K_{oc} , K_d). Compounds adsorbed to particulate matter are mostly found in wet deposition whilst compounds mostly in the vapour phase may be more evenly divided between wet and dry deposition. Recent data show that dry deposition (total from particulate matter and vapour exchange) is quantifiable although expected to be relatively minor in comparison to spray drift deposition at the field edge. At distances further from the field edge, the relative importance of dry deposition rises although the total exposure (dry deposition and spray drift) falls.

Further, the difference between dry and wet deposition is relevant for the distances over which a pesticide may be deposited. Only dry deposition is considered relevant for SRT. This is because normal agricultural practice is to apply pesticides when rain is not expected. By the time that rainfall may cause wet deposition of a pesticide it is considered that it will have moved out of the SRT area. For MRT and LRT wet deposition will be relevant in addition to dry deposition.

For dry deposition (for SRT, MRT and LRT) there is no clear conclusion in the literature cited about the specific effect of the air/water partition coefficient (K_{aw}) in the amount of pesticide deposited (there are competing factors in the partitioning between the vapour phase and the water droplets in air on the one hand and the surface waterbody on the other). Simulation models can predict amounts deposited based on the interaction of the relevant partition coefficients. However these predictions will depend on the way the different phases (i.e. soil, water, air etc) are defined and hence in order to obtain consistent results a single scenario or series of scenarios would probably need to be defined for “the environment”. In addition, it might be argued that the need to run a model in order to determine whether a pesticide may cause concern in the air, does not conform to a simple first tier trigger to identify whether a particular pesticide is likely to give cause for concern. Therefore it is generally not possible to conclude immediately whether higher values of K_{aw} are likely to increase or decrease the amount of dry deposition. In the case of wet deposition (MRT and LRT) the lower the K_{aw} the more likely it is for the compound to be removed in the water droplets but also the less likely it is to enter the atmosphere in the first instance.

The transformation rate in the atmosphere is clearly a generally important factor in the persistence and deposition of a pesticide. However for SRT it is unlikely to exert a significant effect since the pesticide will rapidly move out of the short-range area. In terms of LRT the DT_{50} of the pesticide is likely to be critical and other groups working on the fate of chemicals in air have used a DT_{50} of 2 days as a trigger for further consideration of LRT issues. Multimedia models assess the overall loss of compound from a compartment and hence can potentially provide a more sophisticated assessment of persistence in the form of a P_{ov} (estimate of overall persistence). Other models allow the calculation of half distances (X_t) or atmospheric residence times, which again take into account other loss processes than just transformation.

Of the pesticide properties mentioned during the previous discussions on partitioning, only the vapour pressure, water solubility, octanol/water partition coefficient (K_{ow}) and organic carbon partition constant (K_{oc}) are routinely measured as part of a pesticide registration dossier. Of the other partition coefficients, K_{aw} , (the Henry’s law coefficient) is calculated

from the vapour pressure and water solubility, whilst partition coefficients between soil and air or air and plant are estimated according to empirical relationships that usually involve K_{ow} and/or K_{oc} . This introduces a further degree of uncertainty into the reliability of trigger values based directly on these values or those on model outputs that are based on these values as inputs.

Experimental techniques are generally considered to limit the measurement of vapour pressure to values of 10^{-5} - 10^{-6} Pa. As values are obtained preferentially at ambient temperature, a standard approach for compounds of lower volatility is to raise the temperature and measure the vapour pressure under these conditions (the limit of 10^{-5} - 10^{-6} Pa relates to the vacuum that can be obtained and so is independent of temperature). There is a standard approach for correcting these data back to 20°C but it is noted that this is still an extrapolation that will be outside the range of experimental measurements of the compound in question. Also in the case of older data, these more sophisticated techniques are less likely to have been used and/or the error on the original measurement may have been greater. Water solubility measurements depend largely on the availability of analysis methods with a sufficient limit of quantification. Measuring water solubility of 1 mg/l is considered not to be any difficulty and measurements down to 1 µg/l are achievable depending on compound/analysis method etc. All water solubility measurements must be obtained at the required temperature (20-25°C) and there is no possibility to extrapolate back from solubilities at higher temperatures since compounds do not behave in a standard reproducible manner.

4. INVENTORY OF APPROPRIATE MATHEMATICAL MODELS

4.1. Important Processes

The transfer of pesticides from target to non-target areas can be split into three dominant processes: (i) emission to air (ii) transport and transformation in air (iii) deposition from air. These processes are distinct and require different modelling approaches.

A number of methods can be used to estimate emission. At the simplest level, empirical regression equations, where substance properties are related to the fraction volatilised, can be derived from volatilisation studies on soil and plants (e.g. Smit *et al.*, 1997, Smit *et al.*, 1998, Kördel *et al.*, 1999). More sophisticated approaches that take into account different substance properties, as well as environmental factors, are also available (Jury *et al.*, 1983). At a third, most complex level, volatilisation is included in a number of numerical environmental fate models that describe the behaviour of pesticides in the unsaturated zone of the soil, and in which volatilisation is one possible sink of the substance in the environment (Leistra *et al.*, 2001, Klein, 1995, PRZM, 2001).

Transport in air occurs via dispersion and convection. Convection by wind is generally the dominant process due to the greater transport velocity, hence, the transport of substances in air is mainly dependent on wind speed and wind direction. Convection occurs to pesticides in gas and particulate (i.e. small droplets sorbed to small particles) forms. Degradation in air is of minor importance for short-range-transport (up to 100m), but is one of the crucial parameters to define long-range transport potential and the characteristic travel distance. In contrast, the vertical mixing height is much more variable and thus has more influence on short-range transport compared to long-range transport.

Deposition depends on many influencing parameters. Dry deposition is the most important process for short-range transport, because pesticide application following Good Agricultural Practice will not take place prior to rainfall events. For long-range-transport, deposition is the sum of dry and wet deposition and has to be considered as a sink of the substance in air that additionally lowers the transport potential.

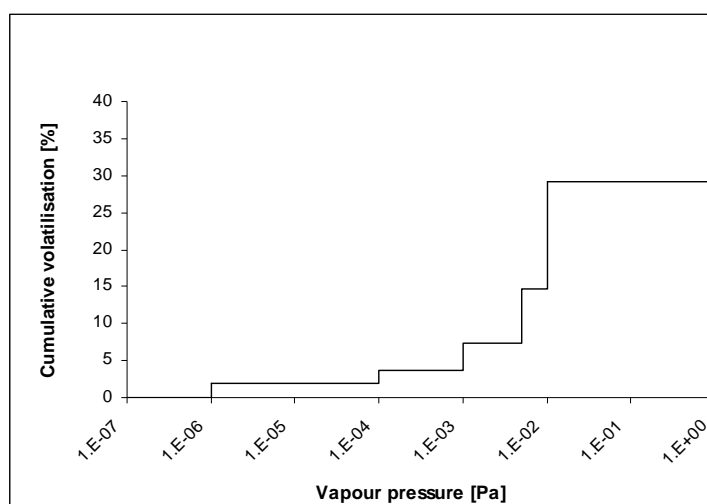
4.2. Emission

4.2.1. Empirical Approaches

4.2.1.1. Volatilisation from soil

No harmonised approach exists to estimate the volatilisation amount from soil and several attempts have been made to relate the volatilisation rate of a pesticide to its physico-chemical properties. Woodrow *et al.*, 1997 describe volatilisation rate as a function of vapour pressure. In contrast, Kördel *et al.*, 1999 consider the total volatilised amount as a function of the vapour pressure. This, latter, approach gives a rough estimate of emission rates and corresponding cumulative daily volatilisation for different vapour pressure classes. Five vapour pressure classes were identified: low volatile substances having a vapour pressure between 10^{-6} - 10^{-4} Pa; semi-volatile substances having vapour pressures between 10^{-4} - 10^{-3} Pa; semi-volatile substances having a vapour pressure between 10^{-3} - $5 \cdot 10^{-3}$ Pa; volatile substances with a vapour pressure between $5 \cdot 10^{-3}$ Pa and 10^{-2} Pa; and highly volatile substances with a vapour pressure $>10^{-2}$ Pa. The corresponding cumulative daily emissions from soil for these classes were one third of the emission from plants yielding 1.8%, 3.7% and 7.3%, 14.6% and 29.3% of the amount applied (see Figure 4.2–1).

Figure 4.2–1: The approach of Kördel *et al.*, 1999, describing the cumulative volatilisation from soil as function of the vapour pressure



Smit *et al.* (1997) used a different approach and derived an equation where the cumulative 21-day volatilisation was a function of the pesticide fraction in the gas phase ($f_{p,gas}$), which in turn was dependent on the partition coefficients of the substances in the three phases air, soil

and water. This equation is shown below:

$$CV = a + b \log(f_{p, gas}) \quad (4.2-1)$$

with $a = 71.9$ and $b = 11.6$ for average conditions, $a = 42.9$ and $b = 9.0$ for dry conditions and $a = 51.1$ and $b = 7.2$ for greenhouse conditions, yielding squared correlation coefficients of 0.76, 0.89 and 0.55, respectively.

Woodrow *et al.* (1997, 2001) correlated pesticide properties to emission rates from soil, water and plants. For volatilisation from soil, they analysed the volatilisation of substances that were applied onto the soil surface and substances that were incorporated. For surface applied substances, they obtained the correlation ($n=15$)

$$\ln(J_v) = a + b (\ln R) \quad (4.2-2)$$

in which:

J_v = volatilisation flux density ($\mu\text{g m}^{-2} \text{h}^{-1}$)

R = ratio

The value for a is 28.36 and that for b is 1.616 ($r^2=0.988$).

The ratio R is given by:

$$R = \frac{P_{v,s}}{(K_{oc} \cdot S_w)} \quad (4.2-3)$$

In which:

R = ratio

$P_{v,s}$ = saturated vapour pressure (Pa),

K_{oc} = organic carbon sorption coefficient (L kg^{-1})

S_w = water solubility in (mg L^{-1}).

In a second correlation for surface applied substances, they included the application rate of the substances resulting in the correlation ($n=15$):

$$\ln(J_v) = a + b (\ln R') \quad (4.2-4)$$

The value for a is 19.35 and that for b is 1.053 ($r^2=0.93$). The ratio R' is then given by:

$$R' = \frac{P_{v,s} \cdot AR}{(K_{oc} \cdot S_w)} \quad (4.2-5)$$

in which:

AR = application rate in (kg ha^{-1}).

Hassink *et al.*, 2003 showed that vapour pressure is the most important quantity in describing the volatilisation of pesticides from soil and plants, although they did not derive any correlations from their data.

4.2.1.2. Volatilisation from plants

Volatilisation from plants can be measured experimentally, however, in the absence of such data, emission can be estimated from knowledge of substance properties and the boundary conditions during emission. Most models, with the exception of the PEM and the Consensus-Pearl model, estimate volatilisation from plants using a volatilisation rate that is input into the model. The only other way to estimate volatilisation from plants is to use one of the following empirical regressions. All of these equations are based on the vapour pressure as the dominant substance property (Kördel *et al.*, 1999, Smit *et al.*, 1998; Woodrow, 1997) and are shown in Table 4.2–1. Note that each attempts to predict a different quantity i.e. cumulative volatilisation after 1 day, 7 days or maximum volatilisation flux. They are not therefore directly comparable and have been included here to show that vapour pressure is used by each to predict volatilisation.

Note that all of the approaches are based upon cumulative volatilisation, except the equation of Woodrow *et al.*, 1997, and that no correlation was performed for the volatilisation classes published in Kördel *et al.*, 1999, who acknowledged that the classes were arbitrary and represented a rough estimate of the cumulative volatilisation versus vapour pressure.

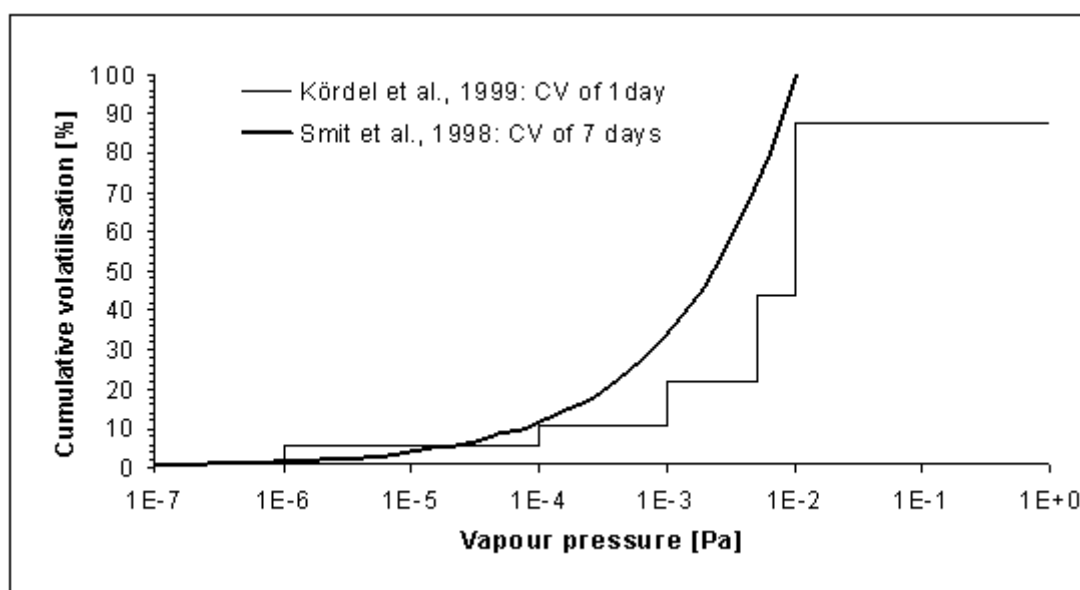
Table 4.2–1 Summary of the correlation between volatilisation from plants and vapour pressure

source	Equation	Variables	r ²	n
Kördel <i>et al.</i> , 1999	CV _{1d} =5.5% for 10 ⁻⁶ Pa < $p_{v,s}$ < 1e-4 Pa CV _{1d} =11% for 1e-4 Pa < $p_{v,s}$ < 1e-3 Pa CV _{1d} =22% for 1e-3 Pa < $p_{v,s}$ < 5e-3 Pa CV _{1d} =44% for 5e-3 Pa < $p_{v,s}$ < 1e-2 Pa CV _{1d} =88% for 1e-2 Pa < $p_{v,s}$	CV _{1d} = cumulative volatilisation after 1 day	N/A	N/A
Woodrow <i>et al.</i> , 1997	$\ln(J_v)=11.78+0.8554 \cdot p_{v,s}$	flux (µg/m ² /h)	0.989	12
Smit, 1998	$\log(CV_{7d})=1.528 + 0.466 \cdot \log(p_{v,s})$	CV _{7d} = cumulative volatilisation after 7 days $p_{v,s}$ in mPa	0.77	24

Figure 4.2–2 shows a comparison between two of the approaches. It was not possible to include the equation of Woodrow *et al.*, 1997, because this equation describes the worst-case volatilisation flux on an hourly basis (whereas the other equations describe cumulative volatilisation), and it does not consider application rate as a factor influencing total volatilisation.

The volatilisation functions of Figure 4.2–2 are in reasonable agreement, although it should be noted that the function of Smit *et al.*, 1998 is based on 7-day cumulative volatilisation and shows a slightly higher volatilisation.

Figure 4.2–2 Different approaches describing the cumulative volatilisation from plants as function of the vapour pressure



4.2.2. Mechanistic Approaches (Analytical Solutions)

4.2.2.1. Volatilisation from Soil

Jury *et al.* (1983, 1984a,b,c) presented the analytical solutions of a screening model that included volatilisation based on the partitioning of a substance in the soil. Volatilisation was therefore strongly dependent on the water-air partition coefficient, the Henry's law constant (K_H), as well as the soil-water partition-coefficient (K_d). The influence of meteorological quantities such as temperature, relative humidity and soil water evaporation from the soil to the atmosphere was also considered. Note, however, that the purpose of this model was to accurately simulate leaching and degradation, rather than volatilisation.

For volatilisation, Jury *et al.* (1983) assumed a stagnant air boundary layer of a particular thickness at the soil surface, yielding the upper boundary condition according to Fick's law:

$$J_v = -h \cdot c_{g,0} \quad (4.2-6)$$

With:

$C_{g,0}$ = gas concentration at the surface layer

$$h = \frac{D_{dif,g}}{d} \quad (4.2-7)$$

where:

$D_{dif,g}$ = diffusion coefficient of the substance in the gas phase of the soil system

d = stagnant air boundary layer thickness.

It was assumed implicitly that the concentration in the air at height d above the soil was zero.

For $D_{dif,g}$ a constant value of $0.43 \text{ m}^2 \text{ d}^{-1}$ was assumed

In contrast to the numerical models, steady state boundary conditions for the soil as well as the atmospheric parameters (e.g. water content, temperature) had to be assumed. One of the output parameters of the model is the volatilisation flux versus time, which can be integrated to obtain the cumulative emission. The greatest limitation of this approach is that it only considers emission from bare soil and cannot be used to estimate the volatilisation rate from plants.

4.2.2.2. Volatilisation from water

Trapp and Harland (1995) give a comprehensive overview of commonly used methods to estimate volatilisation from water. The classical approach to this problem is called stagnant boundary theory (Whitman, 1923; Liss and Slater, 1974) and is often referred to as the two-film model. This approach includes two stagnant boundary layers in both the air and water phase adjacent to the water-air interface. Outside of the stagnant layers, the model assumes well-mixed phases for air as well as for water. Diffusive fluxes across the layer are assumed to follow Fick's first law, and require the diffusion coefficients of the substance in both the water and the air phase. The Henry's law constant determines the air concentration at the air-water interface. The approach of Mackay and Yeun (1983) additionally includes air velocity at a given height, airside friction velocity, as well as the Schmidt-number, which is the dimensionless ratio of viscosity/(density * diffusivity).

For substances with large Henry's law constant (>0.04), Lindner *et al.* (1986) presented an approach where the volatilisation rate was exclusively dependent on the re-aeration rates of the substances in the liquid layer of the Liss and Slater (1974) approach.

4.2.3. Numerical models Simulating Volatilisation

Pesticide fate models were developed to quantify the fate of pesticides after application to crops or bare soil and have been validated against experimental data from the field and from outdoor lysimeters. Their primary purpose is to simulate leaching of pesticides to deeper soil layers, however other processes are also considered.

Models differ in the number of environmental fate processes that they consider. For residues on plants, these can include interception of the applied substance and dissipation from the plant by degradation, uptake, volatilisation and wash-off. For pesticide reaching the soil, either directly at application or after wash-off from the crop, the possible pathways are degradation, leaching to deeper soil layers, surface run-off, drainage, volatilisation, or incorporation into the soil matrix by the formation of bound soil residues.

The dominant characteristic of these models is the potential to simulate particular scenarios with variable, often highly resolved, climatic and soil boundary conditions. Most of the environmental fate (leaching) models are able to calculate volatilisation from soil, but they require a dissipation half-life to calculate volatilisation from plants. However, the new Consensus-PEARL version 2.1.1-C includes an improved description of the processes that are relevant to describe the fate of the pesticide on the plant canopy, i.e. volatilisation, transformation, penetration into the plant leaves and wash-off. Using this model, volatilisation from plants can be estimated from input of the physico-chemical properties of the pesticide and the prevailing meteorological conditions.

Numerical models that can calculate volatilisation from soil, plants or water have been collected and are shown in Appendix 1.

4.3. Transport and Deposition - Gaussian, Lagrangian, Eulerian Type Models

Different approaches have been used to describe the transport of substances through the air. The Gaussian plume concept is an empirical method that has been widely used in many studies. Physically based models have been developed that are Eulerian or Lagrangian. In the Eulerian model, the air compartment is divided into a multidimensional grid with grid cells and the transport of the substance in and out of each grid cell calculated using the mass conservation equation. Using the Lagrangian concept, the trajectory of a parcel of air or particle is simulated and along this trajectory and the removal and emission processes are taken into account. In the Lagrangian models, the convective transport by the wind as well as

the turbulent transport due to wind fluctuations is taken into account. Basically, the simulated system with respect to the earth is fixed in the Eulerian concept, whereas in the Lagrangian concept it follows the average air movement.

All three approaches are only modelling conventions and can be made to give equivalent results for the same scenario e.g. modelling the dispersion of chemical in air or water emitted from a point source. However, one approach may be favoured over another for some applications. For example, if the changing concentration with distance downwind/downstream from a source is required. Eulerian modelling suffers from the disadvantage of having to define multiple mass balance envelopes or compartments.

Van Jaarsveld and Van Pul (1999) have listed the studies in which Eulerian type models and Lagrangian type models have been used for pesticides. Lagrangian type models that have been used are ASTRAP (Voldner and Schroeder, 1989), OPS (Baart and Diederer, 1991) and EU-TREND (Van Jaarsveld *et al.*, 1997). The Eulerian type models are EUROS (Van Pul *et al.*, 1996), MATCH (Persson and Ullerstig, 1996) and ASIMD (Pekar and Van Pul, 1998).

4.3.1. Transport approaches

4.3.1.1. Gaussian type models

The Gausssian plume model is a common atmospheric dispersion model and although these models are in fact Langrangian models they are discussed seperately here due to their broad use. This modelling system is often used to describe turbulent diffusion in the atmosphere, or water bodies, for a chemical after it is emitted from a source. In this type of model, it is assumed that the concentration distributions in the horizontal and vertical directions are Gaussian at each downwind distance. This concept is described as (Pasquill and Smith, 1983):

$$c(x, y, z) = \frac{Q}{2\pi\bar{u}\sigma_y(x)\sigma_z(x)} \exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y(x)^2} + \frac{(z-h)^2}{\sigma_z(x)^2}\right)\right] \quad (4.3-1)$$

in which:

c_a = concentration of substance in air (kg m^{-3})

Q = source strength (kg s^{-1})

\bar{u} = average wind speed in the X direction (m s^{-1})

$\sigma_y(x)$ = standard deviation for the Gaussian distribution in the Y direction

$\sigma_z(x)$ = standard deviation for the Gaussian distribution in the Z direction

Y = crosswind distance (m)

Z = vertical distance (m)

h = source height (m)

In Equation 4.3-1 removal processes such as deposition and transformation are not taken into account. It is possible however to include these processes roughly in the Gaussian model in a very detailed manner (e.g. Van Jaarsveld, 1995). The difficulty in the Gaussian plume concept is to derive correct descriptions of $\sigma_y(x)$ and $\sigma_z(x)$, and various methods have been developed (e.g. Pasquill, 1971; Draxler, 1976; Briggs, 1973). Area sources can be taken into account by considering this source to be represented by a number of evenly distributed point sources. Alternatively, a virtual point source at some distance upwind from the area source can be defined to result in a plume that approximately covers the surface of the area source, thereby representing approximately the area source.

Gaussian plume models have been used in particular to assess exposures on a local scale (Moussiopoulos *et al.*, 1996).

4.3.1.2. Lagrangian type models

A Lagrangian model describes the transport of a fluid element that follows the instantaneous flow. The basic equation in the Lagrangian concept is given by (Zannetti, 1990):

$$c(x, t) = \int_{-\infty}^{t'} \int p(x, t; x', t') \cdot S(x, t) dx dt \quad (4.3-2)$$

in which:

p = probability density function for an air parcel moving from x at time t to x' at time t' .

S = source term ($\text{kg m}^{-3} \text{s}^{-1}$)

The probability function p can be described in various ways, for example by using wind speed measurements, or by using turbulence models, or Monte Carlo techniques (Zannetti, 1990). It should be noted that when assuming a normal distribution for the p function, and assuming turbulence to be stationary and homogeneous, the Gaussian plume expression can be derived.

For non-reactive substances, the p function depends only on the meteorology and, if deposition is taken into account, on the properties of the substance as well. It is difficult however to include chemical reactions in Lagrangian concept.

The Lagrangian models can be divided into different subsets of models. These subsets are the Lagrangian box or trajectory models, the Gaussian segmented plume models, the Gaussian puff models and the particle models (Zannetti, 1990).

4.3.1.3. Eulerian type models

The Eulerian concept is based on the conservation equation for a substance in the atmosphere. So for a 3-dimensional system the conservation equation is given by (Pasquill and Smith, 1983):

$$\frac{\partial c_a}{\partial t} = - \left[\frac{\partial (u c_a)}{\partial x} + \frac{\partial (v c_a)}{\partial y} + \frac{\partial (w c_a)}{\partial z} \right] + S - R \quad (4.3-3)$$

in which:

- c_a = concentration of substance in air (kg m^{-3})
- t = time (s)
- u = wind speed in X direction
- v = wind speed in Y direction
- w = wind speed in Z direction
- x = distance in X direction (m)
- y = lateral distance (m)
- z = height (m)
- S = source term ($\text{kg m}^{-3} \text{s}^{-1}$)
- R = transformation term ($\text{kg m}^{-3} \text{s}^{-1}$)

The wind speed is a vector with components u , v and w in the X, Y and Z directions, respectively. Each component is defined by the average in that direction and the eddy fluctuations around the mean:

$$u = \bar{u} + u' \quad (4.3-4a)$$

$$v = \bar{v} + v' \quad (4.3-4b)$$

$$w = \bar{w} + w' \quad (4.3-4c)$$

in which:

- \bar{u} = average wind speed in X direction (m s^{-1})
- \bar{v} = average wind speed in Y direction (m s^{-1})
- \bar{w} = average wind speed in Z direction (m s^{-1})
- u' = eddy fluctuation in X direction (m s^{-1})
- v' = eddy fluctuation in Y direction (m s^{-1})
- w' = eddy fluctuation in Z direction (m s^{-1})

After replacing each of the first three terms on the right hand side of Equation 4.3-3 by a mean and fluctuation around the mean, the following expression is obtained:

$$\frac{\partial c_a}{\partial t} = - \left[\frac{\partial (\bar{u} \bar{c}_a)}{\partial x} + \frac{\partial (\bar{v} \bar{c}_a)}{\partial y} + \frac{\partial (\bar{w} \bar{c}_a)}{\partial z} \right] - \left[\frac{\partial (\overline{u' c_a'})}{\partial x} + \frac{\partial (\overline{v' c_a'})}{\partial y} + \frac{\partial (\overline{w' c_a'})}{\partial z} \right] + S - R \quad (4.3-5)$$

To solve Equation 4.3-5 a relation has to be specified for the last three terms in this equation. The simplest method is to use K-theory, whereby the differential equation can be solved (Pasquill and Smith, 1983). This method is also described as first order closure.

$$\overline{u' c'} = -K_x \frac{\partial c}{\partial x} \quad (4.3-6a)$$

$$\overline{v' c'} = -K_y \frac{\partial c}{\partial y} \quad (4.3-6b)$$

$$\overline{w' c'} = -K_z \frac{\partial c}{\partial z} \quad (4.3-6c)$$

in which:

K_x = Eddy diffusion coefficient in the X direction ($\text{m}^2 \text{s}^{-1}$)

K_y = Eddy diffusion coefficient in the Y direction ($\text{m}^2 \text{s}^{-1}$)

K_z = Eddy diffusion coefficient in the Z direction ($\text{m}^2 \text{s}^{-1}$)

From Equations 4.3-6a to 4.3-6c it can be noted that the eddy diffusivities can be different in the X, Y and Z directions. The applicability of the K-theory has its limits, especially for systems with point sources under unstable conditions (Zannetti, 1990). Improvement of the description of the last terms in Equation 4.3-5 has been attempted by the use of higher order closure schemes (e.g. Lewellen and Teske, 1976).

4.3.2. Transformation processes

Transformation in air is generally considered not to be relevant for SRT of pesticides (due to the timescale of the relevant processes) and hence many models for SRT do not include this process. In contrast, transformation is a significant process for LRT.

Modelling approaches to transformation generally involve first order equations allowing a transformation rate (frequently obtained via the Atkinson calculation; see Section 3.3) in air to be used as a model input. In theory, transformation in the gaseous and particulate phases should be treated separately, but there is little scientific data on which to base any relationship between particulate and gaseous phase degradation. Additionally, a temperature dependence of transformation would be required for a mechanistic approach to the process, but this currently appears largely beyond the scope of the models.

4.3.3. Deposition processes

Dry deposition

Different approaches exist to simulate dry deposition. One approach is to consider deposition velocity, which considers the deposition velocity of gaseous substances to be much greater than particle-bound substances (Trapp and Matthies, 1996). Consequently, the influence of physico-chemical properties on deposition velocity is limited and the major factor influencing deposition is the air concentration above the deposition surface. This method is therefore used for deposition onto an aquatic as well as a terrestrial surface. Another approach uses the concept of resistance for the exchange of a substance between different air layers, or the exchange between air and any other surface (for example water). The deposition flux onto a surface depends on a number of resistances, such as: turbulent mixing in the air (aerodynamic resistance); a small diffusion zone (laminar boundary layer); and the surface resistance, which is influenced by the partition coefficient (for water dimensionless Henry's law coefficient).

In rapidly running shallow waters the mixing in the upper part of the water body is created by friction at the bottom. The mass transfer coefficients are also a function of the average velocity of the water body, its average depth and the slope. In lakes, slowly running or deep waters and the sea, mixing in the upper part of the water body is caused by the wind and the mass transfer coefficients increase with wind speed. For most pesticides the resistance to transport in the atmosphere limits the dry deposition and not the resistance to transport in the water body.

Wet deposition

In LRT models, wet deposition can often be modelled by a scavenging ratio approach that is used to model the deposition of gases and particles through wet removal. In this approach, the flux of material to the surface through wet deposition is the product of a scavenging ratio times the concentration, integrated in the vertical direction. The scavenging ratio is computed from a scavenging coefficient and a precipitation rate (Scire *et al.*, 1990). The scavenging coefficient depends on the characteristics of the pollutant (e.g., solubility and reactivity for gases, size distribution for particles) as well as the nature of the precipitation (e.g., liquid or frozen). The wet deposition algorithm requires precipitation type (liquid or solid) and precipitation rate. SRT models do not normally consider wet deposition.

4.4. Multimedia Models (including fugacity models)

Multimedia models are widely used as tools to help understand the fate and behaviour of chemicals in the environment. They often use the concept of fugacity (units: Pa), which was first introduced by G. N. Lewis in 1901 as an equilibrium criterion that was a convenient surrogate for chemical potential. The fugacity concept has proven to be an enlightening and elegant method of calculating multimedia equilibrium partitioning of organic contaminants in the environment. Pioneering work in this area was conducted by Mackay and Paterson (1981, 1982). Some multimedia modellers (e.g. SimpleBox, van de Meent, 1993) avoid using fugacity and fugacity capacities (or Z-values) in preference for using concentrations (which are linearly related to fugacities) and partition coefficients. It should be noted that the use of fugacity or concentration in the model equations is a case of personal preference and it does not influence the model output in itself (see Mackay, 2001).

Multimedia models are usually used for describing the fate of non-ionic organic chemicals, although they can be adapted to treat most chemicals including metals (Diamond *et al.*, 1990). Environmental partitioning coefficients are estimated from physico-chemical properties that are easily measured in the laboratory, for example, vapour pressure, water solubility and the octanol-water partition coefficient (K_{ow}). Environmental degradation processes are usually assumed to be first-order and transport between media is described using a set of transport velocities derived from field observations. Mass balance equations are used to balance environmental emissions of a chemical with environmental removal processes and concentrations (or fugacities) are derived in environmental media. The modelling concepts are discussed in some detail in Mackay (2001).

Multimedia models are based on the Eulerian coordinate system i.e. they are compartment or box models. The environment is divided or segmented into a number of volumes or boxes, which are fixed in space and usually treated as being homogenous, i.e. well-mixed in chemical composition. The compartments usually treated are air, surface water, soil, and bottom sediments (Mackay *et al.*, 1996b). Compartments can be added without appreciably increasing complexity, especially if it is assumed that they are in chemical equilibrium with an existing compartment. Examples are aerosol particles added to the air, or suspended solids and biota added to water. The equilibrium assumption avoids the necessity of writing a separate mass balance for the added phase because the concentration is related by a known partition coefficient to that of its companion compartment. Vegetation may significantly affect the environmental fate of some organic compounds and has been included in recently developed models. Vegetation is usually treated as a separate compartment in the mass

balance (Cousins and Mackay, 2001). Media may be subdivided into separate compartments to treat geographical or land use differences e.g. in the SimpleBox/EUSES model soil is divided into three types: industrial soil, agricultural soil and natural soil (van de Meent, 1993).

A number of outputs can be generated from the numerous evaluative fate models that have recently been developed to estimate long-range transport potential. It is useful to define each of these outputs to avoid confusion.

Atmospheric residence time (van Pul *et al.*, 1998)

As discussed in the previous Section, this method calculates an overall residence time of a chemical in the atmosphere including both deposition and reaction removal processes. An atmospheric half-time could be calculated in a similar way. Like all models in this Section, modelling assumptions are required to describe average deposition processes.

Characteristic travel distance (Bennett *et al.*, 1998, Beyer *et al.*, 2000, Beyer and Matthies, 2001) or Half-distance (Van Pul *et al.*, 1998)

The *characteristic travel distance* (CTD) describes the effective loss of a chemical from a mobile phase (e.g. air) and weights it with the advective transport (e.g. wind). It is the distance from the source where the initial mass in the mobile medium (air or water) drops to $1/e$, i.e. approx. 37%. CTD is determined by the balance between competitive rates of transport and loss in a mobile medium, e.g. air. The CTD is independent from the mode of entry. The *half-distance* X is the distance from the source where the initial mass in the air drops to 50%.

Spatial scale (Scheringer and Berg, 1994)

The *spatial scale* of a chemical is referred to as the tendency of a chemical to distribute in space, thus it is a measure for the area or region that might be affected by a certain chemical. The spatial scale does not consider actual amounts of emission, but is based on intrinsic properties of the chemical and the properties of the environment in which it is being transported, for example wind speed and landscape type.

Effective travel distance (Beyer *et al.*, 2000)

The effective travel distance (ETD) extends consistently the idea of the characteristic travel distance for the case of different input patterns. It takes account the fraction f of the totally emitted mass which is initially present in the mobile medium. The mass in the mobile medium

will decrease according to the same profile as the CTD, since constant physical conditions are assumed.

Spatial range (Scheringer, 1996)

The spatial range describes the distance that contains 95% of the total spatial distribution of exposure without specific assumptions on the transport and degradation processes determining the shape of that distribution.

Transport distance (Rodan *et al.*, 1999)

A fixed emission of 3,000 kg/h into each medium is assumed for all chemicals and a multimedia box model is used to calculate the initial concentration of the chemical in the air of the source area. The distance at which the initial concentration drops to 10-11 g/m³ is defined as the chemical's transport distance (TD).

Arctic Accumulation Potential (AAP) (Wania, 2003)

This metric has been developed for assessing POP chemicals and is probably not applicable for currently registered pesticides because it assumes that the chemicals are infinitely persistent in all media. It does, however, identify physical-chemical property ranges for which LRT of persistent chemicals is optimised.

4.5. Collection of models

Many environmental fate models can simulate at least one of the processes of: emission to air, short- or long-range transport, or deposition. In order to distinguish between models, and identify which were suitable for further consideration by the FOCUS Air Group, some simple screening criteria were used. The simplest criteria related to functional and organisational aspects of a model, such as availability of the program and the potential for the program to be run on a standard personal computer. Technical criteria related to the functionalities and processes covered by the models. The criteria used are shown in Table 4.5–1. Models that did not meet the criteria were excluded from further consideration.

Table 4.5–1: Step 1 screening criteria for models

General information		Model Name
		Name or number of most recent release
		Intended use of the model
		Model developers
		Institution
		Year of recent version
1 Availability	1.1	Availability of executable
	1.2	Possibility to run executable on a PC
	1.3	Availability of documentation
	1.4	Transparent version control
2 Substances	2.1	Model can be used/was already used for organic compounds
3 Processes of emission models	3.1	Calculation of emission from plants or soil or water
	3.2	Calculation of emission with help of independent parameters possible
	3.3	Temporal resolution of output ≤ 1 day
4 Processes of transport models	4.1	Consideration of area sources possible
	4.2	Consideration of gaseous and sorbed transport
	4.3	SRT models include dry deposition
	4.4	MRT/LRT models include dry and wet deposition
	4.5	MRT/LRT models consider degradation
	4.6	Model should be appropriate for use under European conditions

The models screened by the working group are shown in Appendices 1 - 3. In total 11 emission models, 63 transport and deposition models and 12 multimedia models (including fugacity type models) were screened. Whereas it was possible to find information for most of the required screening criteria for the emission models, as well as for the multi-media models, only limited information was available for many of the transport and deposition models. If

one of the required screening criteria was not met, or if it was not possible to get sufficient information for a particular model, that model was not considered further.

Seven out of the 11 emission models screened passed the Step 1 evaluation, these were:

- FOCUS-PEARL 2.2.2
- PELMO 3.3.2
- PRZM 2.4.1
- IDEFICS 3.2
- PEM 1.1
- EXAMS 2.98.03
- CONSENSUS-PEARL 2.2.1

Twelve out of 63 transport and deposition models passed Step 1 evaluation, these models were:

- PESTDEP
- ISCST3
- EVA 1.1
- EVA 2.0
- EUROS 5.4
- EUTREND 1.13
- OPS_PRO (OPS) 1.20E
- IFDM
- PLUME-PLUS 3.2
- RAMS 4.4
- ISCLT
- ASDM

Eight out of 12 multimedia models passed the Step 1 evaluation, these were:

- ELPOS 1.0
- TAPL3 2.1
- Chemrange She 2.1
- Simple Box EUSES 1.0
- CemoS 2.0
- CEMC III 3.2.7
- CalTOX 23
- IMPACT 2002

The model TaPL3 was considered to be almost identical to the CEMC Level III model as all the important features of this model are included in the CEMC model. Similarly, the ELPOS and CemoS models are very similar because they are derived from the same models.

Consequently, only ELPOS and CEMC were considered for further evaluation.

4.6. Step 2 Screening: Considerations of Scientific and Technical Quality Criteria

Additional criteria need to be applied in order to further evaluate the suitability of the models that passed the first screening step. The model checklist used by the FOCUS groundwater (FOCUS 1995) and surface water (FOCUS 1997) groups was used as a source for these additional criteria. The checklist is shown below; those criteria marked in bold have been identified as mandatory if a model was to merit further consideration.

1. General information

- **Name of model**
- **Name or number of most recent release**
- **Intended use of the model**
- **Model developers**
- **Sponsoring institution**
- **Date of most recent release**

2. Documentation and system considerations

2.1 *User manual*

- **Availability**
- Language
- Clarity
- **Defines model limitations**
- Includes conceptual model description
- Includes mathematical model description
- Includes sensitivity analysis
- Provides assistance in determining model parameters
- Provides test examples
- Provides references

2.2 *Other documentation considerations*

- **Tightness of version control**
- Availability of source code

2.3 *System considerations*

- Hardware requirements
- Run time for standard scenario
- Reliability
- Clarity of error messages

2.4 *Support*

- Method of support

- Availability of information about bugs, corrections and new versions
- Training for users

2.5 Input

- Pre-processing, e.g. meteorological data
- Meteorological input data
- Digital maps: land use, emissions
- Availability of needed data
- Data range checking
- User friendliness
- Help Utility
- Sample input files
- Database included
- Flexibility

2.6 Output

- Nature of output
- Clarity of output reports
- Echo of input parameters
- Post-processing
- User friendliness
- Help Utility
- Sample output files
- Flexibility

3. Model science

3.1 Compartments considered

- Air, Soil, Water, Plant, Benthic Sediment
- Dispersed phases: i.e. aerosols in air, particles in water droplets (treated as separate compartments or bulk compartments)
- Compartment segmentation (e.g. horizons in soil profile, layers in atmosphere)

3.2 Numerical technique

- adequacy of algorithm
- definitions of boundary conditions
- stability
- numerical dispersion
- time step
- implicit/ explicit
- grid cell size

3.3 Processes considered

- emission, transport, degradation
- only emission
- only transport and degradation

3.4 Emission model

- type of emission: point, line or area source, single source or multiple sources (in time and space), source height
- type of emission: pulse or steady state

3.5 Atmospheric transport model

- type: Gaussian plume, Lagrangian, Eulerian, trajectory or compartment model
- spatial scale: 0-1 km, 1-1000 km, > 1000km (e.g. short, medium and long range transport)
- temporal scale (if dynamic): hour, month, year or steady state?
- possibility to consider dynamic (decreasing) emission rates.

3.6 Deposition model

- wet deposition, dry deposition

3.7 Substance model

- emission: source surface (soil, plant, water), source strength, effect of environmental conditions on source strength
- transformation: type of model, effect of environmental conditions, biotic or abiotic, compartments considered
- distribution in air: dissolution in water droplets, sorption to air-borne particles

3.8 Degree of validation

- List of published validation tests. For each reference, the following items should be specified:
- The names of the chemicals
- The name and version of the model
- Area and sources considered in model test
- Meteo data set used
- Temporal and spatial scale and resolution
- All input independently derived from experiments or observations in the environment (Yes/No)

The evaluation of the models can be found in Appendices 4 through 6. Three models (CALPUFF, CALGRID, MESOPUFF II) passed the Step 1 evaluation but were not evaluated further due to lack of information provided for these models.

4.7. Results from the model evaluation

4.7.1. Estimating volatilisation of pesticides

There are many data on the volatilisation of pesticides measured in laboratory systems and field experiments. These data provide the best estimates of emission and should be used if

available. There are, however, a number of methods that can be used to estimate volatilisation (see Chapter 2). For example, simple regression tools derived from experimental data (see Section 4.2.1), or alternatively, more sophisticated tools that take into account more influencing factors and varying boundary conditions.

4.7.1.1. Numerical models to calculate volatilisation from soil

The models PEARL, PELMO and PRZM simulate pesticide behaviour in the soil (e.g. leaching to deeper soil layers). They consider volatilisation from soil an emission pathway and calculate the partitioning between soil air and water by using partition coefficients. However these volatilisation routines have a poor validation status. One aim of the APECOP project (Vanclooster *et al.*, 2003) was to test and to develop these routines. They found that the FOCUS versions of these models did not adequately reproduce measured volatilisation from soil and needed improvement. Van den Berg *et al.* (2003) suggested improvements to the PEARL and the PELMO models that lead to better agreement between measured and simulated volatilisation rates. However more testing of the modified models is necessary, and the modifications have yet to be included into the FOCUS versions of the models.

FOCUS-PRZM (version 2.4.1)

The FOCUS-PRZM model (Carsel *et al.*, 1998 and PRZM, 2001) considers volatilisation according to the boundary air layer concept of Jury *et al.* (1983). In contrast to the PELMO approach, a fixed 5mm boundary layer is used (Carsel *et al.*, 1998) and the molecular diffusion coefficient is set to 0.43 m d^{-2} (the same value is used in FOCUS PELMO) and cannot be changed. Volatilisation flux through the plant canopy uses a simplified micrometeorological approach where the wind speed at a fixed height (10m) and height of the plant canopy are used as input parameters. Wind speed is input via meteorological files. Volatilisation from plants cannot be calculated directly, but is estimated by means of a first-order dissipation process governed by a rate constant input by the user.

FOCUS-PELMO (version 3.3.2)

Volatilisation in FOCUS-PELMO depends on the concentration in the air phase of the soil, which is calculated by water-air and water-soil partition coefficients (K_f and K_H values). Transport of the soil air to the atmosphere is controlled by the aerial diffusion rate as well as the so-called “active boundary layer”, representing the effective diffusion length of the soil air to the atmosphere. The default value for the diffusion coefficient is $0.05 \text{ cm}^2 \text{ s}^{-1}$ according to Jury *et al.* (1983) assuming a 1mm active boundary layer. Volatilisation varies inversely with boundary layer thickness, thus, higher volatilisation occurs through thinner boundary layers.

Volatilisation from plants is calculated by a linear or exponential process using a rate constant input by the user.

FOCUS-PEARL (version 1.1.1)

FOCUS-PEARL was developed from the SWAP hydrology model (Van Dam 1997) and the pesticide fate models PESTLA (Van den Berg and Boesten, 1998) and PESTRAS (Tiktak *et al.*, 1994). Soil water transport is described by Richard's equation, which distinguishes this model from FOCUS PELMO and PRZM. Volatilisation is, however, treated in a similar way. Concentrations of the active substance in the various phases are calculated using partition coefficients (Freundlich parameters and Henry's law constant) and transport within the gas phase is according to Fick's law and the boundary layer approach of Jury *et al.* (1983). Following the suggestion of Jury *et al.* (1983) a default value for the diffusion coefficient (D_G^{air} of Jury) of a pesticide in air is $0.43 \text{ m}^2 \text{ s}^{-1}$. An exponential approach is used to consider the temperature dependence of the diffusion coefficient. The model provides three possibilities to estimate the relative diffusion coefficient for transport in the gas phase of the soil as described by Jin and Jury (1996). Volatilisation is dependent on the gradient of the concentration in the upper compartment of the soil, as well as diffusion through the stagnant boundary layer. An overall resistance of diffusion from the centre of the upper layer to the atmosphere is calculated which determines the volatilisation flux.

Film volatilisation from the soil surface has not yet been implemented. Again, volatilisation from plants can only be taken into account as a first order dissipation process with input of a dissipation half-life of volatilisation.

CONSENSUS PEARL (version 2.1.1)

Consensus-PEARL was developed from FOCUS-PEARL. Hourly meteorological data can be input into the model leading to an hourly calculation of water and pesticide fluxes. The volatilisation process has been improved by the inclusion of an option that calculates the volatilisation using the concept of resistance to transport from the soil surface into the atmosphere. Resistances depend on the prevailing meteorological conditions. In addition, the decrease in the volatilisation flux as the soil dries is described by an increase in the coefficient of soil sorption at moisture conditions higher than the wilting point.

4.7.1.2. Volatilisation from soil and plants

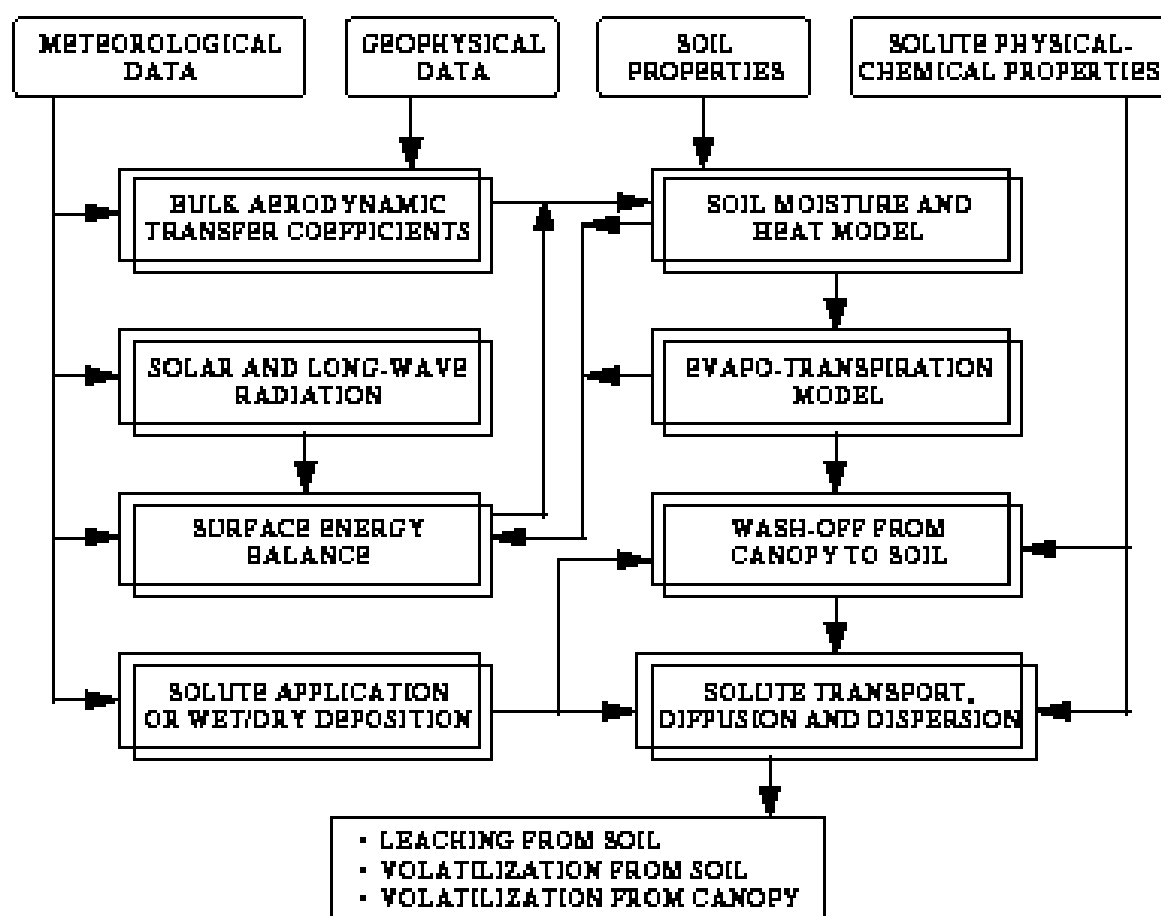
PEM

In contrast to the FOCUS leaching models, PEM was specifically developed for the simulation of volatilisation of pesticides from soil and plants. Emission from soil was tested by comparison against the analytical solution of the Jury model (BAM - Jury *et al.*, 1983). Sufficient agreement between the numerical and the analytical solution was found (Scholtz *et al.*, 2002b). The emission flux of triallate and trifluralin was in reasonable agreement with field data (Scholtz *et al.*, 2002b). However, more testing of the model is necessary, especially against experimental data on cumulative emission.

The following description of the PEM model is taken from Scholtz *et al.* (1999) and Scholtz and Van Heyst (2001). The PEM model is a numerical volatilisation model that concentrates on the volatilisation of pesticides. It considers the advection and diffusion of heat, moisture and pesticide concentration in agricultural soils in either the presence or absence of a crop canopy. The model is driven by hourly meteorological data available from climate observing stations or from meteorological models. Figure 4.7–1 shows the main modules of the pesticide emission model and the input data requirements. Horizontal diffusion and advection are neglected in the soil column, which is divided into 45 variable spaced levels over a 1 m soil depth. The time dependent, one-dimensional governing equations for heat, moisture and pesticide concentration are solved using a finite element technique with a time step of 20 minutes.

At the surface, PEM is coupled to the atmospheric surface layer through a surface energy balance. The sensible and latent heat fluxes are modelled using similarity theory for the atmospheric surface layer, while the radiative heat fluxes are modelled using a simple radiation model that employs the incoming solar radiation at the ground surface. Soil moisture and heat fluxes at the surface are modelled by PEM. A comparison of modelled and measured volatilisation fluxes from bare soils for spray applied triallate and trifluralin has been conducted and shows good agreement between the field data and model estimates over a five day period following pesticide application (Scholtz *et al.*, 1994). PEM is also coupled to a modified ‘big leaf’ canopy sub-model that includes interception of post-emergent spray by the canopy, as well as the subsequent volatilisation and/or wash off during precipitation events. Complete details of the pesticide emission model can be found in Scholtz *et al.* (1997).

Figure 4.7–1: Processes implemented in the PEM model.



PEM supports three different modes of pesticide application. In the seed treated mode, the pesticide is applied at the time of planting in the form of treated seed or in-furrow application centred at a depth of 7 cm. This mode effectively buries the pesticide beneath the soil surface with little pesticide exposed to the atmosphere. The soil-incorporated mode involves the application of the pesticide at the time of tilling during the preparation of the soil for planting. In this mode, it is assumed that the pesticide is uniformly mixed in the upper 10 cm of the soil column. In the spray-applied mode, the pesticide is applied to the soil and/or canopy surface in the form of a spray or dust. There is little penetration of the pesticide into the soil column (assumed to be all within the upper 1 cm) and the applied pesticide is immediately exposed to the atmosphere. PEM allows for four different timings associated with the spray application: a pre-emergent spray, an early growing season post-emergent spray, a mid-growing season post-emergent spray and a late growing season post-emergent spray. In the case of the post-emergent sprays, part of the applied pesticide will remain on the crop canopy.

A comprehensive overview of the equations implemented in PEM is given in Scholtz *et al.* (2002a), and evaluation is presented in Scholtz *et al.* (2002b).

CONSENSUS PEARL

Consensus PEARL describes the fate of a pesticide on the canopy, i.e. volatilisation, transformation, penetration into the plant tissue and wash-off. The volatilisation rate can either be calculated on the basis of the laminar boundary layer concept, or the transport resistance concept. The rate depends on the vapour pressure of the substance and the prevailing meteorological conditions (e.g. air temperature). The rate of phototransformation depends on the solar radiation. A detailed description of the processes included in the new version is given by (Leistra and Wolters, 2004; Leistra *et al.*, 2004)

The new Consensus-PEARL can be used to calculate the volatilisation from plant surfaces on an hourly basis under the prevailing meteorological conditions. Conservative estimates of the cumulative volatilisation during the first 24 hours can be made assuming that competing processes such as transformation, penetration into the plant tissue and wash-off do not occur. The cumulative volatilisation then depends only on the physico-chemical properties of the substance (in particular the vapour pressure) and the meteorological conditions. The model was used to predict the cumulative volatilisation of seven different pesticides having different vapour pressures by assuming the boundary layer concept. Results are shown in Table 4.7–1. From this Table it can be seen that the model predicted almost complete volatilisation for the substance having the highest vapour pressure and only 0.06% volatilisation for the substance having the lowest vapour pressure.

Table 4.7–1: Cumulative volatilisation 24 hours after application computed by Consensus-PEARL. Meteorological data obtained from wind tunnel experiment (Fent, 2004). Average air temperature 15 °C.

	Vapour pressure [§] (Pa)	Cumulative volatilisation during first 24 hours (%)
fonofos	2.8E-02 [†]	99.5
lindane	5.6E-03	70.7
chlorpyrifos	2.7E-03 [†]	31
fenpropimorph	2.2E-03 [‡]	40
ethofumesate	6.5E-4 [†]	7.1
triforine	2.7E-5 [†]	0.31
simazine	3.0E-6 [†]	0.06

§ Values taken from Linders *et al.* 1994.

† At 25 °C

‡ At 20 °C

A single substance, fenpropimorph, was chosen to investigate the effect of other processes on the prediction of volatilisation. The model was set up to mimic the conditions in the wind tunnel experiment for lindane at 15 °C (Fent 2004). A laminar boundary layer was therefore assumed, as was a boundary layer thickness of 1mm, which was obtained by calibration against wind tunnel data (Leistra and Wolters 2004). Firstly, no competing processes were considered, which yielded a value of 39.5% volatilisation over 24 hours, then each of the competing processes was added in turn starting with phototransformation. Fenpropimorph is known to undergo phototransformation on leaf surfaces with a rate coefficient of about 1.6 d⁻¹. When this process was added the cumulative volatilisation fell to 26.7%. Leistra and Wolters (2004) determined the rate constant for penetration of fenpropimorph into leaves to be 2.1 d⁻¹. The cumulative volatilisation fell to 15.3% when this process was included in the calculations. To investigate the effect of wash-off a 2mm/hour rainfall event was assumed to occur between 7 and 12 hours after application, a wash-off coefficient of 0.05% mm⁻¹ was also assumed. Cumulative volatilisation decreased slightly to 14.4%. The calculated cumulative volatilisation values are shown in Table 4.7–2.

Table 4.7–2: Computed mass balance terms for fenpropimorph 24 h after application. Meteorological data obtained from wind tunnel experiment (Fent, 2004). Average air temperature 15 °C.

Processes considered	Mass balance terms for fenpropimorph at 24 h after application (% of dosage)				
	Remaining on plant	Volatilisation	Transformation	Penetration	Wash-off
Volatilisation	60.5	39.5	0	0	0
Volatilisation + Transformation	20.6	26.7	52.6	0	0
Volatilisation + Transformation + Penetration	2.5	15.3	27.7	54.5	0
Volatilisation + Transformation + Penetration + Wash-off	1.5	14.4	25.2	49.7	9.2

Consensus PEARL was also used to compute the cumulative volatilisation of lindane in three experiments done in the Neustadt wind tunnel at different temperatures (Fent 2004). Here, lindane was applied in a mix with 8 other pesticides at a rate of 200 g/ha. Results of the computations are shown in Table 4.7–3.

Table 4.7–3: Computed cumulative volatilisation of lindane 24 hours after application using Consensus PEARL (version 2.1.1-C). Meteorological data obtained from wind tunnel experiment (Fent , 2004). Average air temperature 15 °C.

Experiment	Average temperature (°C)	Cumulative volatilisation during first 24 hours (%)
1	5.6	27.2
2	10.8	50.5
3	14.9	70.7

The model predicted cumulative volatilisation to increase with temperature with about 71% volatilisation in the first 24 hours at 14.9 °C and 27% at 5.6 °C. In the wind tunnel experiment, however, this relationship was not observed, indeed, the volatilisation rate at 5.6 °C was slightly higher than that at 10.8 °C. It is unclear why no temperature relationship was observed in the experiments, although it should be noted that no measurements of the source strength were made.

The wind tunnel studies measured concentrations of lindane in the air of the wind tunnel and deposition of lindane into water. Neither of these quantities were found to increase with increasing temperature in an obvious way. Air concentration was highest at a temperature of 15.9 °C but was lowest at 10.8 °C, conversely the highest deposition was measured at the lowest temperature, whereas that for the other two temperatures was similar. The predictions of the consensus PEARL model and the data of the wind tunnel are not directly comparable as no measurement of cumulative volatilisation was made in the wind tunnel. It is clear however that further data are required to establish the ability of models to predict volatilisation observed in field and semi-field experiments.

4.7.1.3. Volatilisation from water

EXAMS

EXAMS is a pesticide fate model of the aquatic environment. It includes numerous processes, such as transport within the aquatic body, degradation, and exchange with sediment and aquatic plants. Volatilisation is one loss pathway. Transport across the air-water interface uses a two-resistance model. The rate of interphase transport is estimated by calculating the sequential resistance to movement through an aqueous and a gaseous “film” at the air-water interface. The flux of a compound through the aqueous film is described using Fick’s first law in combination with a stagnant boundary layer. Gas exchange processes are then formulated by calculating the flux with the help of a conductivity parameter (also known as the mass transfer coefficient, permeability coefficient, adsorption/exit coefficient, or piston velocity) for the liquid and gas phases. The partitioning of the (unionized) substance across the air-water interface is calculated according to Henry’s Law. The volatilisation routine is poorly validated against experimental data.

4.7.2. Estimating transport and deposition of pesticides

The dispersion of pesticides in air at different scales can be assessed using a number of different models, ranging from simple multimedia box models to advanced deterministic models that require detailed input data (e.g. meteorological data, land use data).

4.7.2.1. Multimedia Box Models

Six multimedia box type models passed the Step 1 screening criteria. The EVA model is appropriate for estimating transport and deposition at the short-range; the other models that passed the screening criteria, CalTox, CEMC Level III, Chemrange, ELPOS and Simple Box, are more appropriate for estimating transport and deposition at the medium- and long-ranges. The EVA 1.1 model estimates the emission during the first 24 h after application for each of 5

vapour pressure classes. The aerial concentration in a box with predefined dimensions above the target area is then calculated assuming a steady state within the box. The decrease in concentration with distance is then calculated according to the Gaussian plume concept, assuming neutral atmospheric conditions and a constant wind speed. Dry molecular and particle deposition on the surface is calculated from the concentration in air and the deposition velocities for each phase. Wet deposition is not considered.

The advantage of EVA 1.1 is that only a few basic input data are required, such as the vapour pressure and application rate, and that the model is easy to use. The disadvantage is that substantial simplifications have been made (e.g. representation of the source by a box, selection of dispersion parameters), so the model is better suited to rank chemicals with respect to their deposition than to obtain a reliable value for the deposition in a specific field situation.

Fent (2004) measured the effect of physico-chemical and environmental factors on deposition in a series of wind-tunnel experiments. He found substantial deviations between the expected relationships between these factors (i.e. those implemented in models like EVA 1.1) and those observed, and concluded that deposition was dependent upon these processes in a complex and as yet unexplained way. The effect of a single factor, such as wind speed or air temperature, on the aeric mass deposited could not be assessed because the source strength (volatilisation rate) was not measured separately, and no set of experiments was available in which unintended variation of other factors could be completely avoided. Confirmation of expected relationships between temperature or wind speed was therefore not possible. Consequently, further work is required to understand the processes governing deposition in order that process-based models, such as EVA 1.1, could be improved.

In the absence of this improved understanding, the results of the wind-tunnel study were used to establish an empirical model that calculates realistic, worst-case deposition derived from the wind-tunnel data. This approach forms the basis of a new model termed EVA2.0, which is an empirical model in which the individual processes of emission, transport and deposition are not described separately. As a consequence, a completely empirical version, EVA 2.0, was developed based on the measured deposition data of substances volatilized in an outdoor windtunnel. In EVA 2.0 only the vapour pressure and the deposition after volatilization was correlated. As a confirmation of its conservatism, EVA 2.0 provides a higher prediction for deposited pesticides than measured in two available field volatilization trials. Lindane was used to define a worst-case deposition scenario since significantly higher lindane deposits were observed than expected from the series of vapour pressures of substances involved in the windtunnel trials.

It should be noted that the depositions observed in the wind tunnel experiments were in the range of those observed in field studies (Siebers *et al.* 2003b, Gottesbüren *et al.*, 2003) for lindane. This is reasonable because, on the one hand, the wind tunnel design is more conservative than a field study due to the walls of the tunnel preventing dispersion and diffusion, on the other, the limited length of the cropped area (25m) may reduce the amount of substance volatilised compared to the field, where the plot length is likely to be considerably larger. The German UBA (Federal Environmental Agency) has now adopted the EVA 2.0 model into the authorisation procedure for short-range transport on the basis of the wind tunnel results.

The deposition data in EVA 2.0 relate to the deposition onto water. These data can be used as a first rough approximation to estimate deposition onto soil. Currently, all experimental data on deposition after volatilisation measure deposition onto water. When data become available on deposition onto soil, then these data should be considered to improve the estimation of this quantity in the assessment scheme outlined in Chapter 5.

The EVA 2.0 model uses the assumption that deposition after volatilisation from soil is one third of the deposition after volatilisation from plants. The justification for this assumption comes from Kördel *et al.* (1999) who derived this value from measured volatilization data of an interlaboratory study with two substances and 11 different comparisons reported by Walter *et al.* (1996).

The wind tunnel results (Fent 2004) and field experiments (Siebers *et. al.*, 2003b, Gottesbüren *et. al.*, 2003) show that vapour pressure is the most important parameter influencing environmental exposure via air. Using these data, five vapour pressure classes were established in the EVA 2.0 model. These are shown in Table 4.7–4.

Table 4.7– 4.: Vapour pressure classes and corresponding deposition rates at 1 m distance as implemented in EVA 2.0 (volatilisation from arable crops)

Vapour pressure range at 20 °C	Deposition (% of application rate)
$vp < 10^{-5} \text{ Pa (plant)}$ $vp < 10^{-4} \text{ Pa (soil)}$	0.00 %
$10^{-4} \text{ Pa} > vp \geq 10^{-5} \text{ Pa}$	0.09 %
$5 \cdot 10^{-3} \text{ Pa} > vp \geq 10^{-4} \text{ Pa}$	0.22 %
$vp \geq 5 \cdot 10^{-3} \text{ Pa}$	1.56 %

The deposition rates shown in Table 4.7–4 are the 90th percentile deposition for the substance having the highest deposition in each vapour pressure class measured at 1m in the wind tunnel

studies. Figure 4.7–2 shows the cumulative deposition for the vapour pressure classes in EVA 2.0 compared to the experimental data upon which they are based.

Figure 4.7– 2 Vapour pressure classes of EVA 2.0 and observed deposition rates from the wind tunnel experiment at 1 m from the treated field (deposition is expressed as percent of applied mass per unit area)

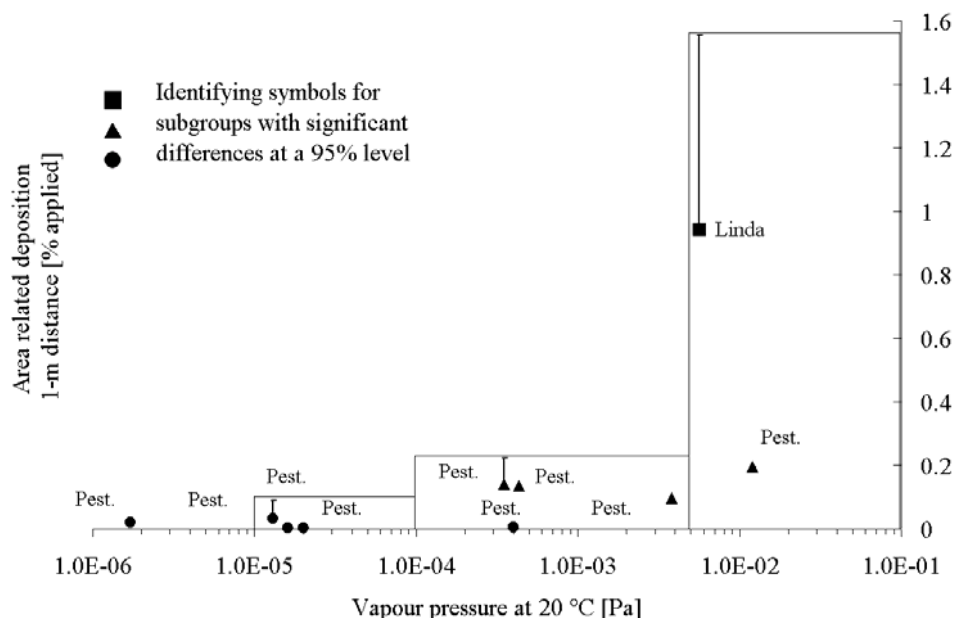
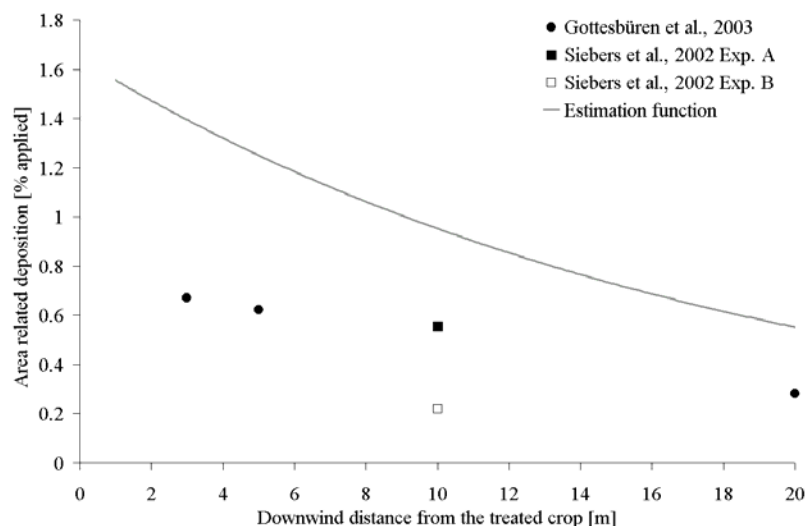


Figure 4.7–3 shows the deposition for lindane estimated by EVA 2.0 compared to field data for the same substance. From this Figure it can be seen that the deposition calculated by EVA 2.0 is conservative.

Figure 4.7– 3 EVA 2.0 predicted deposition of lindane compared to observed deposition rates from field experiments (deposition is expressed as percent of applied mass per unit area)



The following relationship was derived from the wind tunnel data for the decrease of deposition with distance: $DEP(x) = DEP(1) \cdot \exp(-0.05446 \cdot (x-1))$ ($r^2 = 0.985$),

where x is the distance from the field edge in metres, and $DEP(1)$ is the deposition value 1 m from edge of the field for the relevant vapour pressure class. The following assumptions were made when constructing the EVA 2.0 model from the wind tunnel data:

- A vapour pressure trigger of 10^{-4} Pa for application to soil and 10^{-5} Pa for application to plants.
- Vapour pressure classes and deposition at 1m as given in Table 4.7–4
- Interception values according to the FOCUS groundwater report (FOCUS, 2000) to calculate the fraction of the application on plants and soil.
- deposition after volatilisation from plants is 3-times that from soil
- deposition after volatilisation from orchards, vines and hops is twice that of field crops.
- Single volatilisation events only are considered even in the case of multiple applications.
- First order degradation kinetics is used for the calculation of PEC_{actual} and PEC_{twa} values.

Although 15 experiments were carried out and 10 different pesticides were investigated, the number of measurements on which the 90th percentile of deposition class is based is limited. Furthermore, experimental conditions in the wind tunnel did not cover the whole range of conditions that can occur in the field. Therefore, more measurements for different pesticides under different weather conditions are needed to further verify the worst-case nature of the proposed exposure assessment. It should be noted that EVA 2.0 contains only one built-in scenario and it cannot be determined at the moment whether this model is worst-case in all scenarios in all EU Member States.

4.7.2.2. Gaussian Lagrangian and Eulerian Models

The Gaussian plume models (see Section 4.3) are widely used to calculate the dispersion of pollutants in air from a variety of sources, both urban and non-urban. The following models passed the screening criteria detailed in Section 4.5 and could, in principle, be used to estimate dispersion and deposition of pesticides: CTDM Plus IFDM, OML-Multi, PAL-DS and Plume Plus. These models can be used to calculate dispersion of vapours up to tens of km from the source. PlumePlus also considers the dispersion of aerosols and both wet and dry

deposition are included. No information was available on the testing of PlumePlus. The OML model has, however, been tested (Berkowicz *et al.*, 1986 and Olesen, 1995a,b).

The following Eulerian models passed the screening phase: EUROS (medium-range), RAMS-HYPACT (medium and long-range), and CALGRID (medium-range). Emission sources and meteorological data are specified on a gridcell basis in Eulerian models.

EUROS describes the partitioning of the substance between the air, aerosol surface and water droplets; transformation is described using first order kinetics. Input is specified on an hourly basis. The transport and deposition (wet and dry) routines have been tested by Van Loon (1994, 1995, 1996). Detailed analysis of the distribution of lindane in the air, water and soil compartments have been reported by Jacobs and Van Pul (1996). The EUROS model has also been used to compute lindane deposition patterns over EUROPE using emission data from the ESQUAD project (Van Pul *et al.*, 1996).

The CALGRID model can be used to calculate the dispersion at the medium-range scale. Dry deposition and transformation in the gas phase only are considered. No information could be found regarding the testing of CALGRID against measurements.

RAMS and HYPACT can be used in conjunction. RAMS uses meteorological data from the European Centre for Medium Range Weather Forecasting (ECMWF) to calculate the dispersion of pollutants in the atmosphere. These data are then input into HYPACT to calculate dry deposition (wet deposition is not considered). There are no data available on the validation of these models against experimental data.

The following models use a combination of the Gaussian and Lagrangian approaches and passed the screening criteria: EU-TREND, ISCST3, OPS, and PESTDEP. The ISCST3 and PESTDEP models can be used to calculate the dispersion of vapours (not aerosols) and deposition on the short-range and beyond (up 10 km for PESTDEP and tens of km for ISCST3).

PESTDEP was developed to estimate the dry deposition of gaseous pesticides into water up to a distance of 10km from the source. Volatilisation from crops and soil is described by empirical relationships between measured volatilisation rates of pesticides and their physico-chemical properties (Smit *et al.*, 1997, 1998). Cumulative volatilisation is calculated up to 21 days after application to normal moist soil.

Atmospheric transport and mixing considers the pesticide to be released at a low height; mixing in the air column occurs by turbulence, which increases with height according to a

logarithmic wind profile. Three zones are considered: the emission zone, the non-spray zone, and the water body. No deposition occurs in the no-spray zone in order to maximise deposition into the water body, which occurs via dry deposition only. Similarly the emission area is always assumed to be perpendicular to the water body, and the wind direction is always from the direction of the emission towards the water body.

Asman and Hoffmann (personal communication) tested PESTDEP against the wind tunnel data of Fent (2004). They found that the deposition predicted by the model was 2 to over 10 times that measured in the experiment. Although they noted that it was difficult to parameterise the model to reproduce the conditions of the wind tunnel, especially the wind profile and the effect of the tunnel wall on dispersion.

The OPS model can be used to estimate the deposition (wet and dry) of pesticides transported in gaseous and particulate phases for both the short- and medium-ranges. It is intended to calculate long-term exposures (i.e. over months or years). A short-range version of the model is available but has not yet been fully documented.

The OPS model was tested by Van Jaarsveld (1995, 2004). Basic testing was done against data for SO₂ and NO_x in order to test parameters such as the depth of the mixing layer. These test compounds were used because good national and European emissions data were available. The short-range performance of the model was tested against data for a number of field experiments (Asman and Van Jaarsveld 1992, Van Jaarsveld and Schutter, 1993). In addition, Derwent *et al.* (1989) carried out a comparison between different models, including OPS. Duyzer and Vonk (2003) calculated deposition for several pesticides using estimates of emissions and compared them with deposition measured at 18 locations spread over the Netherlands. Measured and calculated depositions were within a factor of 2 for 8 out of the 16 substances studied. Larger differences were attributed to inaccuracies in the emission estimates.

The model was also used to estimate the dispersion and deposition of lindane as observed in the wind tunnel experiments of Fent (2004). Some simplifying assumptions had to be made in order to represent the conditions of the wind tunnel, such as assuming that the source height was 0.25m. There were no experimental data on the volatilisation rate; consequently, measured concentrations in air were used to estimate the source strength.

The model described the relative decrease of concentration with distance well. There were no experimental data on the volatilisation rate, consequently, the source strength was estimated from measured concentrations in air. The highest emission was calculated by the model for

the experiment conducted at an average temperature of 15.8 °C; the model calculated emission for the experiments conducted at 5.8 and 10.8 °C to be about the same. The model predicted comparatively high volatilisation (85% of the applied dose) of lindane for the first hour of the experiment, which is probably due to emissions being estimated from air concentrations.

Estimated dry deposition at 1m from the emission source was 17% of the dose. At these short distances, model estimates of deposition are very sensitive to the source height – the lowest air compartment was assumed to be 25cm thick, which lead to a dry deposition velocity of 0.0175 ms^{-1} . Further work is needed to understand the fate of lindane on plant leaves and its emission and deposition characteristics in order to better understand the differences between modelled and experimental depositions.

The ISCST3 model is designed to calculate the deposition of pesticides carried in the gaseous phase up to a distance of 10km from the emission source. Both wet and dry depositions are calculated, there are separate versions of the model for short- and medium-range transport.

The EUTREND model is a version of the OPS model that is designed to model the deposition of pesticides at the European scale. Both gaseous and particulate transport are considered as are wet and dry deposition. Transformation in air is via a first-order process. EUTREND was used in a study of the distribution of benzo(a)pyrene and lindane on the European scale (Van Jaarsveld *et al.*, 1994; Van Jaarsveld *et al.*, 1997; Van den Hout *et al.*, 1999).

Testing of transport models has been limited since there are very few measured data suitable for comparison and there is a need for more high quality data, particularly on emissions, against which to test models.

4.7.3. Multimedia models

4.7.3.1. Levels of complexity

Multimedia fugacity models exist in four levels of complexity with each increasing level introducing new data input requirements, and providing a more complete description of environmental fate (see Mackay *et al.*, 2001).

Level I fugacity calculations describe a situation in which a fixed quantity of chemical is allowed to come to thermodynamic equilibrium within a closed and defined environment. There is no resistance to chemical migration between environmental phases, and each phase is considered to be homogeneous and well mixed. Level II calculations describe a situation in

which chemical is continuously discharged at a constant rate and reaches steady state and equilibrium conditions at which the emissions are balanced by advective and degradation losses. The Level II software is consistent in appearance and operation with Level I. Degradation half-lives, not required for Level I, must be supplied. New information obtained includes the overall environmental persistence of a chemical, and the relative importance of chemical degradation versus transfer to adjacent regions as mechanisms of removal.

Level III fugacity calculations introduce resistance to chemical migration between environmental compartments, and are the most useful and enlightening evaluative calculations. Level III describes a situation in which chemical is continuously discharged at a constant rate to one or more of the four environmental compartments and achieves a steady-state, non-equilibrium condition. Additional input parameters that characterize the environment are required to calculate transfer rates between environmental media. The Level III calculation shows the dependence of overall environmental fate on media of release and highlights the dominant intermedia transport pathways (e.g. air-water or air-soil exchange). This is the most popular type of model used for regional modelling exercises of which the best-known examples are SimpleBox/EUSES (van de Meent, 1993; EC, 1996), ChemCAN (Mackay *et al.*, 1996c) and CalTOX (McKone, 1993).

Level IV unsteady state (or dynamic) models can also be formulated to analyse short-term (e.g. seasonal) effects on environmental concentrations, or to determine the effect of changing environmental emissions over a period of decades. There are several examples of the use of this type of model in the literature (e.g. Wania and Mackay, 1999; MacLeod *et al.*, 2002b; Sweetman *et al.*, 2002).

4.7.3.2. Model Applications

Multimedia models are often only used to provide an evaluative picture of environmental fate including environmental persistence and long-range transport potential, which is useful for rapid prioritisation and comparison of chemical substances. They are also used to provide a regional, continental or global mass balances and to understand chemical fate and exposure on these different scales. These two distinct uses of multimedia models are discussed in more detail below.

Evaluative or generic assessment of fate

Evaluative assessments use defined hypothetical environments to assess the eventual environmental fate of a chemical and to identify potential compartments of concern. The use of a common environment is particularly valuable for ranking chemicals against the behaviour

of known contaminants (Mackay *et al.*, 1996a,b,c). This type of assessment does not seek to validate measured concentrations, or predict absolute concentrations, it is primarily to gain insight into the potential behaviour of a chemical and to identify candidate chemicals for more detailed assessment. In this way evaluative modelling is particularly valuable as part of tiered chemical assessment strategy.

Assessment using an evaluative model translates chemical properties into a simple, generic fate profile that reveals potential for persistence, transport over great distances, and bioaccumulation (Webster *et al.*, 1998; Beyer *et al.*, 2000). Applying this assessment to new and existing chemicals can identify potential problems before they become evident in the environment, and help to prevent repeating past mistakes. In all cases when assessments of priority chemicals have been done “after the fact” the evaluation has revealed the potential for adverse behaviour. For example, generic modelling assessments of PCBs and DDT indicate that these chemicals would be both highly persistent and bioaccumulative (Mackay 2001), which is largely the reason for their adverse effects on bird populations. Further, models designed to assess long-range transport potential (Beyer *et al.*, 2000) indicate that hexachlorocyclohexanes will be transported long distances by atmospheric and ocean transport, which is consistent with their observed accumulation in polar regions (Wania and Mackay, 1996). General considerations regarding the environmental persistence and long-range transport potential have already been discussed in the Chapter 3 (Section 3.2.2).

A number of models designed to specially estimate environmental persistence or travel distance (CTD or half-distance) have been developed (see Table 4.7–1). Wania and Mackay (2000) and more recently an OECD working group (OECD, 2004) quantitatively compared the output of these models for a large number of organic chemicals with a wide range of physico-chemical properties. They concluded that the absolute values of estimated persistence or travel distance varied between models because of differences in model design (e.g. size of compartments, organic carbon content etc.). However, the ranking of chemicals for persistence and LRT potential was very similar between the different models, indicating that the different methods for estimating travel distances were broadly comparable.

Table 4.7– 1: Examples of models used to predict contaminant persistence and long-range transport.

Model	E/L	Reference	Brief description
ATP	L	Van Pul <i>et al.</i> (1998)	Estimates half-distance
BENN1	E	Bennett <i>et al.</i> (1998)	Model estimates a characteristic time (persistence)
BENN2	L	Bennett <i>et al.</i> (1999)	Model estimates CTD
Chemrange	E	Scheringer <i>et al.</i> (1996)	Circular multi-box model for calculating persistence and LRT
SCHE	E	Scheringer <i>et al.</i> (1997)	Modified model
ELPOS	E	Beyer and Matthies (2001)	Modified EUSES/SimpleBox to calculate persistence and CTD
TaPL3	E	Beyer <i>et al.</i> (2000) Mackay <i>et al.</i> (1996b)	Persistence and LRT model based on EQC
VDMX	E	Brandes <i>et al.</i> (1996) and van de Meent (1993)	Persistence and LRT models based on SimpleBox
WANX	E	Wania (1998)	Models for estimating persistence and LRT

E/L = Eulerian or Lagrangian

Regional, Continental and Global Mass Balance Models

In the evaluative fate assessment the focus was on understanding how a chemical's properties affect its environmental fate. In the regional fate assessment the focus shifts to how the characteristics of the specific region, sometimes referred to as landscape parameters, affect a chemical's environmental fate. For example, effects of changes in temperature, hydrology, meteorology, proportions, and compositions of water and soil can be evaluated. The other main objective of a regional fate assessment is to input reliable discharge data for a region into the model and obtain predicted regional average environmental concentrations for each media. This is useful for regional exposure assessments, when there is limited monitoring data available.

The area treated in a near-field or local chemical evaluation will usually be between 1 and 100 km² thus this type of modelling is highly site-specific and specialized local models are required. Multimedia models are more usually applied to regional-scale assessments when the evaluation area is between 10 000 km² to 1 000 000 km² and represents a state, province, nation or ecological region. For example, ChemCAN is a steady-state Level III model that has been specifically developed to describe the multimedia behaviour and fate of organic and inorganic chemicals in 24 defined regions of Canada (Mackay *et al.*, 1996c), although it is easily adapted to other regions, for example, France (Devillers *et al.*, 1995) and North-Rhine Westphalia in Germany (Berding *et al.*, 2000). Other regional type models include CalTOX (McKone, 1993) and SimpleBox (van de Meent, 1993), which is used within the EUSES

(European Union System for the Evaluation of Substances) modelling framework for risk assessment in Europe. The characteristics of the environmental media, meteorology, hydrology, soil type, and temperature are calibrated for the region of interest, but many of the underlying process representations are the same as the evaluative type model. In some cases it may be desirable to employ an unsteady-state (Level IV) model to analyse short-term (e.g. seasonal) effects on environmental concentrations, or to determine the effect of changing environmental emissions over a period of decades (Sweetman *et al.*, 2002; MacLeod *et al.*, 2002b).

Regional models can be partially validated by inputting reliable discharge rates and comparing available data on ambient environmental concentrations with model predictions. It is expected that the agreement of model predictions with environmental concentration data will be approximate, i.e. a factor of 2 or 3 rather than, for example, plus or minus 20%. This level of accuracy, however, is often adequate to determine if concentrations are significant. In risk assessment applications, toxicity data are rarely more accurate than the above ranges. Furthermore, environmental concentrations can readily vary by such factors spatially and temporally. As mentioned previously, obtaining ambient environmental concentrations for a region is sometimes difficult because measurements are often made where high concentrations are expected.

When comparing against monitoring data, it is recommended that modellers express the uncertainty and variability in model output by examining model sensitivity and the propagation of uncertainty through the model. As a starting point for assessing model uncertainty, sensitive input parameters should be identified by making small changes in individual input parameters and observing the corresponding change in output parameters of interest. MacLeod *et al.* (2002a) demonstrate how model sensitivities can be combined with estimates of uncertainty in input parameters to quantitatively estimate total uncertainty in model outputs. The propagation of uncertainties through the system of equations that make up the model is revealed, and can be used to guide efforts to reduce uncertainty in key input parameters. Model results can thus be expressed as a range of concentrations that reflect uncertainty in input data and in the model's description of the real environment. In a regional modelling exercise, the range of predicted concentrations can then be compared with the range of concentrations observed in the environment.

It is possible to connect a number of multimedia models to express chemical fate on a larger scale e.g. continental or global scale. There are initiatives to develop multi-segment regional models of chemical fate in North America (BETR-NA, MacLeod *et al.* 2001; Woodfine *et al.*, 2001; MacLeod *et al.*, 2002b) and Europe (BETR-Europe: in development) with region-to-

region transport. For example, the BETR-NA model contains 10 regions in Canada, 10 in the USA, 4 in Mexico, and includes surrounding coastal water. Each region, which is a separate 7-compartment multimedia model, has defined climatic, soil, land-use, and hydrological characteristics, and region-to-region transport of air and water is quantified. The net result is that an emission or source in any one region can be tracked to give quantities and concentrations transported to all other regions. It thus directly assesses trans-boundary pollution and long-range transport.

It is sometimes desirable to scale up regional models to describe chemical fate on a continental or global scale, especially when modelling highly persistent and mobile compounds. Globo-POP, a model that describes global chemical fate has been developed by Wania and Mackay (1993, 1995) and has been shown to provide a satisfactory description of the global transport of technical hexachlorocyclohexane (HCH) (Wania *et al.* 1999, Wania and Mackay, 1999). This global model consists of a series of nine connected models representing meridional segments of the planet with appropriate volumes and temperatures.

A number of different regional, continental and global models have been developed or are under development. These models are summarised in Table 4.7–2.

Table 4.7– 2.: Examples of multimedia models used to estimate regional, continental and global fate

Model	Reference	Description
SimpleBox 2.0/EUSES 1.0	van de Meent (1993); EC (1996)	Commonly used tool for risk assessment of organic chemicals within the European Union. Contains specific pesticide module
CemoS	Beyer and Matthies, 2001	Model used to evaluate exposure of pesticides and POPs
ChemCAN 4.0, BETR-NA, BETR-Europe	MacLeod <i>et al.</i> (2001, 2002b), Woodfine <i>et al.</i> (2001)	Regional fugacity models for North America and Europe
CalTOX	McKone (1993)	Regional multimedia model used for assessment of hazardous waste sites
IMPACT 2002	Jolliet <i>et al.</i> (2003)	A spatially explicit European scale fate model
CoZMo-POP	Wania <i>et al.</i> (2000)	A generic, dynamic coastal zone fugacity model
Globo-POP	Wania and Mackay (1993, 1995, 1999)	Multi-compartmental mass balance model for evaluation of fate in the global environment

A common criticism of the multimedia models is their treatment of the environment as a series of well-mixed boxes. Atmospheric transport processes are in particular greatly simplified. This has been partially addressed by dividing the atmosphere into several well-mixed boxes (Wania and Mackay, 1995, MacLeod *et al.*, 2001), but this is not always regarded as satisfactory by chemical fate modellers with a meteorological background. Atmospheric transport is averaged over long-time periods so the models are only suitable for describing long-term fate rather than short-term events. The advantage is considerable reduction in complexity and thus computing time. Similar arguments could be made for treating all of the compartments in multimedia models in much more detail. In general, single medium models are usually far more complex in the treatment of their medium of interest. However, it should be borne in mind that it is preferable to use the simplest model that can generate the desired result. A simple model has the advantage that its results can be easily explained.

In summary, regional or far-field modelling provides an opportunity to focus the assessment on geographic locations that are of interest to the assessor. Model results can be compared with available environmental monitoring data, and inconsistencies between the modelled and observed behaviour of the chemical can be used to identify weaknesses in data describing the chemical, or its emissions. The principal challenge in verifying the environmental fate profile provided by the models is obtaining reliable and applicable data for chemical properties (especially degradation half-lives), emissions and environmental concentrations. Rigorous “validation” of regional or far-field models is impossible, since this requires comparison of predictions with observed environmental behaviour for every contaminant of possible interest. A more feasible approach is to build confidence in the model as a descriptor of chemical fate by conducting several studies examining different classes of contaminants with varied behaviour, such as volatile organics, PAHs and surfactants. Different classes of chemicals are likely to experience different migration pathways, and may reveal areas where the model could be refined or recalibrated. Examples of model evaluation exercises include MacLeod and Mackay (1999), Kawamoto *et al.* (2001), Sweetman *et al.* (2002), MacLeod *et al.* (2002b) and Berding (2000).

4.7.3.3. Conclusions

Multimedia models are tools for synthesising information on chemical and environmental properties with a view to estimating environmental fate and exposure. They can range in complexity and be configured to represent different environments of interest.

Evaluative models can be useful for assessing a chemical's overall environmental persistence (as expressed by an overall residence time) and their long-range travel potential (as expressed by a half-distance or characteristic travel distance). Persistence and long-range transport potential can be assessed with a variety of different models, but it is likely that these different modelling approaches will give similar results, at least on a ranking basis. Evaluative models are thought to be valuable as part of a tiered chemical assessment strategy.

Regional, continental and global scale multimedia models are useful for performing chemical mass balances, exposure assessments and for tracking chemicals from region to region. A variety of different models have been developed which could have applications for assessment of pesticide fate in Europe.

The largest limitation of multimedia models may be in their treatment of the atmosphere. There are certainly more complex treatments of atmospheric transport by meteorologically based models. Another limitation is their lack of spatial resolution, although this is being addressed in a number of on-going modelling efforts that couple multimedia models to Geographical Information Systems (GIS) (Woodfine *et al.*, 2001). The simplicity of the multimedia models, however, makes them appropriate for use as rapid screening tools to assess long-range transport potential.

A variety of MMMs have been developed using both evaluative (e.g. TaPL3) and region-specific environments (BETR-Europe). The evaluative MMMs provide a range of different model outputs. While evaluative models have generated interest amongst regulators, there is some concern that the metrics such as CTD (characteristic travel distance) depend strongly on the design of the evaluative model environment (e.g. soil organic matter, inclusion of vegetation, wind speed etc.). Intercomparison studies of these models (Wania, and Mackay 2000) have shown that the outputs from these different models compare favourably, especially when comparing the rankings of travel distances for large lists of chemicals.

Several of this class of models have been recommended for use in this Chapter (6 multimedia models passed the Step 2 criteria and two of these, Chemrange and ELPOS, were evaluative models see Sections 4.7.3.2 and 4.7.3.3). Evaluative multimedia models are not suitable for use in risk assessment since they do not generate PECs. Furthermore, a calculated travel distance from one of these models currently has no regulatory significance. These models could potentially be used for comparing/benchmarking calculated travel distances for currently registered pesticides with travel distances for known long-range transport chemicals such as PCBs, lindane and hexachlorobenzene. They are useful tools for rapidly evaluating the LRT potential of pesticides using limited input data. Site specific MMMs do produce

regionally averaged PECs, but there has been little validation of these models to date. A common criticism of regional MMMs is that atmospheric transport is greatly simplified compared to some of the other models reviewed in this chapter.

4.8. Application of air models in a regulatory context

Application of air models in a regulatory context is currently limited to short-range transport. Long-range transport models, including multi-media models, have not been used for regulatory purposes in the context of pesticide registration.

4.8.1. Current approaches for short-range transport

Germany

A requirement to estimate the deposition after volatilisation first appeared in Germany in 2002 (Winkler *et al.*, 2002). Before this date deposition from spray drift only was considered. The guideline mandated the use of the EVA 1.1 model to estimate deposition into the aquatic and terrestrial environments. A PEC was calculated by summing the contributions from drift and deposition after volatilisation.

Wind tunnel data taken by Fent (2004) found deviations between measured deposition data and those estimated by the EVA 1.1 model. No simple explanation could be given for these differences. Consequently, a new version of the EVA model (version 2.0) was developed incorporating these new data. This model categorizes pesticides into three vapour pressure classes and calculates the deposition for each class. Volatilisation is assumed to occur within the first 24 hours after application. EVA 2.0 has only a few input parameters (see Section 4.7.2.1).

The most recent scheme for short-range assessment by the German authorities uses a vapour trigger for volatilisation at the first Tier. Substances with a vapour pressure less than 10^{-5} Pa and are applied to plants, or are applied to soil and have a vapour pressure less than 10^{-4} Pa, need not be evaluated further for deposition after volatilisation. Those that exceed these triggers require the deposition after volatilisation to be calculated with EVA 2.0. The depositions due to drift and deposition after volatilisation are summed together and a PEC is calculated. Unacceptable exposure concentrations derived from modelling results in the requirement for further experimental data i.e. either wind tunnel tests or field tests.

Denmark

The Danish EPA uses the PestSurf model for the national assessment of the potential for pesticides to enter surface waters. Deposition after volatilisation is one entry pathway considered in addition to entries from spray drift runoff and drainage. The PESTDEP model (Asman *et al*, 2002) calculates the magnitude of the deposition after volatilisation. The PESTDEP calculation uses worst-case assumptions (such as the wind always blows toward the water body) and many parameters are fixed to be representative of Danish conditions. Consequently, the user only has control over a few input parameters.

4.8.2. Requirements for use of short-range transport air models in EU regulatory context

Chapter 5 detailed an exposure assessment scheme for short-range transport. This scheme recommends that a calculation of deposition after volatilisation needs only be done if vapour pressure triggers are exceeded, and Step 4 modelling is required for FOCUS Surface Water, or if drift mitigation is required for the terrestrial assessment. Since the deposition after volatilisation model needs to be included into the FOCUS Surface Water assessment at Step 4, it is important that any model fits into the FOCUS concept i.e.:

- 1.) Validation status:** The most important requirement of a model to be used in the context of FOCUS is a sufficient validation status. For the entrance pathway drainage and runoff, the models have been successfully tested. Some testing against experimental data has to be carried out with the air models however this has not been as extensive as the testing of the drainage and runoff models.
- 2.) Time dependence of the deposition process:** Deposition after volatilisation is a time dependent process in contrast to deposition by direct spray drift, which occurs within a few seconds and minutes after application. There is experimental evidence that volatilisation of pesticides is highest during the first hours after application and becomes less afterwards. In general volatilisation is negligible 24 hours after application. The time taken for volatilised residues to be transported from the site of application to a water body will be short – assuming a 100m distance between the water body and emission source and a 2m/s wind speed in the direction of the water body gives a travel time of < 1 minute. This means that the dynamics of deposition can be related directly to the dynamics of the emission.

The deposition model must therefore have a sufficient temporal resolution to represent the emission and deposition processes. The drainage and runoff entries in FOCUS Surface

water have a resolution of 1 hour, the deposition model should also have this scale of resolution.

3.) Definition of scenarios: The use of a simulation model requires the definition of a scenario that describes or fixes the initial and boundary conditions influencing the relevant processes of the model. For deposition after volatilisation these processes are: the wind direction, temperature and the size and shape of the treated field.

The simplest way that a scenario can be defined is to fix input parameters at appropriate values. FOCUS Surface Water uses a number of scenarios and the realistic worst-case nature of these scenarios with respect to deposition after volatilisation still needs to be established. Once this has been done models can be parameterised accordingly.

4.9. Conclusions and recommendations

4.9.1. Short range transport

Emission can be calculated by simple regression equations or by (process-based) environmental fate models. Only limited testing of the environmental fate models has so far been carried out, and improvements to their volatilisation routines (as suggested by Vanclooster *et al.* 2003) have not yet been incorporated into the official versions of the FOCUS models. In contrast, regression equations are based upon experimental data, however they typically estimate cumulative volatilisation over 24 hours or 7 days and do not therefore have the temporal resolution required for FOCUS Surface Water Step 4 calculations.

The following transport and deposition models passed the Step 2 screening criteria:

- PESTDEP
- ISCST
- EVA
- OPS_PRO (OPS)
- IFDM
- PLUME-PLUS
- ASDM

The models listed above deal with short-range deposition after outdoor application. No models were available to estimate short-range deposition after emission and transport from indoor applications such as greenhouses.

The exposure assessment scheme in Chapter 5 requires that exposure is calculated at Tier II by means of modelling. However none of the models available completely fulfils the requirements for use within a regulatory context for the following reasons:

- No model currently has sufficient validation status. New experimental data (Fent, 2004, Siebers *et al.*, 2003a, Gottesbüren *et al.*, 2003) have become available during the lifetime of the FOCUS Air Group, and these may raise the validation status of air models in time.
- Emission is a factor not fully understood
- There are no defined scenarios that cover worst-case conditions for deposition after volatilisation under European conditions.

Further work is therefore required to collate information on the basic processes involved in deposition after volatilisation. Once this has been done and once experimentally-tested process-based models become available the SRT scheme requires reevaluation.

EVA 2.0[†] is a simple, empirical model derived from the wind tunnel data of Fent (2004). It has been shown that this model calculates deposition values that are conservative compared to those observed in the wind tunnel study of Fent (see Figure 4.7–2) and compared to the field dissipation data of Siebers *et al.*, 2003a and Gottesbüren *et al.*, 2003 (see Figure 4.7–3).

For pragmatic purposes therefore, the FOCUS Air Group recommends that the EVA 2.0 model can be used as an interim solution for calculating the deposition after volatilisation for short-range transport.

4.9.2. Long range transport

Three long-range transport models passed the Step 2 screening criteria, these were: EUTREND, RAMS-HYPACT and IMPACT 2002. Six of the Multimedia Models CEMC, SimpleBox/EUSES, CalTOX, ChemRANGE, ELPOS, IMPACT2002 passed the Step 2 screening criteria. In principle any of these models would be acceptable for modelling long-range transport, however, the validation status of these models is poor, so no recommendation can be made on the choice of a particular model until further data become available.

†

http://www.bvl.bund.de/cln_027/nn_496790/DE/04__Pflanzenschutzmittel/00__doks__downloads/zul__umwelt__eva20__erl-EN.html__nnn=true

Long-range transport models can still be of use for exposure assessment. Multimedia models can shed light on the potential fate of a compound in the environment, and offer the possibility of ranking chemicals against those having known behaviour. These models, however, tend not to be very sophisticated in their treatment of the atmosphere, and this casts doubt over their ability to predict concentrations in the environment arising from a specific application scenario.

The process based Eulerian and Lagrangian models offer a greater potential to predict residues in and deposition from air. However, these models require the definition of emission and deposition scenarios and no such scenarios are currently available within Europe for long-range transport. ISCST3 has been used in the USA in conjunction with field experiments (Cryer *et al.* 2003); field data were used to parameterise the model, which was then used to predict results under different meteorological conditions and scenarios. However Cryer *et al.* (2003) concentrated on medium range transport of highly volatile soil fumigants to nearby communities, rather than transport of pesticides having a much lower volatility over thousands of kilometres. Nevertheless it may still be possible to demonstrate safety by concentrating on a scale less than long-range on the principle that residues of a substance should generally be higher closer to the source of emission.

The validation status of long-range transport models is poor due to the difficulties of obtaining data on pesticide use and emissions and therefore the difficulty of relating deposition to the emission source. Considerable work would be required to increase the validation status of long-range transport models and to establish relevant scenarios.

5. EXPOSURE ASSESSMENT OF PESTICIDES APPLYING TO SHORT-RANGE TRANSPORT VIA AIR

5.1. Introduction

Directive 91/414 provides detailed guidance on how exposure from spray-drift, runoff and drainage should be calculated, and how the risk assessment for aquatic and terrestrial organisms should be conducted. Deposition of volatilised residues is not explicitly covered by 91/414 and represents a new exposure term to be included into the exposure assessment, where appropriate.

The intention of the FOCUS Air group was to determine which pesticides do not volatilise significantly and could therefore be excluded from further consideration; the short-range trigger was established to identify these substances. For pesticides exceeding the short-range trigger, guidance would be provided on how to calculate exposure resulting from volatilisation, and how it should be included into the existing exposure assessment. The aim was to include deposition of volatilised residues as an additional exposure term into the existing framework; risk assessment could then proceed using current guidance with the refined exposure estimate.

A key consideration is the level at which deposition of volatilised residues should be included into the exposure assessment. In order to determine the appropriate level, the group compared exposure estimates from existing routes with that resulting from deposition after volatilisation. Deposition of volatilised residues should only be only considered where exposure is significant compared to other exposure routes.

Few data are published on the exposure and risk assessment of off-site transport and short-range deposition of airborne pesticides. A first approach has been made by the German BBA (Federal Biological Research Centre for Agriculture and Forestry) in Guideline Part IV 6-1 on volatilisation of pesticides (Nolting *et al.*, 1990).

Short-range deposition of pesticides in “aerosol form”, during and shortly after application (spray drift), can already be estimated from publications of standard drift values by Rautmann *et al.*, (2001). These data are currently used in aquatic exposure assessment of FOCUS Surface Water (FOCUS 2001).

However, field studies conducted by the BBA with semi-volatile pesticides suggest that deposition into water bodies close to a treated field can be underestimated if deposition due

only to spray drift is considered (Siebers *et al.*, 2003a). In addition, studies conducted by the German registration authorities with indoor applications (greenhouses and warehouses) showed that deposition of volatilised substances into non-target areas was possible after opening and ventilation.

5.2. Basic Consideration on Risk Assessment of Air-Borne Pesticides

Risk assessment is a process that comprises the evaluation of scientific information on the hazardous properties of pollutants and the extent of exposure to non-target organisms. This process is generally described by comparison of exposure and toxic effect levels within a certain time at the site of interest. For man, this evaluation generally is performed by comparison of the exposure through the inhalative, oral and dermal routes to toxic effect levels, e.g. the AOEL (Acceptable Operator Exposure Level) or ADI (Acceptable Daily Intake). For organisms other than man, this evaluation is described by other ratios, such as: TER = Toxicity-to-Exposure-Ratio; HQ (Hazard Quotient for arthropods) = ratio between exposure and LR50 (50% lethal rate in the standard glass plate test); or PEC/PNEC = ratio between Predicted Environmental Concentration and Predicted No Effect Concentration (the later is preferred for industrial chemicals). The remit of the FOCUS Air group was to consider exposure, appropriate endpoints for short-range risk assessment are therefore not considered any further.

Exposure to air-borne pesticides can occur directly within the gaseous phase and indirectly after deposition from the gaseous phase on to a non-target area. In the current risk assessment schemes pesticides in the gas phase are assessed for their risk to humans via inhalation, whereas the environmental risk to terrestrial (e.g. mammals, birds, arthropods, plants) and aqueous non-target organisms (e.g. fishes, daphnids, algae) is assessed via deposition.

5.2.1. Human Exposure

The gaseous concentration of a volatilised pesticide substance in the air varies greatly with time after the start of emission and with distance from the emission source. Highest levels are observed directly after application and very close to the source. These peak concentrations of air-borne pesticides are already covered in the risk assessment for operators and bystanders by comparison of the potential exposure (inhalative and dermal route) with the AOEL (Lundehn *et al.*, 1992; UK-POEM, 1992). Operator exposure is a worst-case assessment as the operator (i. e. the farmer during application of a pesticide) receives the highest exposure. Inhalative exposure is expected to be lower for bystanders (considered to be beside the sprayed field).

Inhalation of pesticides by workers re-entering the field and in greenhouses is addressed in the draft EUROPOEM II report, Project FAIR3-CT96-1406 (2002), which states that formulation of an active substance also needs to be taken into account: “Active substances which are contained by a barrier, i. e. micro-encapsulated formulation, granule/dust, or even particles of undissolved active substance from suspension concentrate spray solutions will have a lower potential for vapour phase inhalation exposure.” Inhalative exposure of re-entry workers caused by volatilisation post-application is considered to be of minor importance compared to total exposure, which is mainly by the dermal route.

The inhalative exposure route is thus covered by the operator and re-entry worker exposure assessment and therefore does not need to be additionally evaluated this Report.

5.2.2. *Environmental Exposure*

Peak exposure of man to pesticides in the air occurs shortly after application and decreases rapidly thereafter. In contrast, deposition of volatilised residues in non-target areas may lead to the accumulation of residues over the time that volatilisation occurs. Therefore, this time is a relevant parameter for environmental exposure assessment in addition to the extent of volatilisation.

5.2.2.1. *Time Scale of Volatilisation*

Off-site deposition following volatilisation is a cumulative process as volatilisation, aerial transport and deposition last some time (seconds - days). Cumulative volatilisation is usually completed within one day for volatilisation from plants, but can last for up to several days from soil, depending on the environmental conditions. However, even with long-term volatilisation from soil, the major portion of the volatilisation occurs within the first few days (Rice *et al.*, 2002). In addition, evaporation from soil is generally lower than from plants (see Chapter 2, Section 2.4). Consequently, aerial concentrations (and in turn deposition) resulting from long-term volatilisation from soil will be comparatively low, and will be further reduced by processes such as degradation in soil and atmospheric dispersion, which become more important over longer times. As a result, exposure assessment for short-range transport should only consider the short-term.

It should be noted, however, that “long-term” evaporation from soil can occur under special conditions. After application to the soil, drying of the upper soil layer can result in a diminished volatilisation shortly after application as a result of increased sorption, which can cause an accumulation of a substance at the soil surface. Subsequent re-moistening of the soil surface (by a light rainfall or dew) can then result in a significant volatilisation some days

after application. It is also possible that rainfall shortly after application to soil can leach the substance to the subsurface soil layer resulting in a decrease of volatilisation. Volatilisation flux increases again when rainfall stops as a result of back-migration due to the “wick effect” (See Chapter 2, Section 2.3). Again, it should be noted that dissipation processes become more relevant over the long-term and reduce the effective peak concentration.

The FOCUS Air group considered that maximum exposure would occur in the 24 hour period following application. Although significant emission to the air can occur after 24 hours, this is only true for certain compounds and the degree to which it occurs is dependent upon meteorological conditions. In addition the highest exposure is likely from substances that volatilise quickly, and when meteorological conditions are such that deposition from spray drift and following volatilisation coincide. Over a longer time it is likely that changes in meteorological conditions (e.g. changes in wind speed and direction) will cause dilution and dispersion of residues. For these reasons the FOCUS Air group took the decision to limit the consideration of deposition after volatilisation in the short-range assessment scheme to the 24 hour period following application.

5.3. Current Relevant Exposure Assessment Schemes

5.3.1. EU Surface Water Exposure Assessment

Guidance on exposure assessment under 91/414 for deposition to surface waters has already been established by the FOCUS SurfaceWater Group (FOCUS 2001). They proposed four evaluation steps taking into account the entry routes spray drift, run-off and drainage.

At Steps 1 and 2 drift values are obtained from standard values available from the literature (Rautmann *et al.*, 2001). A fixed distance between the edge-of-field and water is assumed and the corresponding drift is deposited into the water body according to crop type. For arable crops, a 1m distance is assumed at minimum, leading to a deposition of 2.8% of the application into the water body. For vineyards and orchards a minimum distance of 3m is assumed leading to deposition of 2.7 – 8.0% for vines and 15.7 – 29.2% for orchards for a single application (see Appendix 10). An additional 10% of the application is deposited into the water body as the sum of run-off and drainage loadings for Step 1, for Step 2 this may vary between 2 and 5 percent depending upon the season and area of use (northern and southern Europe). In Step 3, different types of water body are considered, and the distance from the edge-of-field to the water body varies with water body type as well as with crop type. For arable crops, distances vary between 1 – 1.5m for ditches, 1.5 – 2.0m for streams and 3.5 – 4.0m for ponds. The corresponding distances for citrus, hops, olives and vines vary

between 3.5 and 6m. Run-off and drainage entries are calculated by the PRZM and MACRO models respectively. In Step 4 mitigation measures (e.g. implementation of vegetative filter strips, drift reducing equipment) are introduced. These measures cause a decrease of the exposure (i.e. PEC_{sw}), and might be required if the previous PEC_{sw} derived from the conservative low-step assessment indicate unacceptable ecological exposure levels.

For an evaluation of unacceptable exposure effect levels guidance is given in the Guidance Document on Aquatic Ecotoxicology, SANCO/3268/2001 rev.4 (final) (2002) using the short-term ecological endpoints.

5.3.2. EU Terrestrial Exposure Assessment

Assessment under 91/414 requires the estimation of exposure of non-target arthropods and plants, exposure of wildlife, and soil organisms. Document SANCO/10329/2002 rev.2 final (2002) governs how risk assessment for non-target arthropods and plants should be done, and proposes that minimum drift distances of 1m for arable crops, and 3m for vineyards and orchards, be considered in the standard risk assessment. Failure at this Tier requires a consideration of drift mitigation measures, higher Tier fate data or ecotox data.

Potential exposure to wildlife animals (e.g. mammals, birds) is highest in the field. Therefore, the off-site risk assessment for wildlife animals is covered by an in-field risk assessment. For the estimation of the terrestrial exposure (in- or off-field) and the comparison to respective toxicity data to birds and terrestrial vertebrates guidance given by the guidance document SANCO/4145/2000 (2002).

Finally, terrestrial organisms not dwelling on the soil surface (e.g. earthworms, soil micro-organisms) are in general not exposed by a deposit of a volatilised pesticide to the top of the soil. An exposure/risk assessment with volatilisation is therefore not applicable.

5.3.3. Existing Exposure Schemes for Short-Range Transport of Airborne Pesticides

An off-site risk assessment for airborne pesticides was first developed by Kördel *et al.* (1999). This work was funded by the German UBA (Federal Environmental Agency) and provided a risk-assessment approach for long-range transport of pesticides in air and for short-range transport followed by deposition to non-target plants. A very extensive scheme was proposed by the EPPO (European and Mediterranean Plant Protection Association, EPPO, 2003), which contains a module for emission from field and indoor use into air, followed by subsequent short-range transport and deposition. The EPPO scheme that applies to the short-range

transport is shown in Appendix 7. Pesticide regulation in Germany already requires an assessment of deposition of pesticides in air (Winkler *et al.*, 2002). This assessment scheme used the modular simulation tool EVA 1.1 (Exposure Via Air) to estimate deposition. The tool was tested against a limited number of field studies and calculated the volatilisation rate; the concentration in air; and the off-site terrestrial and aquatic deposition as a function of distance from the edge-of-field. This model has now been updated using an extended set of data on deposition after volatilisation measured in outdoor wind tunnels (Fent, 2004).

This new version is called EVA 2.0 and it calculates deposition according to vapour pressure. If the predicted deposition, and consequently derived TER data, are not acceptable for non-target organisms, field trials on the experimental quantification of deposition rates are proposed. A similar scheme as for the EPPO evaluation has been constructed from the German assessment report. It is shown in Appendix 8.

5.4. Exposure Assessment Schemes Proposed by FOCUS AIR

Deposition following volatilisation is an exposure term not explicitly considered under 91/414. Other FOCUS groups have reported on how to estimate exposure from spray-drift, run-off and drainage for example. The FOCUS Air Group did not consider these exposure calculations and only considered how deposition following volatilisation could be included into existing exposure schemes. Separate recommendations were made for aquatic and terrestrial deposition; both use a three-tiered approach, which is outlined in Table 5.4–1.

Table 5.4–1: Tiered Approach Proposed by FOCUS AIR

Tier 1	Examination of the application conditions, Entrance trigger for volatilisation, i.e. vapour pressure Requirement of mitigation measures based on exposure by other routes
Tier 2	Model calculation of the off-site deposition and the resulting PEC Including a potential refinement using experimental data for basic processes
Tier 3	Volatilisation/deposition experiments And/or mitigation measures to reduce deposition to the off-site area

5.4.1. Tier I:

Tier I considers the potential of a substance to reach the atmosphere. Some application techniques such as baits, granular formulations, seed treatment, and incorporation into the soil can reduce the amount of substance reaching the air to such an extent that it may require no further evaluation.

5.4.1.1. Deposition to surface water

If the application technique is such that there is the potential for a substance to reach the air, then an assessment is made of the potential of the substance itself to reach the air. In Chapter 2, Section 2.7 the vapour pressure was established as a trigger for volatilisation from plants and soil. Using these data, and taking into account the potential uncertainties of volatilisation and vapour pressure measurements, the following conservative values are proposed by the FOCUS Air group to establish whether a substance has the potential to reach the air:

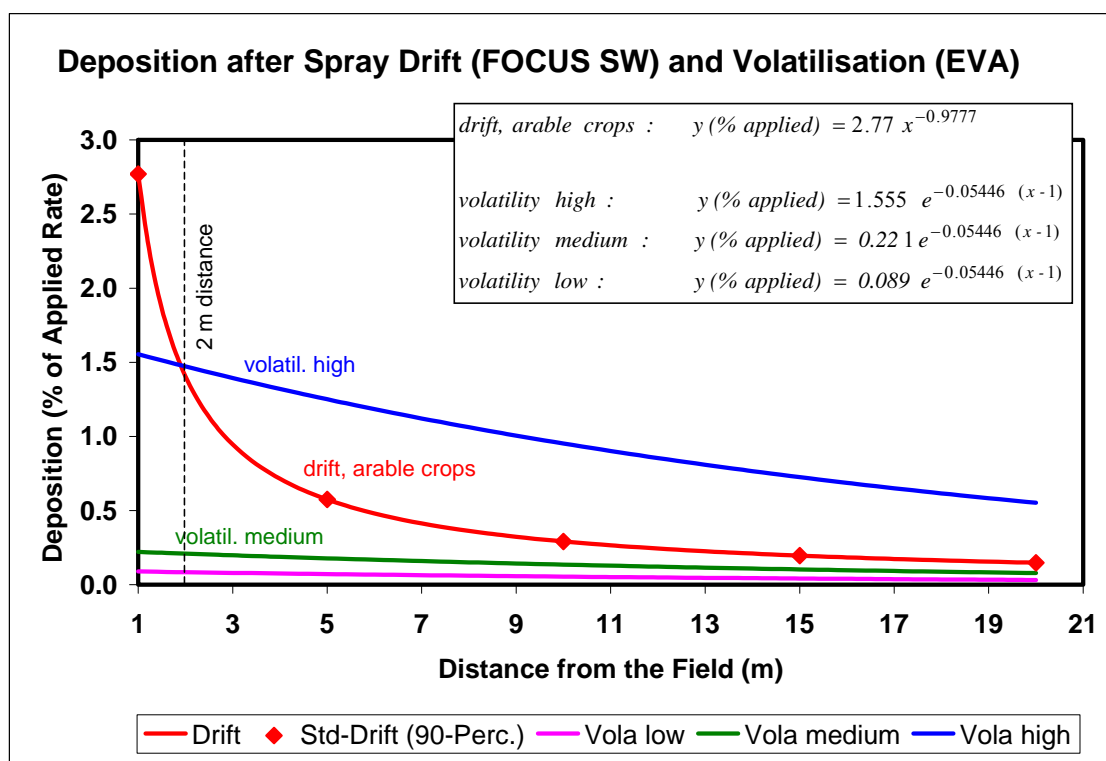
$V_p \geq 10^{-4}$ Pa (20°C) for volatilisation from soil and

$V_p \geq 10^{-5}$ Pa (20°C) for volatilisation from plants

Exceedence of these triggers indicates the potential for a substance to be emitted to air, but does not automatically mean that an exposure assessment has to be made. FOCUS Surface Water Steps 1 and 2 use highly conservative assumptions regarding exposure from spray-drift, run-off and drainage and any additional component for exposure via volatilisation is considered to be incorporated in the inherent conservativeness of the assessment (FOCUS 2001). Step 3 calculations are aimed to be realistic worst-case estimates of exposure from spray drift and run-off/drainage. Experimental data (see Section 3.4.1, Fent, 2004) indicate that total exposure from the aerial route, as a result of both spray drift and volatilisation, may be only slightly greater than the FOCUS SW default spray drift value of 2.77% of the applied rate at 1 m for arable fields (i.e. the additional contribution of deposition from volatilisation close to the treated field is not significant compared to the existing regulatory value used for spray drift input).

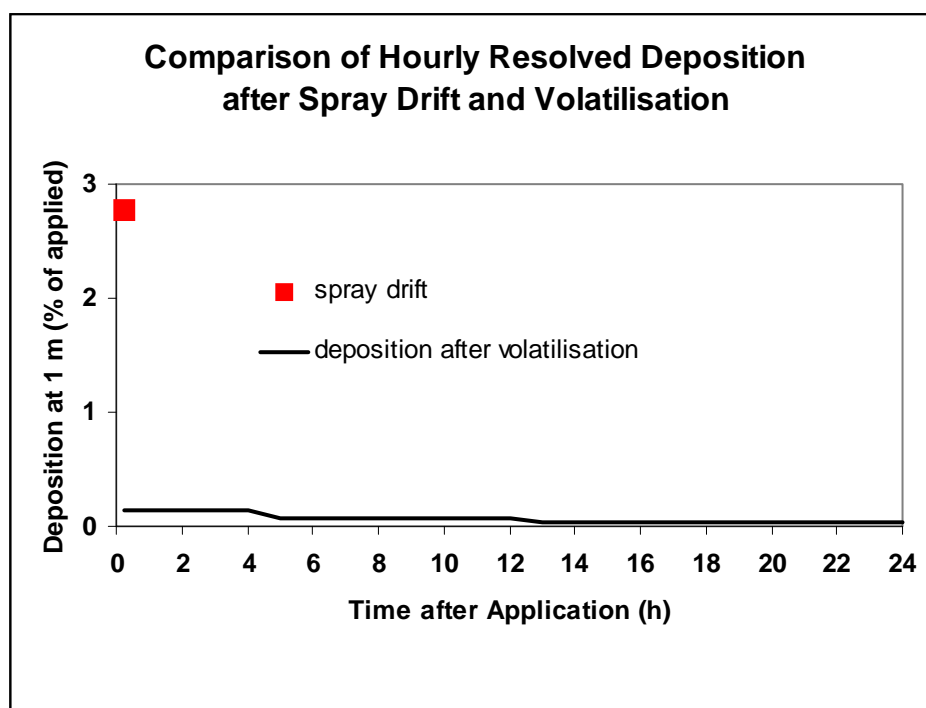
The EVA 2.0 model for short-range deposition was developed from the data of Fent (2004). Figure 5.4–1 shows deposition following volatilisation calculated by EVA 2.0 compared to spray drift deposition (instantaneous) for arable crops used in FOCUS Surface Water assessments. This Figure shows that drift generally dominates the deposition for compounds in the low and medium volatility classes implemented in EVA 2.0, but even for highly volatile substances the drift route dominates the aerial pathway for distances less than 2 m from the edge of the field. Beyond 2 m, however, the volatilisation route appears to exceed the drift route for compounds in the high volatile class.

Figure 5.4–1: Comparison of deposition caused by spray drift (FOCUS SW, arable crops, instantaneous event) and by volatilisation from arable crops (as predicted by EVA 2.0, cumulative over 24 h)



Note that in Figure 5.4–1 cumulative deposition arising from volatilisation over 24 h is compared to deposition after spray drift, which can be considered as an instantaneous event. Figure 5.4–2 shows hourly deposition from volatilisation of highly volatile compounds (highest deposition class of EVA 2.0) compared to a spray drift event at 1 m distance from the treated field. The Figure shows that hourly deposition from volatilisation is less than 10 % of the deposition after spray drift.

Figure 5.4–2: Comparison of temporally resolved deposition caused by spray drift (arable crops) and by volatilisation from arable crops (as predicted by EVA 2.0) at 1 m distance



FOCUS SW Steps 1-3 propose a minimum 1-m distance between edge of the field and a surface water body (i.e. ditch) for arable crops,. The above two Figures show that deposition after volatilisation is not significant compared to spray drift within the short-range (i.e. < 2 m). Consequently, deposition from volatilisation need only be considered in addition to drift for distances greater than 1 m (i.e. Step 4). For other types of crops (e.g. orchards, vines), spray drift according to FOCUS SW is higher than for arable crops. In the absence of specific data on volatilisation and deposition from orchards, vines and hops the FOCUS Air Group has taken the pragmatic decision that the percentage of deposition after volatilisation is also unlikely to be significant in comparison with the increased spray drift percentages for these crops at the distances used for evaluation at FOCUS SW step 3.

If surface water concentrations resulting from FOCUS SW Step 1-3 calculations are not acceptable in the risk assessment, Step 4 assessments can be performed including drift mitigation measures such as the use of drift reducing nozzles or buffer zones. These mitigation measures would, however, only slightly affect the deposition of volatilised substances, but would change the ratio between the volatilisation and the drift.

In conclusion, deposition after volatilisation need only be considered in the surface water assessment if drift mitigation at FOCUS SW Step 4 is required. In this case the deposition

after volatilisation should additionally be considered, taking into account the temporal dynamics of the process.

5.4.1.2. Deposition to a terrestrial surface

Tier I for terrestrial exposure is the same as that for surface water i.e. a consideration is first made whether the application technique is such that a pesticide can reach the air taking into account the use conditions. Consideration of exposure from deposition after volatilisation should be made in the same way as for non-target arthropods and plants given in guideline SANCO/10329/2002 rev. 2 (2002). A further evaluation is only needed if a substance exceeds these triggers. The terrestrial deposition following volatilisation should only be taken into account, if a risk assessment according to SANCO/10329/2002 rev.2 (2002) results in the requirement of drift mitigation measures for 1 m (field crops) or 3 m (other crops). In the same way as for the aquatic assessment, for pragmatic reasons it was considered that a further component of the exposure via deposition after volatilisation did not need to be considered if the compound passed the risk assessment using exposure from spray drift at 1 m for field or 3 m other crops, respectively.

The assessments should be separately conducted for the relevant species mentioned in the SANCO document (non-target arthropods, non-target plants). Guidance for the assessment of terrestrial vertebrates and birds is given in the document SANCO/4145/2000 (2002). It should be applied in a similar way as for non-target arthropods and plants.

5.4.2. Tier II:

Further assessment is needed if the relevant vapour pressure trigger is exceeded and mitigation measures are required in the basic exposure and risk assessments (FOCUS 2001, SANCO/10329/2002 rev.2 (2002) and SANCO/4145/2000 (2002)). This group propose that at Tier II the assessment is done by means of a model that estimates deposition as a function of distance from the edge of field. Several short-range transport models passed the first step of FOCUS AIR model evaluation. However, their use in an exposure assessment scheme is currently limited for reasons outlined in Section 4.9.1. During the lifetime of the working group new information on the aquatic deposition of volatilised pesticides after application onto plants became available (Fent, 2004). These data are the best currently available. Based on these data, EVA 2.0 was developed using an empirical relationship between vapour pressure and deposition after volatilisation to a non-target surface. In order to obtain a sufficiently conservative estimate for the deposition after volatilisation, EVA 2.0 is calibrated

to the 90th percentile of measured deposition. As stated in Section 4.9.1 the EVA model can be used as an interim solution for the assessment of short-range deposition.

No model is currently appropriate to specifically address the dry deposition of pesticides to terrestrial areas. However, deposition calculations of EVA 2.0 are carried out on an aerial basis (e.g. % of applied rate) they can therefore be used to estimate deposition onto terrestrial non-target areas. It is recognized that the scientific processes controlling dry deposition to terrestrial areas can be different to those applicable for aquatic areas. Nonetheless, in the current absence of direct knowledge regarding deposition to terrestrial surfaces, FOCUS AIR recommends that EVA 2.0 can also be used for this exposure route as an interim solution.

In general, FOCUS AIR proposes EVA 2.0 could be used in Tier II of the exposure assessment for volatilisation and short-range transport of pesticides in the air and subsequent deposition to an adjacent non-target area as an interim solution. The proposed scheme should be reviewed as soon as a better, experimentally tested, model becomes available. Moreover, an analysis of the uncertainty in the input data for this model and their propagation to the calculated exposure concentrations would give valuable information on the reliability of these exposure concentrations. It should be noted that the use of EVA 2.0 for FOCUS AIR is limited to the estimation procedure of the deposition after spraying outdoor agricultural crops. Other functionalities of EVA 2.0 such as the calculation of predicted environmental concentrations, toxicity exposure ratios as well as emissions from indoor uses should not be used within the procedures proposed by FOCUS AIR.

If this first approach using simple deposition classes as implemented in EVA 2.0 does result in unacceptable exposure concentrations it should be considered whether a refined modelling approach using more sophisticated process description could be taken into account. As an example it could be shown that the volatilisation of a substance is reduced if degradation on the plant surface is fast (e.g. by photolytical processes), or if penetration into the plant occurs. As shown in Section 4.7.1.2, these additional processes can be considered by using a model such as Consensus PEARL. In future, process-based models may be used for modelling dispersion in air as well as deposition. For the time being, however, no recommendation can be given how existing process-based models should be used due to the lack of process understanding and scenarios.

5.4.3. Tier III:

If modelling finally results in unacceptable PECs real deposition data can be determined experimentally and/or mitigation measures can be applied to reduce the PECs to an acceptable

level. No detailed guidance can be given here; as this would be a case-by-case decision. In terms of mitigation measures, examples are increased edge-of-field distances, use of spray reducing equipment, or modified application conditions. In terms of experiments, the performance of a field or a semi-field volatilisation experiment would be proposed with a more realistic quantification of the deposition after volatilisation. Different experimental approaches are currently available (Siebers *et al.*, 2003a; Gottesbüren *et al.*, 2003, Hoffmann *et al.*, 2003, Fent, 2004).

Figure 5.4–3 shows a flow diagram for the proposed short-range scheme for aquatic deposition, Figure 5.4–4 shows a flow diagram for the proposed terrestrial deposition scheme.

5.4.4. Very volatile pesticides

Volatilisation and subsequent deposition of very volatile compounds e.g. fumigants ($V_p > 10^{-2}$ Pa at 20°C) can result in a substantially higher emission and off-site exposure rates than from other exposure routes, even when they are incorporated into the soil (e.g. methyl bromide, Yates *et al.*, 1997). Therefore these substances would not adequately be assessed by the given exposure assessment schemes for SRT and a study would be required to determine the deposition from this type of substance. The nature of this study would need to be agreed by the registrant and the authority concerned.

Figure 5.4–3: Assessment Scheme for Aquatic Deposition

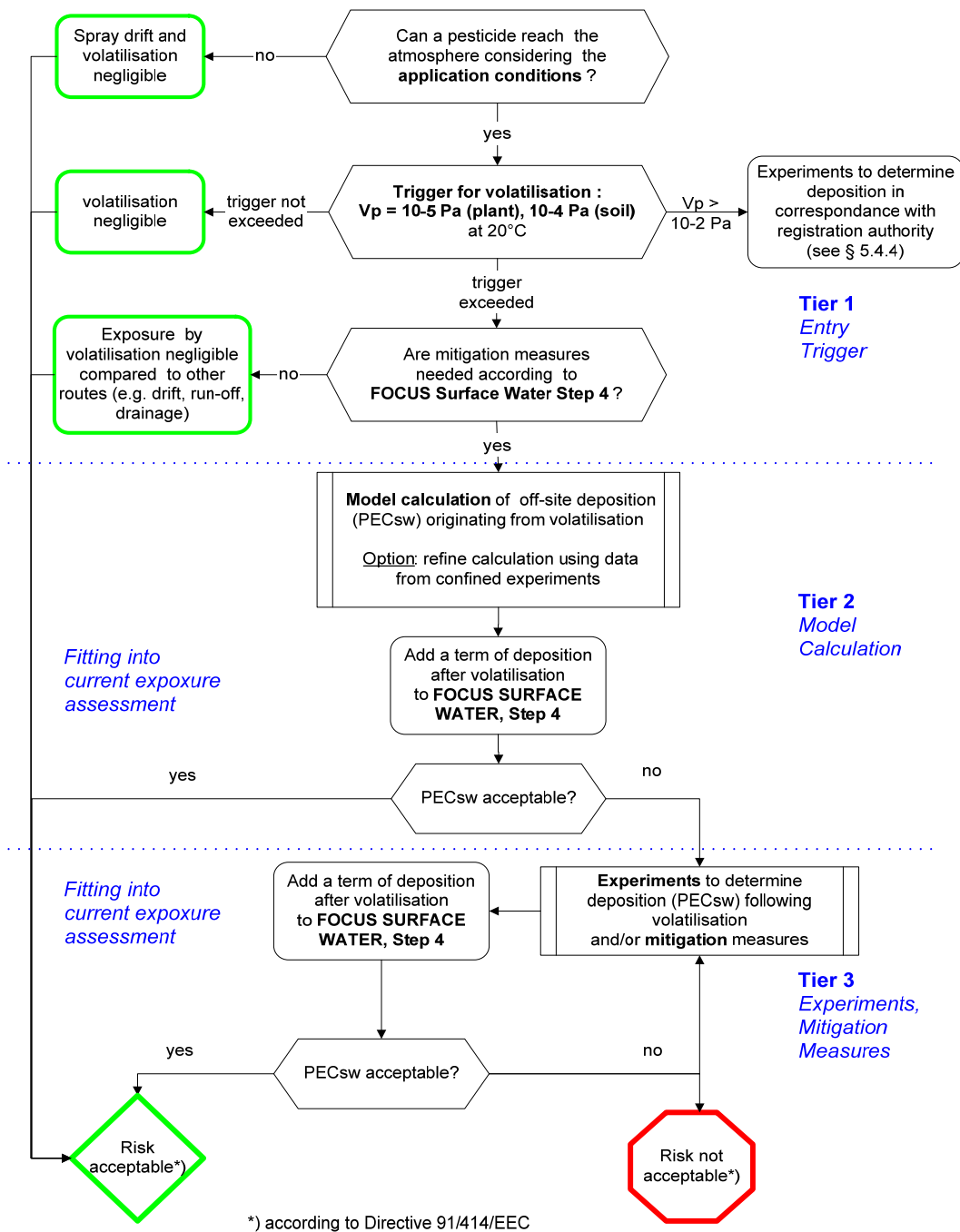
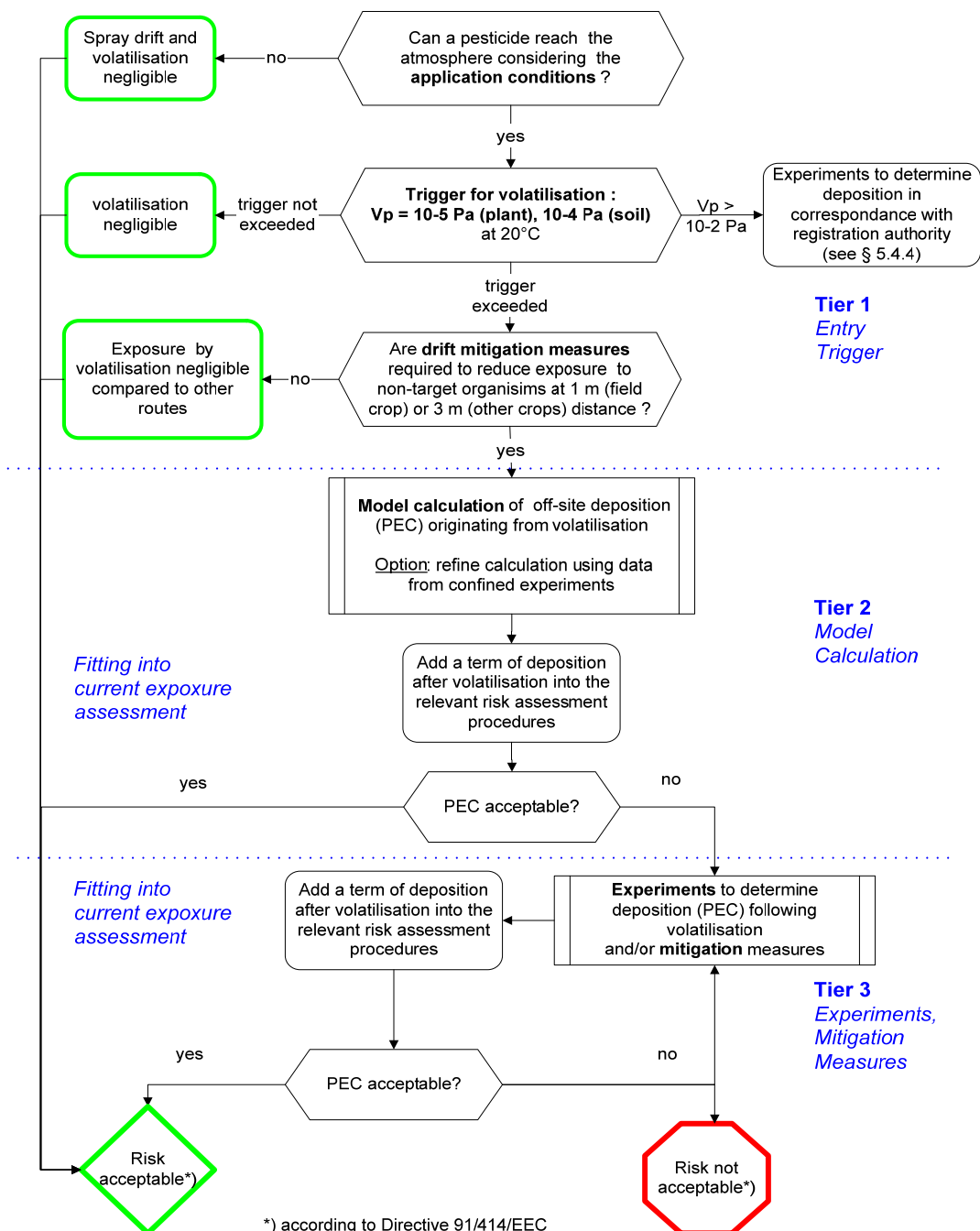


Figure 5.4–4: Assessment Scheme for Terrestrial Deposition



5.5. Special Cases Not Included in Proposed Schemes

5.5.1. *Exposure Assessment for Application to Rice Fields*

Volatilisation from water, for example after application to flooded rice fields, needs to be considered separately to that from plants and soil. In this case, Henry's law constant, rather than the vapour pressure, is a better indicator for potential emission to the atmosphere. However, no simple trigger for volatilisation could be obtained from the literature.

Exposure of surface water from rice agriculture was considered by the MED-RICE group (MED-RICE 2003). However their assessment considered exposure of an adjacent drainage canal from spray drift and outflow only. It is likely that volatilisation is negligible compared to outflow, if the same magnitude of volatilisation as from plants and soil is assumed – this is shown by a model calculation in Appendix 9.

5.5.2. *Environmental Exposure from Indoor Use*

Few data are available for a potential exposure of surface waters and terrestrial sites adjacent to greenhouses and storehouses where pesticides have been used (see Chapter 2, Section 2.6). Experiments for single standard greenhouses have been conducted by BBA and UBA, in which the ventilation can be considered as worst case (Siebers *et al.*, 2003b). At 5 m distance between greenhouse and a model surface water body, the total deposition to the water body over the first 24 hr after application was between <0.001 % for procymidone and tebufenpyrad and 0.05 % of the application rate for lindane using high volume application techniques.

Considering the measurements carried out in the German greenhouse studies, the aquatic deposition percentages are lower than the spray drift percentages used in the FOCUS SW step 3 assessment (FOCUS 2001) for outdoor field spray uses (e.g. the drift from arable crops is 0.57% of the application at 5m distance, drift from other crops is even higher). Therefore as a first step for exposure assessment the drift percentages for outdoor applications could be used. (Note that the drift percentages are independent of compound properties, whilst the deposition percentages of the emission from a greenhouse are dependent on the properties of the compound).

Where there are indoor uses only, and safe use cannot be demonstrated using the FOCUS SW step 3 drift percentages, then the deposition percentage of 0.05 % (based on lindane deposition) should be used for compounds where the application method is by high volume

application (and also low volume application - by comparison to the Dutch emission data). Where the application is by ultra low volume (for a definition see Chapter 2, Section 2.6) no experimental data are available on deposition. In the absence of these data, and based on the emission percentages from Dutch measurements relative to high and ultra-low volume applications, a conservative estimate of a four-fold increase in deposition percentage (i.e. 0.2 %) for ultra-low volume applications could be included.

Environmental conditions from the German studies may not be the worst case in terms of the percentage deposition occurring. However in conjunction with the use of the deposition percentage from the pesticide lindane (considered on the basis of available data to be worst case pesticide for deposition), the FOCUS AIR Group considers that the percentages recommended are sufficiently conservative for the range of likely experimental conditions and pesticide properties. Experimental deposition data measured at 5 m in the German studies can further be considered as a reasonable estimate of the deposition at 1 m (expected to be highest) since the decrease of the deposition percentage with distance is relatively low in the first 10 m range (see Figure 5.4–1).

If the risk assessment still does not show safety using these revised exposure percentages, then the exposure assessment would need to be further revised on a case-by-case basis using scientifically defensible justifications.

6. LONG-RANGE TRANSPORT POTENTIAL

Currently, there are various decision-making schemes for the assessment of substances (including pesticides) for long-range transport (EPPO 2003, UNEP 2001, Guicherit *et al.*, 1999, Rodan *et al.*, 1999, Pennington *et al.*, 2001). However these schemes tend to be tiered decision making frameworks based largely on simple trigger values (e.g. partition coefficients and half-lives) and do not contain risk assessment strategies in which predicted environmental concentrations (PECs) are compared to toxicity endpoints for various species and safe levels defined. In the absence of clear risk assessment guidance, the aim of the FOCUS Air group was to firstly provide a simple means to screen out substances that are of no concern for long-range transport; and secondly, to provide generic guidance on how to evaluate those substances identified as having the potential for long-range transport. A tiered risk assessment scheme for long-range transport would require the definition of exposure scenarios and was therefore specifically beyond the remit of this group.

Pesticides are unique for the amount of ecotoxicological and environmental fate data that are required in order to gain registration within the EU. Thus more is known about the effects of pesticides than other substances, such as PCBs, that have also been detected in so-called “pristine” areas. However, no guidance is available on appropriate species in remote environments, and there are no long-range transport scenarios available for PEC calculation. Risk is therefore difficult to quantify. Nonetheless, a concentration limit (equivalent to a limit of detection) for long-range transport of pesticides is impractical and unscientific and decisions on individual substances should be made on a risk basis.

This Chapter establishes an appropriate way to identify substances for which long-range transport is not a concern, and provides general guidance on how to evaluate substances identified as being of potential concern.

6.1. Assessment of Long-range Transport Potential

Earlier chapters assess the relevant processes involved in the Long-Range Transport (LRT) of pesticides (Chapter 3) and the model types/approaches to simulating these (Chapter 4) as well as emissions of pesticides into the atmosphere (Chapter 2).

Transformation and deposition are the major pesticide-related processes whilst meteorological factors can be incorporated through the use of models. It is important to recognise that these models can provide an interpretation of the effect of the compound properties on its LRT potential. However, the models cannot compensate for, or otherwise over-ride, any basic

uncertainty or inaccuracy in the experimental determination of these pesticide-specific properties, or uncertainty in the emission data.

There are thus 3 levels of modelling complexity that can be applied for estimating the potential for a pesticide to be transported long distances in the atmosphere, depending on the level of input data available and complexity required:

1. **Simple LRT physical-chemical trigger values** (requires pesticide-specific chemical properties as provided by Directive 91/414).
2. **Evaluative modelling assessment** (requires pesticide-specific chemical properties as provided by Directive 91/414 and an evaluative model environment – which may require large assumptions in its definition).
3. **Atmospheric transport and deposition modelling** to provide geographical spatial PECs or deposition fluxes (requires detailed meteorological and environmental information, detailed information on chemical properties and their variation with environmental changes as well as emission data).

Each of these modelling approaches is described below.

6.1.1. Simple Trigger Values

These are based on the processes considered and discussed in Chapter 3 (Transport, Transformation and Deposition). The most straightforward parameter for a simple trigger would be DT_{50air} .

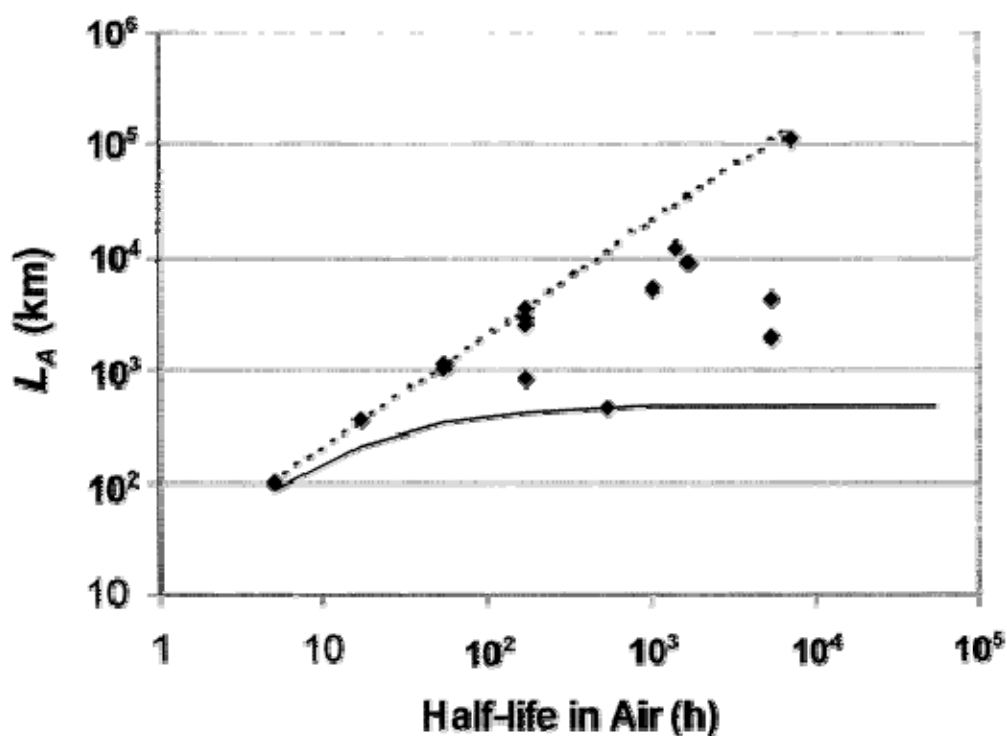
A DT_{50} for air of 2 days is already applied as a POP criterion (UNEP, 2001; UNECE, 1998) in other global initiatives. What this value essentially means is that if a chemical has a DT_{50} of 2 days then 50% of the chemical has the potential of being transported as far as parcel of air can travel in 2 days. Assuming a typical average wind speed of 5 m/s (18 km/h), a parcel of air can travel $18 \times 48 \text{ h} = 864 \text{ km}$ in 2 days (48 h). This distance of 864 km (about the distance from Berlin to Stockholm) is also known as the half-distance (i.e. the distance at which the air concentration will have dropped by half relative to the source air).

However, the DT_{50} is a slightly simplistic measure because it only accurately reflects the residence time of chemicals that partition 100% to the air. Many chemicals will not volatilise to air from the terrestrial surface or will be significantly deposited back to the terrestrial surface and will thus not travel as far as the above calculation suggests. The DT_{50} is a conservative trigger in this regard. This is illustrated in Figure 6.1–1 using a plot of the

estimated characteristic travel distance (CTD) (see Chapter 4 for more information) against the air DT_{50} . The CTD also accounts for atmospheric deposition. The points below the dotted line represent chemicals that do not travel as far as predicted from the DT_{50} alone because they are deposited.

To take account of the tendency of pesticides to partition to surfaces (soils, water, vegetation etc.), the evaluation could be complicated further. One way to do this is to combine the DT_{50} trigger with physical-chemical property triggers. For example, for chemicals with a $\text{Log } K_{OA} > 9.0$ or $\text{Log } K_{AW} < -6.0$, less than 0.1 % of the total chemical in a multimedia box model environment is predicted to partition to air from terrestrial/aquatic surfaces (see Figure 6.1–2). These chemicals are thus unlikely to be LRT chemicals even if their DT_{50} is more than 2 days because the vast majority of chemical used will remain partitioned to terrestrial surfaces.

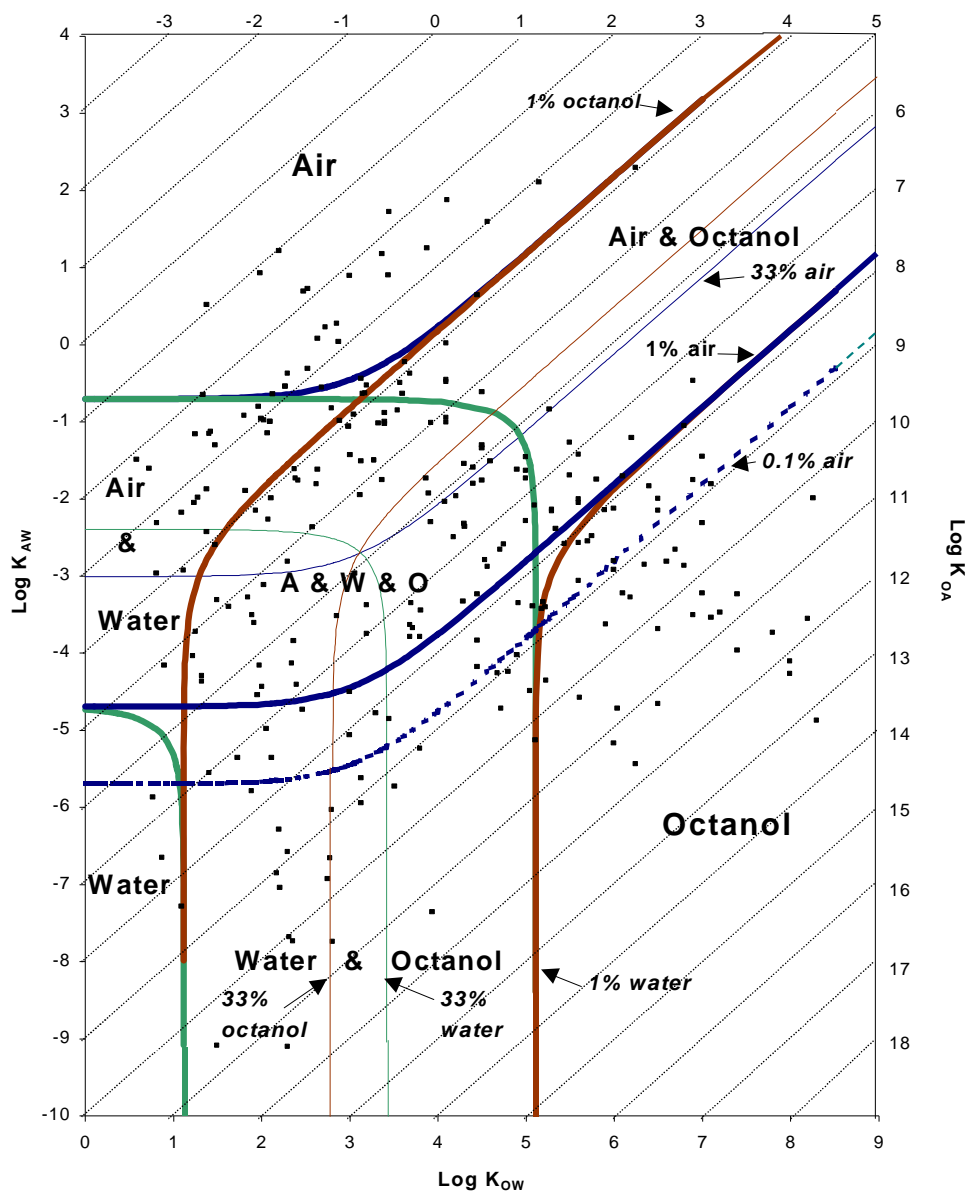
Figure 6.1–1. Characteristic travel distance in air (L_A) as a function of half-life in air (L_A) for a range of chemicals. The dashed line is the maximum L_A , i.e., when the chemical is 100% partitioned to air (this is simply wind speed multiplied by DT_{50}). The solid line represents a “minimum travel distance” i.e. for a chemical that will deposit as soon as possible. Reproduced from Beyer *et al.* (2000)



Another process that is not accounted for well in a simple DT_{50} trigger is particle bound transport. If a pesticide in air partitions appreciably to small airborne particles it may be transported long distances by “piggybacking” a ride with the particles before they deposit. Pesticides may degrade more slowly if sorbed to a particle and could theoretically travel long

distances even if their DT_{50} in the free phase is <2 days, however, there is no experimental information to back up this judgement. Very fine atmospheric particles have long residence times in the atmosphere and thus have the potential to travel distances further than 1000 km. Larger particles will be more efficiently scavenged by rain and will travel much shorter distances. Discussion of the residence times and removal processes of different types of particulate matter in the atmosphere can be found in general texts on atmospheric chemistry and physics (e.g. Seinfeld and Pandis, 1997). There is a paucity of literature information presenting data on the size fraction of particulate matter to which pesticides are associated. The partitioning of a pesticide between the gaseous and particulate phase depends on the vapour pressure or K_{OA} (Bidleman and Harner, 2000). If the mass of particulate matter in air is comparatively small, then a low vapour pressure or high K_{OA} could still result in a substantial fraction ($>>50\%$) of the total amount in the atmosphere sorbed to particulate matter (Bidleman and Harner, 2000). Partitioning between the vapour and particulate phases and deposition processes are discussed in more detail in Chapter 3.

Figure 6.1–2. Plot of $\text{Log } K_{AW}$ vs. $\text{Log } K_{OW}$ for 233 organic chemicals on which dotted lines of constant K_{OA} lie on the 45 diagonal. This graph shows the wide variation of properties. Volatile compounds tend to lie in the upper left, water-soluble compounds tend to lie in the lower left. The thicker lines represent constant percentages present at equilibrium in air, water and octanol phases, assuming a volume ratio of 656,000:1300:1 (taken from Mackay, 2001). Note that pesticides generally form a very small sub-set of all chemicals in respect of their range of $\text{Log } K_{AW}$ (generally < -1) and $\text{Log } K_{OW}$ (generally < 5)



6.1.2. *Evaluative Transport Models*

These models, discussed at more length in Chapter 4, provide an estimate of the potential for a pesticide to be transported long distances in the atmosphere by calculating travel distances (or other metrics defined in Chapter 4) in an evaluative model world. These calculations combine reaction and partitioning information for chemicals to provide a more sophisticated assessment than can be provided by the DT₅₀ in air alone.

A variety of evaluative models have been developed, which provide a range of different model outputs (see Chapter 4 for a list of models and types of outputs) including the Characteristic Travel Distance (CTD). One criticism of these models is that model generated metrics such as CTD depend strongly on the design of the evaluative model environment (e.g. soil organic matter, inclusion of vegetation, wind speed etc.). Intercomparison studies of these models (Wania and Mackay, 2000; OECD, 2004) have shown that the outputs from these different models compare favourably, especially when comparing the rankings of travel distances for large lists of chemicals. Although these models have generated interest amongst regulators, a model-generated metric such as CTD currently has little regulatory significance. These models could potentially be used for comparing/benchmarking calculated travel distances for currently registered pesticides with travel distances for known long-range transport chemicals such as PCBs, lindane and hexachlorobenzene. In this way the models could be used to support other experimental evidence.

6.1.3. *Atmospheric Transport and Deposition Models*

Complex models are available (see Chapter 4) that can provide PECs at geographical locations remote to the site of application. For some models these PECs are provided only for the well-mixed troposphere. Atmospheric modellers have recently added other media to their models and PECs can now be additionally provided for water, soil, sediments and even vegetation (e.g. EUROS, ISCST-3). Multimedia box modellers have also generated highly spatially resolved models with improved description of atmospheric transport (e.g. BETR-NA and BETR-Europe), which can also provide multimedia box PECs.

Overall it is now possible with some models to get highly spatially resolved PECs for the European continent, which could potentially be used to provide exposure estimates for risk assessment (see review by van Jaarsveld and Van Pul, 1999). However the reliability of such models is uncertain due to the extremely limited validations that have been undertaken for the calculation of PEC (and model validations to date have been for persistent pesticides such as lindane, and toxaphene as well as PCBs, which are not representative of currently registered

pesticides) (e.g. Jacobs and Van Pul, 1996, Baart *et al.*, 1995). It should be noted that the concepts for the description of atmospheric transport and deposition as implemented in these models can be tested using persistent compounds.

6.1.4. FOCUS Proposal for Long-range Transport Entry Trigger

Following consideration of the options stated in the previous sections, the proposal of the group is to establish a simple trigger to rapidly exclude those compounds not considered to have realistic potential for LRT. Both the evaluative models and the more detailed atmospheric transport and dissipation models require input of the pesticide-specific parameters as a starting point for their more detailed consideration of potential exposure. Therefore at the initial trigger stage we consider that an appropriate pesticide-related property could be considered directly. The transformation rate in air has previously been identified as the major (although not only) property influencing the potential for LRT. In common with other initiatives (UNEP, 2001; UNECE, 1998) we therefore propose that the DT₅₀ in air of 2 days should be used as the initial screen to determine whether a pesticide has a potential for LRT.

In common with other aspects of regulatory assessment we consider that a tiered approach to measurement of the DT₅₀ in air would be acceptable. Evidence reviewed in Chapter 3 suggests that the theoretical Atkinson calculation is an acceptably accurate basis for a first tier assessment. If the calculated value exceeds 2 days then the possibility to determine the value experimentally is not excluded. If this experimentally derived value leads to a lower DT₅₀ than the theoretical calculation, then this experimentally measured value should be used in preference. However it is noted that there are no current standard procedures for the experimental determination of the DT₅₀ in air (some information is provided in OECD monograph 61 from 1993 and the need for standard methods to measure transformation rates in air and the design of necessary protocols needs further detailed consideration) and hence any experimental result would need to be justified on a scientific basis (e.g. with respect to the hydroxide radical concentrations used etc.). Finally, in order to standardise the input parameters for the Atkinson calculation it is proposed that a 12 hr day is used with a hydroxyl radical concentration of 1.5×10^6 OH radicals/cm³ as this maintains consistency with the current approach of the US EPA (i.e. trigger is two 12 hour days).

6.2. Considerations for Substances Exceeding the Long-Range Transport Trigger

The DT50 of 2 days is a widely accepted trigger value for long-range transport potential. Compounds that have a DT50 greater than 2 days do not necessarily have the ability to undergo long-range transport. The fact that this trigger is based only on the transformation in air is conservative in the sense that other removal processes are not taken into account. The trigger is not a measure of risk. Any evaluation of risk needs consideration of the potential concentration that substances may be found in, as well as the potential impact of that concentration. This means that a substance having a DT_{50air} of 100 days may not pose a greater risk than a substance having a DT_{50air} of 10 days, especially considering that substances may be transported to remote regions in only a few days.

It needs to be borne in mind that at this time there is no framework within Directive 91/414 to assess the risk arising from LRT, and particularly to the possibility of different sensitive species (for instance in polar regions). Also, existing ecotoxicological risk assessments under this Directive concentrate on the field environment (i.e. very short off-target distances) and generate higher predicted exposures than would be expected for long-range distances. Nevertheless, in the absence of any other guidance, the existing framework for ecotoxicological risk assessment for the field environment provides a basis by which the deposition from LRT (wet and dry) may be placed in context of known endpoints and effects.

The levels of pesticides measured in remote environments show that it is extremely unlikely that acute effects will be caused by a single deposition event such as rainfall. Concern over deposition in these environments centres on low-level exposure of species that are regarded as more sensitive than species in agricultural environments, because they are not usually exposed to pesticides. In order to address this concern, deposition over a period of time (ideally the period over which longer-term toxicity endpoints were derived) is more appropriate than deposition from a single event. An extremely conservative assumption would be to consider the total annual or seasonal deposition for substances that show a strong seasonal pattern and are not persistent or bioaccumulate.

It may be possible to adequately demonstrate safety by the incorporation of additional information (e.g. the amount of substance entering the atmosphere; the behaviour of the compound during transport in the atmosphere; the potential concentration that a substance may be found in a remote region) into some of the modelling approaches detailed in Sections 6.1.2 and 6.1.3. However, these should be justified on a scientific basis where undertaken.

Further data and processes that should be considered when assessing the LRT potential of compounds with $DT_{50air} > 2$ days are detailed in Sections 6.2.1 and 6.2.2.

An impressive example of what may be achievable in a given situation can be seen in the work of Cryer *et al.* (2003) where complex process modelling allowed pesticide residues (chiefly for soil fumigants) in air to be calculated directly. Demonstration of safe levels of residues at distances less than the long-range can show that levels in air at greater distances show safety. Note however that this type of approach requires considerable effort to obtain the required dataset and requires the definition of an exposure scenario.

In addition to modelling techniques, the availability of monitoring data also offers the possibility to re-assess the exposure of a pesticide in remote environments and this is discussed further in Section 6.2.3.

6.2.1. Potential for Entry into the Atmosphere

The general principles and processes involved in the emission of pesticides into air are discussed in Chapter 2. Clearly, the amount of a substance entering the atmosphere will influence its concentration in a remote environment. At the most basic level, the amount applied within Europe may need to be considered; for example, dilution in air alone may be enough to make any impact of a substance unlikely, if it is used only in small amounts for a specialised application. It should be noted, however, that data on the usage of pesticides within Europe varies from Member State to Member State and can be difficult to obtain. Uncertainties in estimating emissions (in particular usage) can lead to uncertainty in model estimates of deposition.

Application technique can also have a significant effect upon the amount of residues entering the air (Van den Berg *et al.*, 1999). Granular applications, seed treatments, or applications made in greenhouses can reduce the amount of substance reaching the air to such an extent that it may require no further evaluation. Similarly, changes of application technique may be used to minimise residues entering the atmosphere at the site of application. Note that emissions from an application technique are dependent upon the technique, not the properties of the chemical.

The route of entry into the atmosphere may also be significant. Volatile substances will enter the atmosphere some time after application (typically within 24 hours) and losses of $>50\%$ may occur in extreme cases. Volatility is dependent upon chemical properties and volatilisation from plants and soil can be measured. Conversely, non-volatile substances may enter into the atmosphere as fine droplets created during spray application, and data on the

percentage of chemical entering the air as fine droplets are sparse. Preliminary computations with the IDEFICS model indicate that the emitted fraction can be up to ca. 10% of the dosage, although higher values can be predicted in more extreme cases (see Chapter 2, Section 2.2).

6.2.2. Transport and Deposition of Residues in the Air

The general principles and processes involved in the transport, transformation and deposition of pesticides in air are discussed in Chapter 3. Simple nomograms that categorise the fate of chemicals released into the air on the basis of chemical properties (see Figure 6.1–2) can be useful to estimate the potential fate of a pesticide. Similarly, the evaluative environments used in Multi Media box models can shed light on the potential fate of a chemical (see Chapter 4) and identify any compartments of potential concern.

A key consideration is whether a substance is transported primarily in the vapour or particulate phase. Those transported in the particulate phase may have a significantly shorter residence time than the DT₅₀ in air might suggest, as they may be “rained out” of the atmosphere in precipitation (Van Pul *et al.*, 1998; Asman *et al.*, 2001, Beyer *et al.*, 2000). Substances that are transported primarily in the vapour phase (and have low solubility) can show a lesser tendency to be removed from the atmosphere (Huskes and Levsen, 1997; Dubus and Hollis, 1998), although the Henry constant may be a more important factor than vapour pressure in determining the degree to which a substance is found in rainfall. There is evidence that substances that are transported primarily in the vapour phase, and have low Henry’s constants, do not show the same seasonal deposition compared to pesticides carried predominantly in the particulate phase (Dubus *et al.*, 2000).

The deposition of many pesticides can show a seasonal pattern (Huskes and Levsen, 1997; Goolsby *et al.*, 1997; Charizopoulos and Papadopoulou-Mourkidou, 1999; Halsall *et al.*, 1998; De Rossi *et al.*, 2003; Carrera *et al.*, 2002). Although substances with high vapour pressure and low solubility may be detected in the atmosphere year-round (Dubus *et al.*, 2000). A useful classification of deposition according to substance properties is given in Dubus *et al.* (2000).

Deposition may not lead to the permanent elimination of pesticides from the atmosphere. Although for the majority, adsorption to soil particles and plants; dissipation and degradation in soil and water column will remove deposited residues. Pesticides carried predominantly in the air phase however may be re-emitted into the atmosphere. This is the “grasshopper effect” and is one of the characteristics of POPs. Plotting chemical properties on the type of fate-in-air nomograms mentioned above can identify substances likely to show this behaviour.

6.2.3. The Role of Monitoring

In principle, monitoring can provide the clearest indication of long-range transport potential because concentrations are measured directly, rather than estimated. The literature contains a wealth of data on detections of pesticides in air, precipitation and environmental compartments such as mountain lakes. Unfortunately, the aim of most of these monitoring studies has been detection rather than risk assessment. This means that in practice few of the existing data can be used to estimate risk without making gross simplifying assumptions. Conversely, dedicated monitoring studies offer the opportunity to collect data tailor-made for risk assessment.

As a general rule, the aim of a monitoring study should be to measure deposition (i.e. rate/unit area) in a remote environment, rather than concentration. This is because deposition can later be expressed as a concentration once exposure scenarios have been defined. Although it is possible to measure concentrations directly in environments such as mountain lakes, interpretation of these data are uncertain because no standard protocol exists on site selection and sampling methodology. Measurement of the deposition into, rather than the concentration in, a remote environment allows for site-to-site comparison and the calculation of concentrations in environmental compartments using standard scenarios.

In order that monitoring data can be expressed as a deposition rate it is essential that sample volumes be known. It is well known that pesticide concentration can be related to the size of a rainfall event (Bucheli *et al.*, 1998, Goolsby *et al.*, 1997) with higher concentrations being observed with smaller rainfall events for some pesticides. Pesticides that are carried in the particle phase are effectively rained out of the atmosphere by even small amounts of rainfall (Mackay *et al.*, 1992). So, for a given mass of pesticide in air, a 1mm rainfall event will have a 10-fold higher concentration than a 10mm event, even though the mass deposited will be the same. Concentrations alone, therefore, give no indication of a deposition rate without a report of event volume, alternatively wet deposition can be expressed as a deposition/area/event as in Kuang *et al.* (2003).

Similarly, deposition of pesticides is sometimes aggregated into a total deposition over a large area. In order to assess the relevance of this deposition it needs to be converted into an effective rate per hectare. For example, a deposition of 300kg of a substance over 37,000 km² of the Netherlands is equivalent to an effective deposition rate of 0.08 g/ha/year. This value may be placed in context of an in-field application rate that may be several 100s of g/ha in a single application.

There are a number of quality criteria that need to be applied to monitoring data, not least of which are the analytical methods and limit of detection (LOD) of the pesticide. The ability to measure minute concentrations of some pesticides, and also to sample large volumes of air, means that detect levels of some pesticides can be extremely small. This can mean, in turn, that some pesticides are detected in remote environments, whereas others are not, solely on account of the different LODs of the pesticides, or the analytical methods used, or the sampling methodology. A concentration limit for long-range transport of pesticides is therefore impractical and unscientific.

Long-range transport of pesticides is dependent upon meteorology. There is therefore a chance element involved with deposition. A dedicated monitoring study would have to take this into account by placing the study in an area where the prevailing winds allowed for the chance of exposure, and would have to be conducted for long enough to ensure that precipitation including the active substance could occur. It is likely that this would require a monitoring study to be conducted for more than a single year. Similarly, uncertainties over the chance of exposure at a monitoring site could be minimised by conducting studies at more than one location, although locations would have to be positioned far enough away from each other to ensure that they did not sample the same air mass.

Any monitoring site for long-range transport would, in principle, have to be positioned over 1000 km away from the nearest area of agricultural use. Finding such sites could be problematic for substances that are widely applied in Europe. However, monitoring sites could be placed closer than 1000 km from the target area of pesticide use, because higher residues would be expected at a site that was closer to this area (provided that the direction of wind allows for exposure). Also, existing monitoring data showing detections at less than long-range could also be used to estimate deposition, provided they satisfy the considerations outlined above.

Few of the existing monitoring data for long-range transport measure the deposition of a pesticide annually or over the application period. This quantity may, however, be estimated from existing studies by using some simplifying assumptions. Peak wet deposition may simply be scaled to the required period (provided that sample volumes are available); also a concentration in air could be converted into a deposition by assuming a 2m (typical height of a weather station) column of air if the volume sampled is known and 100% deposition is assumed. Again this may simply be scaled to the required period. These are highly conservative approaches because they assume: wet deposition always occurs at the peak rate; 100% deposition of airborne residues; no dissipation or degradation in the environment concerned. A more refined estimate of deposition would take these factors into account. If it

can be shown that the levels measured are the result from representative use patterns at long-range transport, and that deposition levels are safe, then there would be no need to perform a dedicated monitoring study.

6.2.4. *Toxicity and Behaviour in the Environment*

The current absence of any other definition of a “safe level” of pesticides in remote environments implies that a risk assessment is required to determine whether safe uses can occur. The lack of a framework for risk assessment, and hence any defined scenarios for exposure estimation, means that the evaluation of substances exceeding the long-range trigger must be made on a case-by-case basis, taking into account the known behaviour and toxicity of the compound. Registration of agrochemicals under Directive 91/414 requires the generation of an extensive ecotoxicological data package to assess the potential impact upon biota, and a detailed environmental fate package to elucidate behaviour in the environment. It seems sensible therefore that these data should be used to assess any impact upon a remote environment arising from long-range transport – with due consideration given to the characteristics of the environment in question. The data package mandated by Directive 91/414 should make it easier to make this assessment for pesticides compared to the assessment of chemicals such as PCBs for which no such extensive data are required.

The scenarios used for in-field or edge-of-field assessment under 91/414 could be used to place pesticide loadings from atmospheric deposition and the resulting concentrations in environmental compartments in context of known endpoints and effects. Clearly these scenarios are not long-range transport scenarios, but there is considerable experience of making risk-based decisions using them; they could therefore provide a starting point for evaluating risk.

The use of these scenarios would be temporary measure to allow sensible risk-based decisions to be made for an individual substance. In future, a more detailed analysis of long-range transport of pesticides may recommend specific scenarios, or testing of different species, or may set safety levels. Until that time, the in- or near-field scenarios used under 91/414 make a sensible starting point for evaluation. Note however that consideration of additional safety factors to represent species sensitivity, persistence in remote environments and the potential to bioaccumulate may also have to be made.

Risk assessment of pesticides within the EU is typically done with reference to marker species that are used to represent whole classes of organisms. Including a safety factor into the assessment accounts for species sensitivity. As noted before, concern over the transport of

pesticides to remote environments mainly centres upon the effect of active substances on ecosystems that are regarded as being “more sensitive” than agricultural environments. In principle this could be accounted for by a safety factor approach. However expert ecotoxicological guidance would be required to set a suitable value.

Deposition should be converted into a concentration in a compartment of concern. It is incorrect to simply compare a concentration in rainfall to ecotoxicological endpoints, as it does not reflect the environmental concentration to which organisms are exposed and for which the endpoints were derived. For instance, if 1cm of rainfall containing a pesticide at a concentration of 1µg/L falls into a 30cm ditch (standard environment for aquatic risk assessment under Directive 91/414) it will experience a 30-fold dilution; the concentration of 0.03µg/l (1/30th of the rainfall concentration) should therefore be compared to aquatic endpoints, and not the rainfall concentration, because this is the concentration that aquatic organisms may be exposed to.

Long-range transport of pesticides involves the deposition of small amounts of substance. It is extremely unlikely that acute effects will occur from a single deposition event, chronic low-level loading of environments is therefore a more relevant quantity to consider. The assessment of risk should therefore be made with reference to chronic endpoints.

It is difficult to tell from a single study in a single location and year whether maximum, average, or below-average deposition patterns have been measured. The likelihood of deposition depends on the application(s) of the source substance in the source area(s) and the occurrence of airflow between the source area(s) and the monitoring site. A conservative estimate would be to consider the total annual or seasonal deposition measured (or calculated from) a monitoring study of sufficient quality. This quantity can be used as a conservative estimate of the maximum deposition, provided it can be shown that there was the likelihood of deposition occurring during the length of the study, and that there has been a representative use of the pesticides in the known source area(s) during the monitoring study (i.e. within Europe). The total annual deposition may not be a conservative estimate for substances that bioaccumulate or are persistent.

A conservative way to estimate the potential effects of long-range transport is to convert the annual or seasonal deposition into a concentration using the scenarios under 91/414, assuming that the mass enters the compartment of concern at one time. The resulting concentration can then be compared against chronic endpoints and safety levels estimated.

Using the annual or seasonal deposition in this way is conservative because transformation and other removal processes are not considered. In practice, these processes may mitigate exposure considerably, particularly over longer periods. A more refined assessment would include these processes to reduce the concentration resulting from the annual or seasonal deposition over a period relevant to the chronic endpoint. The annual mass can be equally partitioned over the period considered in the chronic endpoint for the species being considered. A time-weighted average concentration could therefore be calculated and compared to endpoints as before. This would still be conservative, as the annual or seasonal loading is taken as input. It should be noted however that the annual or seasonal loading may not be conservative for substances that bioaccumulate or are persistent.

The most realistic approach would be to consider the concentrations arising from measured deposition events as they occurred. Then the maximum deposition within the time window of interest for chronic toxicity testing can be taken. By setting this window against the measurement period, the period in the year with maximum deposition relevant to exposure of organisms can be found. However this approach would require that there was a realistic deposition pattern during the course of the study. It is highly likely therefore that data from more than one place and for more than one year would be required.

6.3. Conclusions

The DT_{50air} trigger has been set at a value of 2 days in order to identify substances that are not of potential concern for LRT; it is also consistent with other triggers for long-range transport (UNEP, 2001; UNECE, 1998) or pesticide authorisation (BBA). The trigger is not a measure of risk in itself: an exceedence of the trigger indicates the need for further evaluation in order that a decision can be made.

Substances tend to be found in remote environments in amounts that are a small fraction of the application. Some authors (Unsworth *et al.* 1999, Dubus *et al.* 1998) have concluded that the resulting concentrations are unlikely to be affecting remote environments, however other authors express concern over the potential for low-levels of pesticides to impact on environments far removed from agriculture, because species may be more sensitive than those in agricultural regions. It is a matter of debate whether this is true, and if so, which exposure scenarios are relevant, and what safety factors are appropriate for remote areas.

In the absence of any other guidance for setting of safe level of a pesticide in a remote environment, the potential for each substance that fails the entry level trigger to cause an

impact on remote environments should be assessed on a case-by-case basis. This should include a consideration of the following:

- The amount of the substance entering the atmosphere
- The likely behaviour of the substance as it is transported in and deposited from the air
- The potential impact on and behaviour in remote environments.

A concentration limit for long-range transport of pesticides is impractical and unscientific because the concentration at which substances can be detected is dependent upon analytical methods and sampling methodology. Decisions on individual substances should be made on a risk basis instead.

Consideration of atmospheric deposition as a way of entry into the in-field and edge-of-field scale scenarios required by 91/414 could provide a starting point for evaluating the risk arising from long-range transport. Particular attention should be paid to substances that bioaccumulate in food chains and are persistent once they reach a remote environment, as these are mechanisms by which trace concentrations may build up to harmful levels. Additional safety factors may also be required to address species sensitivity. Chronic toxicity endpoints are the most appropriate for assessing risk.

Monitoring data can confirm that a pesticide has been transported to a remote region. The following principles are proposed for using monitoring data to assess the risk posed from long-range transport:

- Monitoring studies should report the sampling methodology (e.g. sample volumes) and measure the input into, rather the concentration in, environments of concern. Deposition should be expressed as a rate/unit area/time.
- For substances which are not persistent or bioaccumulating the total annual deposition or deposition over a season (if deposition has a seasonal pattern) is a conservative quantity to use to estimate a concentration in a compartment of concern. This quantity can be derived (or calculated) from monitoring studies of sufficient quality, preferably at more than one location and more than one year. However if monitoring data are used to estimate this deposition from a single study it must be shown that there was the likelihood of deposition occurring during the length of the study, and that there has been a representative use of the pesticide in known source area(s) during the monitoring study (i.e. within Europe)

- More refined estimates of concentrations in compartments of concern would require a consideration of transformation or other dissipation/removal. Time weighted average concentrations, relevant to toxicity endpoints, could therefore be calculated. The total annual or seasonal deposition can be estimated from existing monitoring data (provided they are of sufficient quality) using a number of conservative simplifying assumptions, or from a dedicated monitoring programme.
- Time-weighted average concentrations could also be calculated arising from measured events and considering the highest cumulative total deposition that occurs during the year over the period of interest for the chronic endpoint of the species. This would likely require a dedicated monitoring study.
- Dedicated monitoring studies would need to be conducted in more than one place and for longer than a year in order to maximise the chance of deposition being detected. The highest residues are likely to occur at sites that are closest to exposing crop, provided that winds can blow in the required direction.
- There is a need for guidance on how to assess the quality of existing monitoring studies, as well as guidance on how to set up a monitoring programme that meets the quality requirements.

Modelling can be used to shed light on the potential behaviour of a substance once entering the air, and also to rank a chemical against others whose behaviour is known. Complex process models can be used to demonstrate that residues in air reach safe levels at scales shorter than long-range (i.e. >1000 km). However due consideration needs to be given to the validation status of any model and the availability of data, particularly on emissions.

7. ADVERSE EFFECTS TO THE ATMOSPHERE

7.1. Introduction

This Chapter investigates the potential for pesticides to adversely affect the atmospheric environment, the following topics are addressed:

- global warming
- ozone depletion
- photochemical smog formation
- acidification and eutrophication

The Chapter takes the work of De Leeuw (1993) and Hauschild and Wenzel (1998) as a starting point for evaluating the hazard posed by all chemicals to the atmosphere. Once criteria for estimating hazard are defined, the risk from pesticides is assessed.

The introduction of a chemical to the environment can occur through emissions during its production and by its use and disposal. After emissions, chemical substances can be transported, dependent upon degradation in air and deposition, to non-target areas (water and soils). The notification of a new substance with a production level greater than 1 tonne/year is required following the European directive 79/831/EEC.

Environmental criteria used for life cycle assessment of products (LCA) in general are the following:

1. use of resources
2. greenhouse effect
3. stratospheric ozone depletion
4. acidification
5. over-fertilisation
6. photo-smog
7. human and environmental toxicity

8. nature use

9. noise

Clearly, not all of these categories are appropriate to pesticides, especially points 5,8 and 9. Point 7 is addressed elsewhere in this document and will not be commented upon further in this Chapter.

Toet and De Leeuw (1993) introduced a method by which the potential for a new substance to cause environmental problems related to the atmosphere could be assessed. They identified the following issues as relevant:

- climate change
- atmospheric ozone, both in troposphere and stratosphere
- acidification and eutrophication.

In general the potential for any chemical to affect the atmosphere is related to its atmospheric residence time. There are also a number of chemical properties that may indicate whether a substance is a cause for concern. These two topics are addressed first in this Chapter, before specific issues related to the atmosphere, such as climate change, are discussed.

7.2. Hazard Potential

Hazard potential may be used as the starting point for the assessment of the potential of pesticides to impact upon the atmosphere. This is a more relevant quantity for assessing this potential than merely considering the absolute amount emitted. The hazard potential can be defined as: *the harmfulness of an emitted amount of specific pesticide relative to the harmfulness of the same amount of a reference compound.*

7.2.1. Atmospheric lifetime

The assessment of the atmospheric hazard of a chemical requires the determination of the atmospheric lifetime, and consequently, the evaluation of the removal processes from the atmosphere.

Removal processes can be summarised as (see Chapter 3) :

- dry and wet deposition
- chemical reaction, mainly photochemical reactions

The atmospheric lifetime of a specific chemical, which may be defined as :

$$\tau = \frac{1}{k_d + k_w + k_c}$$

where k_d and k_w are representative rates for dry and wet deposition removal, k_c is the pseudo first order transformation rate.

7.2.2. Chemical parameters

The wet and dry deposition depend strongly on:

- gas/particle partition
- vapour pressure - compounds with vapour pressure $> 10^{-4}$ Pa are generally present in the gas phase whereas those with vapour pressure $< 10^{-4}$ Pa are bound to aerosols. Wet removal is very efficient for the removal of particle-bound substances whereas the removal of gaseous compounds is dependent upon the Henry constant.

The atmospheric degradation of a chemical can be affected by four processes :

- direct photolysis
- reaction with OH-radicals
- reaction with ozone
- reaction with NO_3 -radicals

The main oxidation pathway for the majority of organic compounds is through the reaction with OH-radicals. Various procedures are available to estimate the reaction rate, k_{OH} , of this process, such as smog chamber experiments and Structure Activity Relationships (SAR). The Atkinson approach (Atkinson 1987; 1988) is the preferred method to obtain a first estimate of k_{OH} . Degradation of pesticides in air is discussed in greater detail in Chapter 3.

Reaction with ozone occurs only for compound with double or triple bonds. Structure activity relationships have also been developed (Atkinson and Carter, 1984) for this process.

Reactions with other oxidants are minor with respect to OH-radicals and O_3 reactions.

The atmospheric lifetime (τ_x) of a chemical X with respect to photochemical processes can be defined as :

$$\tau_x = \frac{1}{k_c}$$

with :

$$k_c = J + k_{OH}[OH] + k_{O_3}[O_3] + k_{NO_3}[NO_3]$$

and J is the photolysis rate (see Leeuw, 1993).

7.3. Climatic changes

The impact of a chemical on global warming depends strongly on its IR absorption characteristics. If a chemical shows absorption bands in the region 8500-11 000 nm (called atmospheric window) it may potentially be identified as a greenhouse gas. If this case is verified, the “global warming potential (GWP) of the chemical needs to be estimated.

The GWP is defined as: as the ratio of calculated warming of each unit of mass of gas emitted into the atmosphere relative to the mass unit of the reference gas CFC-11. The concept of GWP was developed for the assessment of the climatic impact of chlorofluorocarbons (CFCs) and the proposition of substituted hydrogen- chlorofluorocarbons (HCFCs). The application of this process, without recourse to the use of CFC-11 as a reference, requires knowledge of the IR absorption strength and atmospheric lifetime, as these are the dominant factors influencing GWP. The GWP of a substance can be expressed as follows:

$$GWP = \frac{\tau_P}{\tau_{CFC11}} \cdot \frac{M_{CFC11}}{M_P} \cdot \frac{S_P}{S_{CFC11}}$$

where: τ_P is the atmospheric lifetime of the chemical P; M_P is the molecular mass; and S_P is the IR absorption strength in the interval 800-1200 cm^{-1} . Global atmospheric models can be used for the more detailed assessment of GWP (see for example World Meteorological Organisation , WMO 1989, 1991)).

When the IR-absorption strength and the lifetime of a chemical are known, Equation 4 can be used as a first evaluation of the possible impact of this chemical on climatic change.

Substances that have a lifetime of less than 2 – 3 years would generally be expected to have GWP values less than 0.03.

7.4. Atmospheric ozone

Two factors need to be considered in order to assess whether chemicals can have an impact upon atmospheric ozone: the impact upon stratospheric ozone and the impact upon ozone formation in the troposphere.

7.4.1. Stratospheric ozone

A chemical can have an impact on the stratospheric ozone when :

- the atmospheric lifetime is long enough to permit the transport of the chemical to the stratosphere
- the chemical contains one or more Cl or Br substituents. Other halogens do not play an important role in stratospheric ozone depletion (see de Leeuw, 1993).
- chemicals containing N and S can also play a role in the stratospheric ozone depletion, even if they are emitted at high altitudes (volcanoes), or if they have a very long atmospheric lifetime (N₂O for example).

The potential risk of a chemical can be estimated from Ozone Depletion Potential (ODP), which is defined as: the ratio of calculated ozone column change for each unit of mass of a gas emitted to the atmosphere relative to the depletion calculated for an equal mass of the reference gas CFC-11.

The ozone column is defined as the total amount of ozone between the earth surface and space or, mathematically expressed, as the integral of ozone concentration through the entire atmosphere.

Since stratospheric ozone column contributes 90 % of the total ozone column, ODP can be used for the measurement of the potential of a chemical to affect the stratospheric ozone layer. The ODP provides an estimate of the maximum calculated effect of a chemical relative to the maximum calculated effect of an equal amount of CFC-11 and this ODP concept is widely used to evaluate the potential effect on stratospheric ozone of CFCs and HCFCs.

In general, ODP values approach zero for species with atmospheric lifetime less than one year and as first approximation can be obtained for a chemical P by :

$$ODP = \frac{\tau_P}{\tau_{CFC11}} \cdot \frac{M_{CFC11}}{M_P} \cdot \frac{n_{Cl} + \alpha n_{Br}}{3}$$

where τ_P is the atmospheric lifetime of the chemical P; M_P is the molecular mass; n_{Cl} and n_{Br} , the number of Cl and Br atoms in the molecule; and α is a measure of the effectiveness of Br in ozone depletion compared to Cl (α depends on the stratospheric concentrations of Cl and Br). For an estimated stratospheric concentration of Cl of about 3 ppb, a reasonable value of α is 30. ODP can be estimated in a similar way to GWP by means of global 1-dimensional or 2-dimensional atmospheric models (see WMO ozone assessment reports WMO 1989, 1991).

The Montreal protocol has included methylbromide (CH_3Br) as the only pesticide which can be responsible for ozone layer depletion. Under this protocol, developed countries have agreed to reduce the use of methyl bromide by 70 % by 2003 and terminate its use by 01 January 2005, except for minor and specific use (e.g. pre-shipment). Developing countries have until 2015 to stop the use of methyl bromide. Hauschild and Wenzel (1998) have calculated the time-dependant ODP of methyl bromide together with some CFCs and HCFCs (Table 7.4–1).

Table 7.4–1. Time-dependant ODP value for some important halocarbons (Hauschild and Wenzel, 1998).

Substance	Formula	Atmospheric lifetime (years)	5y	10y	15y	20y	30y	40y	100y
CFC11	$CFCl_3$	50±5	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Tetrachloromethane	CCl_4	42	1.26	1.25	1.24	1.23	1.22	1.20	1.14
HCFC142b	CH_3CF_2Cl	19.5	0.17	0.16	0.15	0.14	0.13	0.12	0.08
Halon 1211	CF_2ClBr	20	11.3	10.5	9.7	9.0	8.0	7.1	4.9
Methyl bromide	CH_3Br	1.9	15.3	5.4	3.1	2.3	1.5	1.2	0.69

7.4.2. Tropospheric ozone

Tropospheric ozone production and the rate at which this ozone formation takes place depends on a number of factors :

- the reactivity of the compound and the degradation pathway
- the meteorological conditions (characterised by high temperature, high levels of solar radiation and low wind speed)
- the concentration of other air pollutants, especially ozone precursors such as NO_x in concentrations of ppb and VOCs such as xylene, aldehydes and olefins etc.

Derwent and Jenkins (1991) have proposed to the use of a Photochemical Ozone Creation Potential (POCP) as a way to compare the potential for organic compounds to impact upon ground-level ozone concentration. The POCP index can be defined as *the relative effect of ozone of a unit of mass of an organic compound (i.e. chemical) compared to that caused by an equivalent mass of ethene. By definition, ethene has a POCP value of 100.*

It has been shown that the PCOP value for a new chemical cannot be determined easily since it requires knowledge of the atmospheric degradation pathway and this information is generally not available from laboratory studies. The effect of a chemical on tropospheric ozone cannot be estimated since only very basic characteristics are known.

However, a first indication of episodic ozone formation can be obtained from a reactivity scale based on the rate constant for the (OH + hydrocarbons) reaction and molecular weight as follows :

$$OH - scale = \frac{k_P}{M_P} \cdot \frac{M_{C_2H_4}}{k_{C_2H_4}} \cdot 100$$

where k_P is the OH-rate constant at 298 K of chemical P; and M_P is the molecular weight (OH-scale can easily estimated via structure activity relationship).

7.5. Impact on the chemical composition of the troposphere

The potential impact of a chemical on the composition of the troposphere can be easily assessed. Assuming a well-mixed troposphere, the concentration, C in the troposphere is defined by :

$$\frac{dC}{dt} = fQ - \frac{C}{\tau}$$

where Q is the global emission strength, f is the dilution factor relating to mixing ratio ($f=5.9/M$ where M is the molecular mass and f has units of ppt), and τ is the atmospheric lifetime.

Accumulation in the troposphere occurs when :

$$\frac{dC}{dt} > 0 \quad \text{or} \quad \tau > \frac{C}{fQ}$$

In order to prevent the accumulation of pollutants in the troposphere, the introduction of persistent compounds (lifetime exceeding 20 years) should be avoided.

7.6. Acidification

When, a molecule containing Cl, F, N or S substituent oxidises, acidic molecules, such as HCl, H₂SO₄, HNO₃, can be formed. Deposition of these oxidation products onto to surfaces (soil or water) can lead to the acidification. The Acidification Potential (AP) can be defined as *the number of potential acid equivalents per mass unit compared to the number of acid equivalents per unit of a reference compound (SO₂ is proposed as reference gas)*

The AP is given by the following formula :

$$AP = \frac{M_{SO_2}}{M_p} \cdot \frac{n_{Cl} + n_F + n_N + 2n_S}{2}$$

7.7. Eutrophication

The Eutrophication Potential (EP), can be defined as:

$$EP = \frac{M_{NO_2}}{M_p} \cdot (n_N + n_P)$$

where NO₂ is the reference compound, and the deposition of nitrogen and phosphorous is of importance.

7.8. Discussion and conclusions.

Generally, the hazard potential depends strongly on the atmospheric residence time lifetime, which in turn depends on the rate by which removal processes (wet and dry deposition, chemical conversion) take place. The hazard potential of pesticides depends only on their chemical characteristics; an estimate of their emission is also required to assess risk to the

atmosphere. A full assessment of the atmospheric risk of a pesticide, requires a consideration of both direct and indirect emissions (e.g. volatilisation from soil and water).

Emissions of currently used pesticides are likely to be negligible compared to emissions of other substances such as CO₂, and hence the effects on the atmosphere are likely to be marginal in comparison. This point needs to be bourn in mind when considering the potential effects of pesticides on the atmosphere.

In conclusion it can be stated that for substances that are applied in high volumes the following adverse effects can potentially occur:

- global warming potential (GWP), only if chemical is volatile, has a strong IR absorption (800-1200 cm⁻¹) and long residence time (> 1 year). Global warming potential should be measured relative to CO₂
- ozone depletion potential (ODP) in the stratosphere, only if chemical is volatile and atmospheric residence time > 1 year
- accumulation in the troposphere, only if the chemical is a gas and the atmospheric residence time > 20 years
- photochemical ozone creation potential (POCP) in the troposphere particularly valid for volatile and reactive chemicals
- acidification potential (AP) is compared to SO₂ as reference gas
- eutrophication (EP) is compared to NO₂ as reference compound
- The most relevant physical properties of pesticides to consider are: Henry's law constant, vapour pressure and K_{ow}.

It is very unlikely that these Hazardous Potentials apply to pesticides.

8. CONCLUSIONS

The FOCUS Air Working Group carried out an extensive review of the literature on pesticides in air. From this review it was concluded that considerable uncertainty surrounds the processes that result in the deposition of pesticides from air and that relatively more is known about the emission of pesticides to air than either their transport and transformation in air or their deposition from air.

A detailed model inventory resulted in the selection of 7 models appropriate for modelling short-range transport, 3 models for modelling long-range transport and 6 models for modelling emission. No appropriate **process-based** models could be recommended for modelling short-range exposure of pesticides.

A tiered short-range exposure assessment scheme was established. The first Tier is a vapour pressure trigger to identify substances that need no further evaluation. Substances that are applied to plants and have a vapour pressure less than 10^{-5} Pa (at 20°C), or are applied to soil and have a vapour pressure less than 10^{-4} Pa (at 20°C), need not be considered in the short-range risk assessment scheme. Substances that exceed these triggers, require evaluation at the second Tier, which is done by modelling.

In the light of current uncertainty regarding the modelling of deposition of volatilised pesticide residues, the group recommends that the EVA 2.0 model be used for estimating exposure as an interim solution until a better, experimentally tested, model becomes available. The group considered that dry deposition was quantitatively less important than spray drift at edge-of-field. Therefore, the residues arising from deposition of volatilised residues should be added to exposure estimates currently made under 91/414 only when mitigation measures are required for spray drift assessment. If safety cannot be demonstrated by modelling, further experimental data are required.

Following high and medium volume application in a greenhouse, a maximum deposition of 0.05 % of the application rate was demonstrated at a distance of 5 m from the greenhouse. For ultra-low volume application a deposition four times this amount i.e. 0.2% is assumed to be conservative.

The group proposes that a long-range transport trigger of a $DT_{50\text{air}}$ in air of < 2 days be used to identify substances that require no further evaluation for long-range transport. Substances exceeding this trigger require further evaluation to estimate their potential impact; recommendations have been made on how to conduct such an evaluation.

The different processes that may cause a pesticide to impact upon air quality were addressed. It was concluded very unlikely that currently registered pesticides would have such an impact

9. SUGGESTIONS FOR FURTHER WORK

The FOCUS Air Group make the following recommendations for further work with regard to the exposure assessment of pesticides in air:

- The relevance of the loss to the atmosphere during application (i.e. airborne residues distinct from drift) is not yet clear and this pathway of atmospheric loss should be further investigated.
- Further assessment of the processes governing medium range transport and the implications for exposure assessment at this scale is needed.
- Further data are needed from field or semi-field experiments on the deposition of volatilised pesticides to improve the validation status of EVA 2.0 and short-range emission and transport models in general
- Further work (in particular more experimental data) is required to understand the basic processes involved in deposition after volatilisation in order that process-based models can be improved for modelling short-range transport. In addition more work is needed to understand the driving factors and differences between dry and wet deposition.
- More data are needed on the effect of pesticide formulation on pesticide volatilisation losses during application.
- The validation status of long-range transport models needs to be improved. This would require appropriate data on the usage and emissions of pesticides on a regional scale and research on the link between sources of pesticide emissions and sinks in the environment.
- Further data on the emission from greenhouses and indoor uses would help to refine the recommended estimates of deposition
- Standard protocols for measuring the half-life of pesticides in air need to be established
- There is a need for guidance on how to assess the quality of existing monitoring studies for long-range transport, as well as guidance on how to set up a monitoring programme that meets the quality requirements

- In order to develop an exposure scheme for long-range transport, scientifically based protection goals need to be set i.e. a definition needs to be made of what needs to be protected and how to protect it.

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11. GLOSSARY OF TERMS

Term	Meaning
Calibration	Adjusting one or more input parameters to improve the match between model output and experimental data
Computer model	Model that describes the mathematical model in code that can be executed by a computer
Deterministic model	Mathematical or computer model in which all parameters can have one unique value only and in which one parameter set results in one unique output
Distribution of scenarios	a number of scenarios to be created which reasonably characterise the range of driving forces for the environmental fate mechanism being studied; driving forces are in this context the primary variables controlling the environmental fate mechanism
Dry deposition	Removal of vapours and particles from the air by deposition on soil, plant or water surfaces
Emission	The entry of pesticides into the air by different mechanisms. (i.) During application: by spray drift (aerial transport of spray fog) and volatilisation of the substance from the airborne spray fog. (ii.) After application: by volatilisation from sprayed surfaces (e.g. plants, soil, water and greenhouses)
Fugacity	Escaping tendency of compound in any phase
Glasshouse	Building with natural ventilation rate less than 10 hr^{-1} (i.e. ten exchanges of air to the outdoors per hour)
In-field exposure	Exposure within the treated field
Lee eddy	Air flow structure at the lee side of a wind obstacle
Long range	Distance greater than 1000 km
Mathematical model	model that describes the conceptual model in terms of mathematical equations
Medium range	Distance between 1 and 1000 km
Mixing ratio	Ratio of the amount (or mass) of a substance in a given volume to the total amount (or mass) of all constituents in that volume
Multi media model	Model that describes the exchange of compounds between at least two different media, e.g. soil and air or vegetation and air
Off-field exposure	Exposure outside the treated field
Probabilistic model	Mathematical or computer model which accounts for variability in one or more input parameters and expresses outputs as probability density functions; a probabilistic model is often just a deterministic model run many times
Re-emission	Emission of pesticide from deposit resulting from previous aerial transport out of the treated area
Scenario ¹	a representative combination of crop, soil, weather and agronomic parameters to be used in modelling; representative means in this context that the selected scenarios should represent physical sites known to exist, i.e. the combination of crop, soil, weather and agronomic conditions should be realistic
Short range	Distance between 0 and 1000 m
Spray Drift	Losses of the spray fog during application measurable near the sprayed area (as downwind ground deposit) after sedimentation of the spray fog droplets up to a few minutes after application (~5mins)

Term	Meaning
Travel distance	Distance over which the compound is transported through the air
Validation process	comparison of model output with data independently derived from experiments or observations in the environment; this implies that none of the input parameters is obtained via calibration; note that this definition does not specify any correspondence between model output and measured data
Validity range	that part of reality to which the validation of a model applies
Validation status	the extent to which a model has successfully been validated within its range of validity
Validated model	model which has gone successfully through a validation process for a specified range of validity; this implies that the number of datasets considered is sufficient for the intended use of the model
Verification	examination of numerical technique in the computer model to ascertain that it truly represents the mathematical model and that there are no inherent numerical problems with obtaining a solution; this implies also a check on errors in the code
Volatilisation	The transfer of condensed pesticide residues from surfaces (e.g. leaves, soil water) into the atmosphere after application or from spray droplets during application.
Wet deposition	Removal of vapours and particles from the air in rainfall

12. LIST OF ABBREVIATIONS

Abbreviation	Meaning
AOEL	Acceptable Operator Exposure Level
BBA	Biologische Bundes Anstalt
BCF	Bio-concentration factor
CTD	Characteristic travel distance
CV	Cumulative Volatilisation
DCPA	Chlorthal-dimethyl
DT _{50air}	Time period during which 50% of mass in air is transformed
ECPA	European Crop Protection Association
EPPO	European Plant Protection Organisation
EPTC	S-Ethyl dipropyl thiocarbamate
EUROPOEM	European Predictive Operator Exposure Model
FOCUS SW	FOCUS Surface Water
GC-FID	Gas chromatography – Flame Ionisation Detection
HV	High volume application technique
HQ	Hazard Quotient
IADN	Integrated Atmospheric Deposition Network
IDOE	International Decade of Ocean Exploration
LRT	Long range transport
LR50	50% of the lethal rate
LV	Low volume application technique
LOD	Limit of detection
LOQ	Limit of quantification
LRT	Long Range Transport
MMM	Multi Media box Model
MRT	Medium range transport
OC	Organo-chlorine
PEC	Predicted environmental concentration
PEC _{sw}	Predicted environmental concentration in surface water
PNEC	Predicted No Effect Concentration
POP	Persistent Organic Pollutant
PCB	Polychlorinated biphenyl
SEAREX	Sea Air Exchange Program
SRT	Short Range Transport
SW	Surface Water
TER	Toxicity Exposure Ratio
TGD	Technical Guidance Document
ULV	Ultra low volume application technique
VIF	Virtually Impermeable Film
VOC	Volatile Organic Compound

13. LIST OF SYMBOLS AND UNITS

Symbol	Description	Units
a	Intercept in correlation of Smit et al.	-
A	Surface area	m ²
AR	Application rate	kg ha ⁻¹
b	Slope in correlation of Smit et al.	-
c _a	Concentration of substance in the air	kg m ⁻³
c _{g,0}	Concentration substance in gas phase at soil surface	kg m ⁻³
c _L	Concentration substance in the liquid phase	kg m ⁻³
c _{L,r}	Reference substance concentration in the liquid phase	kg m ⁻³
CV	Cumulative loss by volatilisation	-
d _a	Thickness of boundary air layer	m
D _a	Coefficient of substance diffusion in air	m ² d ⁻¹
D _{a,r}	Coefficient of diffusion in air at reference temperature	m ² d ⁻¹
D _w	Coefficient of diffusion in water	m ² d ⁻¹
D _{w,r}	Coefficient of diffusion in water at reference temperature	m ² d ⁻¹
DT50s	50% transformation time in soil	d
DT50a	50% transformation time in air	d
DT50 _{ov}	The overall half-life of the chemical in the environment	
f _{p,gas}	Fraction of substance in gas phase	-
f _{oc}	Fraction of organic carbon	-
h	source height	m
H	Henry coefficient (dimensionless form)	-
J _{p,dry}	flux of dry deposition of substance	kg m ⁻² s ⁻¹
J _{p,wet}	flux of wet deposition of substance	kg m ⁻² s ⁻¹
J _v	Mass flux of volatilisation of substance	kg m ⁻² s ⁻¹
k _{NO3}	Rate coefficient for transformation by NO ₃ radicals	s ⁻¹
k _{O3}	Rate coefficient for transformation by O ₃ radicals	s ⁻¹
k _{OH}	Rate coefficient for transformation by OH radicals	s ⁻¹
K	constant depending on greenhouse shape and wind direction	-
K _a	Dissociation constant for weak acids	mol m ⁻³
K _{F,eq}	Freundlich sorption coefficient	m ³ kg ⁻¹
K _d	Linear-sorption coefficient	m ³ kg ⁻¹
K _H	Henry coefficient for gas/liquid partitioning	-
K _{aw}	Coefficient for partitioning between air and water	-
K _{oa}	Coefficient for partitioning between octanol and air	-
K _{ow}	Coefficient for partitioning between octanol and water	-
K _{oc}	Coefficient for sorption on organic carbon	-
K _{sa}	Coefficient for partitioning between soil and air	-
K _x	Eddy diffusion coefficient in the X direction	m ² s ⁻¹
K _y	Eddy diffusion coefficient in the Y direction	m ² s ⁻¹
K _z	Eddy diffusion coefficient in the Z direction	m ² s ⁻¹
L _{dis,g}	Dispersion length for the gas phase	m
L _{dis,L}	Dispersion length for the liquid phase	m
M	Molar mass	kg mol ⁻¹
m _{a,p}	Areic mass of substance on the plants	kg m ⁻²
m _{oc}	Mass fraction of organic carbon in soil	kg kg ⁻¹
m _{om}	Mass fraction of organic matter in soil	kg kg ⁻¹
N	Freundlich exponent	-
p	probability density function for an air parcel moving from x at time t to x' at time t'	-

Symbol	Description	Units
pK_a	Negative decimal logarithm of K_a	-
$p_{v,s}$	Saturated vapour pressure of the substance	Pa
$p_{v,sr}$	Saturated vapour pressure of substance at reference temperature	Pa
pH	Negative decimal logarithm of C_H^+	-
P_{ov}	The overall residence time of the chemical in the environment (time to degrade to 1/e of the original mass)	d
Q	Source strength of emission	$kg\ s^{-1}$
Q_v	volumic mass rate of emission	$kg\ m^{-3}\ s^{-1}$
r_a	Resistance for transport through boundary air layer	$s\ m^{-1}$
r_s	Resistance for diffusion through top boundary soil layer	$s\ m^{-1}$
R	Molar gas constant	$J\ mol^{-1}\ K^{-1}$
R_t	Volumic mass rate of substance transformation	$kg\ m^{-3}\ s^{-1}$
$R_{v,p}$	Areic rate of volatilisation from the plants	$kg\ m^{-2}\ s^{-1}$
$R_{w,p}$	Areic rate of wash-off from the plants	$kg\ m^{-2}\ s^{-1}$
RH	Relative humidity	-
$S(x,t)$	Source term	$kg\ m^{-3}\ s^{-1}$
S_w	Substance solubility in water	$kg\ m^{-3}$
S_e	Relative water saturation	-
S_r	Substance solubility at reference temperature	$kg\ m^{-3}$
SC	Fraction of the soil covered by the plants	-
t	Time	d
T	Temperature	K
T_r	Reference temperature	K
\bar{u}	Average wind speed in X direction	$m\ s^{-1}$
u_x	wind speed in X direction	$m\ s^{-1}$
u_y	wind speed in Y direction	$m\ s^{-1}$
u_z	wind speed in Z direction	$m\ s^{-1}$
u_x'	eddy fluctuation in X direction	$m\ s^{-1}$
u_y'	eddy fluctuation in Y direction	$m\ s^{-1}$
u_z'	eddy fluctuation in Z direction	$m\ s^{-1}$
x	downwind distance	m
X_t	Half-distance for atmospheric transport	m
y	crosswind distance	m
z	vertical distance	m
ϵ_g	Volume fraction of gas phase	$m^3\ m^{-3}$
$\theta(h)$	Volume fraction of liquid phase	$m^3\ m^{-3}$
θ_s	Saturated volume fraction of liquid phase (total porosity)	$m^3\ m^{-3}$
λ	wavelength	nm
ρ_b	Dry soil bulk density	$kg\ m^{-3}$
$\sigma_y(x)$	standard deviation for the Gaussian distribution in the Y direction	-
$\sigma_z(x)$	standard deviation for the Gaussian distribution in the Z direction	-
τ_a	Atmospheric residence time	d

APPENDIX 1 STEP 1 EVALUATION OF EMISSION MODELS

Table A1 –1 Step 1 Evaluation of Emission Models

General Information	Model Name		FOCUS-PEARL	CONSENSUS-PEARL	PELMO	PRZM	IDEFICS	PEM
	Name or number of most recent release		FOCUS-PEARL 2.2.2	CONSENSUS-PEARL 2.1.1.	FOCUS-PELMO 3.3.2	FOCUS-PRZM 2.4.1	IDEFICS 3.2	PEM 1.1
	Intended use of the model		Emission (Leaching, behaviour in vadose zone)	Emission; Leaching, behaviour in vadose zone)	Emission (Leaching, behaviour in vadose zone)	Emission (Leaching, behaviour in vadose zone)	Drift	Emission
	Model developers		Tiktak et al.	Van den Berg et al.	Klein, M.	Carsel et al.	Holterman et al.	Scholtz T.
	Institution		Alterra and RIVM	Alterra and RIVM	FHG Schmallerberg	EPA, Waterborn	A&F, The Netherlands	Ortech
	Year of recent version		2003	2004	2002	2002	2002	2003
Availability	1.1	Availability of executable	Yes	Yes	Yes	Yes	Expected	Expected
	1.2	Possibility to run executable on a PC	Yes	Yes	Yes	Yes	Yes	Yes
	1.3	Availability of documentation	Yes	Yes	Yes	Yes	Expected	Expected
	1.4	Transparent type version control	Yes	Yes	Yes	Yes	Yes	Expected
Substances	2.1	Model can be used/was already used for organic compounds	Yes	Yes	Yes	Yes	Yes	Yes
Processes of emission models	3.1	Calculation of emission from plants or soil or water	Yes	Yes	Yes	Yes	From droplets in air	Yes
	3.2	Calculation of emission with help of independent parameters possible		Yes	Yes	Yes	Yes	Yes
	3.3	Temporal resolution of output <= 1 day		Yes	Yes	Yes	N/A	Yes
Further consideration in the FOCUS process			Yes	Yes	Yes	Yes	Yes	Yes

Table A1 – 1 Step 1 evaluation of Emission models (contd)

		Model Name	EXAMS	RICEWQ	Sesoil	MACRO	LEACHP /LEACHV
General information		Name or number of most recent release	EXAMS 2.98.03	RICEWQ 1.4		MACRO 4.3	
		Intended use of the model	Emission from water (behaviour in surface water)	Emission	Emission (Leaching, behaviour in vadose zone)	Emission (Leaching, behaviour in vadose zone)	Emission (Leaching, behaviour in vadose zone)
		Model developers		Williams, Ritter Cheplick		Jarvis N.	Hutson & Wagenet
		Institution	EPA	Waterborne Environmental Inc	Waterborne Environmental Inc		
		Year of recent version	2001			2002	
Availability	1.1	Availability of executable	Yes	Yes	Yes	Yes	No
	1.2	Possibility to run executable on a PC	Yes	Yes	Yes	Yes	Yes
	1.3	Availability of documentation	Yes	Yes	Yes	Yes	?
	1.4	Transparent type version control	Yes	Yes	Yes	Yes	?
Substances	2.1	Model can be used/was already used for organic compounds	Yes	Yes	Yes	Yes	Yes
Processes of emission models	3.1	Calculation of emission from plants or soil or water	Yes	No	Yes	Yes	?
	3.2	Calculation of emission with help of independent parameters possible	Yes	No	Yes	Not yet	?
	3.3	Temporal resolution of output <= 1 day	Yes	Yes	No information	Yes	Yes
Further consideration in the FOCUS process			Yes	No	No	No	No

APPENDIX 2: STEP I EVALUATION OF TRANSPORT AND DEPOSITION MODELS

Table A2 –1 Step 1 evaluation of transport and deposition models (Part I)

General information	Model Name		PESTDEP	ISCST	EVA		EUROS
	Name or number of most recent release		PESTDEP	ISCST3	EVA1.1	EVA2.0	5.4
	Intended use of the model		Emission - SRT - Deposition	SRT / LRT Deposition	Emission - SRT - Deposition	Deposition after volatilisation	Emission, Transport and Deposition at European scale
	Model developers		Asman	EPA	Winkler, R., Koch, W,		Sauter et al.
	Institution		Danish Institute of Agricultural Sciences (DIAS), Denmark	EPA	German UBA		RIVM, Bilthoven, NL
	Year of recent version		1999	2000	2002	2004	2002
Availability	1.1	Availability of executable	Yes	Yes	Yes	Yes	Yes
	1.2	Possibility to run executable on a PC	Yes	Yes	Yes	Yes	Yes
	1.3	Availability of documentation	Yes	Yes	Yes	Yes	Yes
	1.4	Transparent version control	Yes	No info	Yes	Yes	Yes
Substances	2.1	Model can be used/was already used for organic compounds	Yes	Yes	Yes	Yes	Yes
Process of transport models	4.1	Consideration of area sources possible	Yes	Yes	Yes	Yes	
	4.2	Consideration of gaseous and sorbed transport					
	4.3	SRT models include dry deposition	Yes		Yes	Yes	
	4.4	MRT/LRT models include dry and wet deposition	n.a.		n.a.	n.a.	
	4.5	MRT/LRT models consider degradation	n.a.		n.a.	n.a.	
	4.6	Model should be appropriate for use under European conditions	Yes		Yes	Yes	
Further consideration in the FOCUS process			Yes	Yes	Yes	Yes	Yes

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General information	Model Name		EU-TREND	OPS	OPS_Pro	2-D OSLO
	Name or number of most recent release		1.13	1.20E	4	
	Intended use of the model		Emission,Transport and Deposition at European scale	Emission,Transport and Deposition in the Netherlands	Emission,Transport and Deposition in the Netherlands	Emission and Transport at global scale
	Model developers		Van Jaarsveld et al.	Van Jaarsveld	Van Jaarsveld	Fuglestvedt et al.
	Institution		RIVM, Bilthoven, NL	RIVM, Bilthoven, NL	RIVM, Bilthoven, NL	Univ Oslo
	Year of recent version		1995	1994	2003	1994
Availability	1.1	Availability of executable	Yes	Yes	Yes	No info
	1.2	Possibility to run executable on a PC	Yes	Yes	Yes	No info
	1.3	Availability of documentation	Yes (but no manual)	Yes	Yes	No info
	1.4	Transparent version control	Yes	Yes	Yes	No info
Substances	2.1	Model can be used/was already used for organic compounds	Yes	Yes	Yes	No
Process of transport models	4.1	Consideration of area sources possible				
	4.2	Consideration of gaseous and sorbed transport				
	4.3	SRT models include dry deposition				
	4.4	MRT/LRT models include dry and wet deposition				
	4.5	MRT/LRT models consider degradation				
	4.6	Model should be appropriate for use under European conditions				
Further consideration in the FOCUS process			Yes	Yes	Yes	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General information	Model Name		3-D OSLO	ASIMD	AUSTAL	CALGRID	Cambridge model
	Name or number of most recent release				AUSTAL 2000	1.6c	
	Intended use of the model		Emission and Transport at global scale	?	Stack Emissions	Dispersion and transformation of reactive pollutants	Emission, Transport and Deposition at global scale
	Model developers		Berntsen and Isaksen	EMEP/ MSC-E	Ing.- Büro Janicke, Gesellschaft für Umweltphysik	Yamartino and Scire.	Law and Pyle
	Institution		Univ Oslo	Moscow	TA-Luft	Atmos. Studies Group, Earth tech, Concord MA, USA	Univ Cambridge
	Year of recent version		1994	?	2000	1998	1993
Availability	1.1	Availability of executable	Yes	No info	Yes	Yes	No info
	1.2	Possibility to run executable on a PC	Yes	No info	Yes	Yes	No info
	1.3	Availability of documentation	Yes	No info	Yes	Yes	No info
	1.4	Transparent version control	No info	No info	Yes	Yes	No info
Substances	2.1	Model can be used/was already used for organic compounds	Yes	No	No	Yes	No
Process of transport models	4.1	Consideration of area sources possible	Yes				
	4.2	Consideration of gaseous and sorbed transport	?				
	4.3	SRT models include dry deposition	Yes				
	4.4	MRT/LRT models include dry and wet deposition					
	4.5	MRT/LRT models consider degradation					
	4.6	Model should be appropriate for use under European conditions					
Further consideration in the FOCUS process			No	No	No	No	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General information	Model Name		CAR	CAR-FMI	CIT	CONTI-LINK	CTDM-PLUS
	Name or number of most recent release						
	Intended use of the model		Road Pollution	Road Pollution	Ozone formation in alpine regions	Road Pollution	Stack emissions in complex terrain
	Model developers		Eerens et al.	Harkonen and Karppinen	McRae	Larssen	Perry et al.
	Institution		RIVM, Bilthoven, NL	Finland Meteorological Institute	CCR ISPRA	Norwegian Institute for Air Research (NILU)	US-EPA
	Year of recent version		1993	1998	1988	1993	1989
Availability	1.1	Availability of executable	No info	Request needed to model developers	No info	No info	Yes
	1.2	Possibility to run executable on a PC	No info	Yes	No info	No info	Yes
	1.3	Availability of documentation	No	Yes	No info	No info	Yes
	1.4	Transparent version control	No	Yes	No info	No info	No info
Substances	2.1	Model can be used/was already used for organic compounds	No	No	No info	No	Yes
Process of transport models	4.1	Consideration of area sources possible					
	4.2	Consideration of gaseous and sorbed transport					
	4.3	SRT models include dry deposition					
	4.4	MRT/LRT models include dry and wet deposition					
	4.5	MRT/LRT models consider degradation					
	4.6	Model should be appropriate for use under European conditions					
Further consideration in the FOCUS process			No	No	No	No	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General information	Model Name		TMK	DISPERSION	DMU	DRAIS	ECHAM
	Name or number of most recent release			2.1	?	?	
	Intended use of the model		Emission and Transport at global scale	Urban air quality	Emission, Transport and Deposition at European scale	Ozone formation	Emission, Transport and Deposition at global scale
	Model developers		Velders et al.	Backstrom and Omstedt	Zlatev	Nester et al.	Roelofs and Lelieveld
	Institution		KNMI, The Netherlands	Swedish Meteorol. Institute (SMHI)	Nat Environm. Research Inst. Denmark	KfK	Univ Wageningen
	Year of recent version		1994	2001	1995	1987	1995
Availability	1.1	Availability of executable	No info	Yes	No info	No info	No info
	1.2	Possibility to run executable on a PC	No info	Yes	No info	No info	No info
	1.3	Availability of documentation	No info	Yes	No info	No info	No info
	1.4	Transparent version control	No	Yes	No info	No info	No info
Substances	2.1	Model can be used/was already used for organic compounds	No	No	Yes	No info	No
Process of transport models	4.1	Consideration of area sources possible					
	4.2	Consideration of gaseous and sorbed transport					
	4.3	SRT models include dry deposition					
	4.4	MRT/LRT models include dry and wet deposition					
	4.5	MRT/LRT models consider degradation					
	4.6	Model should be appropriate for use under European conditions					
Further consideration in the FOCUS process			No	No	No	No	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General information		Model Name	EKMA/OZ IPM4	EMEP /MSC- E/ acid deposition	EMEP /MSC- W/ photochemistry	EMEP/MS C-W/ acid rain	EMEP/MSC- W/ sulphur
		Name or number of most recent release	Unknown				
		Intended use of the model	Urban Air Quality: Ozone formation			Acid rain in Europe	Sulphur in Europe
		Model developers	Jeffries and Sexton	MSC-E	Simpson	Barrett et al.	Jakobsen et al.
		Institution	US EPA	Russian HydroMeteorological Office	DNMI	DNMI	DNMI
		Year of recent version	2000	1993	1993	1995	1995
Availability	1.1	Availability of executable	Yes	No info	No info	No info	No info
	1.2	Possibility to run executable on a PC	Yes	No info	No info	No info	No info
	1.3	Availability of documentation	Yes	No info	No info	No info	No info
	1.4	Transparent version control	Yes	No info	No info	No info	No info
Substances	2.1	Model can be used/was already used for organic compounds	No	No	No	No	No
Process of transport models	4.1	Consideration of area sources possible					
	4.2	Consideration of gaseous and sorbed transport					
	4.3	SRT models include dry deposition					
	4.4	MRT/LRT models include dry and wet deposition					
	4.5	MRT/LRT models consider degradation					
	4.6	Model should be appropriate for use under European conditions					
Further consideration in the FOCUS process			No	No	No	No	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

		Model Name	EMEP MSC POP	EURAD (CTM)	HARM	HARWELL	HPDM
General information		Name or number of most recent release		EURAD CTM 3.0	10.4		
		Intended use of the model	LRT potential and overall persistence of POPs; emission scenario evaluation	Daily short-term forecasts of air pollution (NO _x , SO ₂ , O ₃ , CO, PM ₁₀ , according to the EU-directive 96/62 and its daughter directives 99/30	Emission, Transport and Deposition at European scale	Emission and Transport at global scale	Stack emissions
		Model developers	Shatalov, Strukov, Vulykh, Mantseva and Fedyunin	H.J. Jakobs, M. Memmesheimer, H. Elbern, E. Friese, H. Feldmann	Metcalf et al., 1995	Hough	Hanna and Paine
		Institution	Meteorological Synthesizing Centre-East of EMEP	Rhenish Institute for Environmental Research (RIU) at the University of Cologne	UK Met Office	Harwell Laboratory	Sigma Research Corp, USA
		Year of recent version	2003	2001	Unknown	1991	1989
Availability	1.1	Availability of executable	Yes	Standard version available for scientific purposes	Permission needed from principal investigator	No info	Yes
	1.2	Possibility to run executable on a PC	Yes	Yes	Yes	No info	Yes
	1.3	Availability of documentation	Yes	No	No information	No info	Yes
	1.4	Transparent version control	No	Yes	Yes	No info	No info
Substances	2.1	Model can be used/was already used for organic compounds	Yes	No	No	No	No
Process of transport models	4.1	Consideration of area sources possible					
	4.2	Consideration of gaseous and sorbed transport					
	4.3	SRT models include dry deposition					
	4.4	MRT/LRT models include dry and wet deposition					
	4.5	MRT/LRT models consider degradation					
	4.6	Model should be appropriate for use under European conditions					
Further consideration in the FOCUS process			No	No	No	No	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General information	Model Name		HYPACT	IFDM	IMAGES	INPUFF	UK-ADMS
	Name or number of most recent release		No info				
	Intended use of the model		Emission, transport and deposition of pollutants	Stack emissions	Emission, Transport and Deposition at global scale	Stack emissions	Stack emissions
	Model developers		Tremback et al.	Cosemans, R.	Mueller and Brasseur	Petersen and Lavdas	Carruthers et al.
	Institution		Colorado State university & ASTeR Inc.	VITO, Mol, Belgium	BISA, Brussel and NCAR, Boulder, USA	US EPA	UK Met Office and CERC
	Year of recent version		1993	1992	1995		1992
Availability	1.1	Availability of executable	No info	Yes	No info	Yes	Yes
	1.2	Possibility to run executable on a PC	No info	Yes	No info	Yes	Yes
	1.3	Availability of documentation	No info	Yes	No info	Yes	Yes
	1.4	Transparent version control	No info	Yes	No info	No info	Yes
Substances	2.1	Model can be used/was already used for organic compounds	No info	Yes	No	No	Yes
Process of transport models	4.1	Consideration of area sources possible		Yes			Yes
	4.2	Consideration of gaseous and sorbed transport					
	4.3	SRT models include dry deposition		Yes			Yes
	4.4	MRT/LRT models include dry and wet deposition		Yes			Yes
	4.5	MRT/LRT models consider degradation		Yes			
	4.6	Model should be appropriate for use under European conditions		Yes			Yes
Further consideration in the FOCUS process			No	Yes	No	No	Yes

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General information	Model Name		IVL	Liège model	LOTOS	Mainz model	MARS
	Name or number of most recent release				Lotos4		MARS 2.0
	Intended use of the model		Emission, Transport and Deposition at European scale	Emission, Transport and Deposition at global scale	Point and area emissions in Europe	Emission, Transport and Deposition at global scale	Photosmog formation in urban areas
	Model developers		Moldanova, Andersson-Skold	Hauglustaine et al.	Roemer and Builtjes	Kanakidou et al.	Moussiopoulos
	Institution		Swedish Environmental Institute	Univ Liege, Belgium	TNO	Max Planck Institute	Aristotle Univ Thessaloniki, Univ Karlsruhe
	Year of recent version		1992	1994	1996	1991	1995
Availability	1.1	Availability of executable	Not public domain	No info	No	No info	Not public domain
	1.2	Possibility to run executable on a PC	Yes	No info	No	No info	Yes
	1.3	Availability of documentation	Yes	No info	Yes	No info	Yes
	1.4	Transparent version control	No	No info	No	No info	Yes
Substances	2.1	Model can be used/was already used for organic compounds	Yes	No	Yes	No	No
Process of transport models	4.1	Consideration of area sources possible					
	4.2	Consideration of gaseous and sorbed transport					
	4.3	SRT models include dry deposition					
	4.4	MRT/LRT models include dry and wet deposition					
	4.5	MRT/LRT models consider degradation					
	4.6	Model should be appropriate for use under European conditions					
Further consideration in the FOCUS process			No	No	No	No	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General information	Model Name		MATCH	MEMO	MERCURE	MOGUNTIA	OML_Point
	Name or number of most recent release		4.2.0	6.0	3.2		2.1
	Intended use of the model		Urban air quality	Air motion and dispersion of inert pollutants	Atmpsrpheric dispersion of pollutants	Emission,Transport and Deposition at global scale	Dispersion of pollutants at local scale
	Model developers		SMHI Persson et al.	Moussiopoulou s and Kunz	Carissimo and Elkhalfi	Zimmermann	Olesen
	Institution		Swedish Meteorol. Institute (SMHI)	Aristotle Univ Thessaloniki, Univ Karlsruhe	EDF	Funke Consult	NERI, Denmark
	Year of recent version		2003	1997	1997	1992	1999
Availability	1.1	Availability of executable	Yes	Not public domain	Yes	Yes	Yes
	1.2	Possibility to run executable on a PC	Yes	Yes	Yes	Yes	Yes
	1.3	Availability of documentation	Yes	Yes	Yes	No	Yes
	1.4	Transparent version control	Yes	Yes	Yes	No	Yes
Substances	2.1	Model can be used/was already used for organic compounds	Yes	No	Yes	No	No
Process of transport models	4.1	Consideration of area sources possible			No		
	4.2	Consideration of gaseous and sorbed transport			No		
	4.3	SRT models include dry deposition					
	4.4	MRT/LRT models include dry and wet deposition					
	4.5	MRT/LRT models consider degradation					
	4.6	Model should be appropriate for use under European conditions					
Further consideration in the FOCUS process			No	No	No	No	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

		Model Name	OSPM	PLUME-PLUS	RAMS	REM3	ROAD AIR
General information		Name or number of most recent release		3.2	RAMSv4.4 and HYPACT v1.2		
		Intended use of the model	Road pollution	Atmpspheric dispersion of pollutants	Atmospheric dispersion and transport in complex terrain	Emission, Transport and Deposition in NW Europe	Road Pollution
		Model developers	Berkowicz	DenBoeft et al.	many	Freie Univ Berlin	Larssen and Torp
		Institution	NERI, Denmark	TNO, The Netherlands	TNO, MEP	Freie Univ Berlin	Norwegian Institute for Air Research (NILU)
		Year of recent version	1985	2003	2002		1993
Availability	1.1	Availability of executable	No info	Yes	Yes	Yes	No info
	1.2	Possibility to run executable on a PC	No info	Yes	Yes	No info	No info
	1.3	Availability of documentation	No info	Yes	Yes	No info	No info
	1.4	Transparent version control	No info	Yes	Yes	No	No info
Substances	2.1	Model can be used/was already used for organic compounds	No	Yes	Yes	No	No
Process of transport models	4.1	Consideration of area sources possible					
	4.2	Consideration of gaseous and sorbed transport					
	4.3	SRT models include dry deposition					
	4.4	MRT/LRT models include dry and wet deposition					
	4.5	MRT/LRT models consider degradation					
	4.6	Model should be appropriate for use under European conditions					
Further consideration in the FOCUS process			No	Yes	Yes	No	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General information	Model Name		STOCHEM	TVM	UAM	UDM-FMI	UiB model
	Name or number of most recent release		7		1.3		
	Intended use of the model		Atmpspheric dispersion of greenhouse gases and pollutants		Pollutants in urban airsheds	Industry and traffic emissions	Emission, Transport and Deposition at global scale
	Model developers		Johnson and Derwent	Schayes et al.	System Applications Int.	Karppinen and Harkonen	Strand and Hov
	Institution		UK Met Office	CCR ISPRA	ICF, System Applications Ltd	Finland Meteorological Institute	Univ Bergen
	Year of recent version		Unknown	1995	1999	1997	1994
Availability	1.1	Availability of executable	Permission needed from MetOffice	No info	Yes	Currently not public domain	Yes
	1.2	Possibility to run executable on a PC	No	No info	Yes	No	Yes
	1.3	Availability of documentation	No	No info	Yes	Yes	Yes
	1.4	Transparent version control	Yes	No info	Yes	No	No info
Substances	2.1	Model can be used/was already used for organic compounds	Yes	No	Yes	No	No
Process of transport models	4.1	Consideration of area sources possible				Yes	
	4.2	Consideration of gaseous and sorbed transport				No	
	4.3	SRT models include dry deposition				Yes	
	4.4	MRT/LRT models include dry and wet deposition					
	4.5	MRT/LRT models consider degradation					
	4.6	Model should be appropriate for use under European conditions					
Further consideration in the FOCUS process			No	No	No	No	No

Table A2 – 1 Step 1 Evaluation of Transport and Deposition models (contd)

General Information	Model Name		SCAL-TURB	UK photochemical model	EPISODE	ASTRAP
	Name or number of most recent release				2.2	
	Intended use of the model		Stack emissions	Emission, Transport at European scale	Inert and photochemical pollutant dispersion	Calculation of acid deposition on LRT scale
	Model developers		Gryning et al.	Derwent and Jenkin	Walker and Grønskei.	Voldner + Schroeder
	Institution		Norwegian Institute for Air Research (NILU)	UK Met Office	Norwegian Institute for Air Research (NILU)	University of Chicago
	Year of recent version		1987	1991	1997	1996
Availability	1.1	Availability of executable	No info	Yes	Not public domain, available under conditions	Yes
	1.2	Possibility to run executable on a PC	No info	Yes	Yes	Yes
	1.3	Availability of documentation	No info	Yes	Yes	Yes
	1.4	Transparent version control	No info	No info	Yes	No info
Substances	2.1	Model can be used/was already used for organic compounds		No	No	No
Process of transport models	4.1	Consideration of area sources possible				
	4.2	Consideration of gaseous and sorbed transport				
	4.3	SRT models include dry deposition				
	4.4	MRT/LRT models include dry and wet deposition				
	4.5	MRT/LRT models consider degradation				
	4.6	Model should be appropriate for use under European conditions				
Further consideration in the FOCUS process			No	No	No	No

**APPENDIX 3: STEP 1 EVALUATION OF MULTIMEDIA MODELS
(INCLUDING FUGACITY MODELS)**

Table A3 – 1 Step 1 Evaluation of Multimedia Models (to predict persistence and LRT)

General Information	Model Name		ELPOS	TAPL3	Chemrange Sche	BENNX	ATP
	Name or number of most recent release		ELPOS 1.0	TAPL3 2.1	ChemRange 2.1	BENNX 1.0	ATP 1.0
	Intended use of the model		Regional / LRT	Regional / LRT	Regional / LRT	Regional / LRT	Regional / LRT
	Model developers		Beyer & Matthies	Beyer et al.	Scheringer et al.	Benett et al.	van Pul et al.
	Institution		University Osnabrück	Trent University, Can Lancaster Univers, UK	Swiss Federal Institute of technology, Zurich,	University of California at Berkeley	RIVM, Bilthoven, Netherlands
	Year of recent version		2001	2000	1996	1999	
Availability	1.1	Availability of executable	Yes	Yes	Yes	Limited	Yes
	1.2	Possibility to run executable on a PC	Yes	Yes	Yes	Yes	Yes
	1.3	Availability of documentation	Yes	Yes	Yes	No	No
	1.4	Transparent version control	Yes	Yes	Yes	No	No
Substances	2.1	Model can be used/was already used for organic compounds	Yes	Yes	Yes	Yes	Yes
Process of transport models	4.1	Consideration of area sources possible	Yes	Yes	Yes	?	?
	4.2	Consideration of gaseous and sorbed transport	Yes	Yes	Yes	Yes	Yes
	4.3	SRT models include dry deposition	n.a.	n.a.	n.a.	n.a.	n.a.
	4.4	MRT/LRT models include dry and wet deposition	Yes	Yes	Yes	Yes	Yes
	4.5	MRT/LRT models consider degradation	Yes	Yes	Yes	Yes	Yes
	4.6	Model should be appropriate for use under European conditions	Yes	Yes	Yes	Yes	Yes
Further consideration in the FOCUS process			Yes	Yes	Yes	No	No

Table A3 – 2 Step 1 Evaluation of Multimedia Models (regional, continental and global fate models)

General information	Model Name		Simple-Box EUSES	CemoS	Chem-CAN BETR-NA, EVn-BETR	CEMC Level III
	Name or number of most recent release		EUSES 1.0	CemoS 2.0	CHemCan4.0	Level 3 2.7
	Intended use of the model		regional scale	regional scale	Regional / LRT	regional scale
	Model developers		van de Meent	Beyer, Trapp, Matthies	Matt Macleod, Don Mackay and Kevin Jones	Mackay, D. et al.
	Institution		RIVM, Biltoven, NL	University Osnabrück	Trent University, Canada and Lancaster University, UK	Trent University, Canada
	Year of recent version		1993	2001	1991	2002
Availability	1.1	Availability of executable	Yes	Yes	Yes	Yes
	1.2	Possibility to run executable on a PC	Yes	Yes	Yes	Yes
	1.3	Availability of documentation	Yes	Yes	Yes	Yes
	1.4	Transparent version control	Yes	Yes	Yes	Yes
Substances	2.1	Model can be used/was already used for organic compounds	Yes	Yes	Yes	Yes
Process of transport models	4.1	Consideration of area sources possible	Yes	Yes	Yes	?
	4.2	Consideration of gaseous and sorbed transport	Yes	Yes	Yes	Yes
	4.3	SRT models include dry deposition	n.a.	n.a.	n.a.	n.a.
	4.4	MRT/LRT models include dry and wet deposition	Yes	Yes	Yes	Yes
	4.5	MRT/LRT models consider degradation	Yes	Yes	Yes	Yes
	4.6	Model should be appropriate for use under European conditions	Yes	Yes	No	Yes
Further consideration in the FOCUS process			Yes	Yes*	No	Yes**

* Although fulfilling Step 1 criteria no further consideration due to similarity to ELPOS

** Although fulfilling Step 1 criteria no further consideration due to similarity to TaPL

Table A3 – 2 Step 1 Evaluation of Multimedia Models (regional, continental and global fate models) – continued

General information	Model Name		Globo-POP	CalTOX	CoZMo-POP
	Name or number of most recent release		Globo-POP 1.0	CALTOX 23	CoZMo-POP 1.0
	Intended use of the model		regional scale	regional scale	Regional / LRT
	Model developers		Wania, F.	McKone	Wania, F.
	Institution		University of Toronto	University of California at Berkeley	University of Toronto
	Year of recent version		2000	1993	2000
Availability	1.1	Availability of executable	Yes	Yes	Yes
	1.2	Possibility to run executable on a PC	Yes	Yes	Yes
	1.3	Availability of documentation	Yes	Yes	Yes
	1.4	Transparent version control	Yes	?	Yes
Substances	2.1	Model can be used/was already used for organic compounds	Yes	Yes	Yes
Process of transport models	4.1	Consideration of area sources possible	Yes	Yes	Yes
	4.2	Consideration of gaseous and sorbed transport	Yes	Yes	Yes
	4.3	SRT models include dry deposition	n.a.	n.a.	n.a.
	4.4	MRT/LRT models include dry and wet deposition	Yes	Yes	Yes
	4.5	MRT/LRT models consider degradation	Yes	Yes	Yes
	4.6	Model should be appropriate for use under European conditions	No	Yes	No
Further consideration in the FOCUS process			No	Yes	No

APPENDIX 4: STEP 2 EVALUATION OF EMISSION MODELS

Table A4 – 4 Step 2 Evaluation of emission models

Model	FOCUS-PEARL	CONSENSUS-PEARL	PELMO	PRZM
1. General information				
Name of model	PEARL	PEARL	PELMO	PRZM
Name or number of most recent release	FOCUS-PEARL 1.1.1	CONSENSUS-PEARL 2.1.1	FOCUS-PELMO 3.3.2	FOCUS-PRZM 2.4.1
Intended use of the model	Emission from soil (leaching, behaviour in vadose zone)	Emission from soil and plant; fate in soil and fate on plant	Emission (Leaching, behaviour in vadose zone)	Emission (Leaching, behaviour in vadose zone)
Model developers	Tiktak et al.	Van den Berg et al.	Klein, M.	Carsel et al.
Sponsoring institution	Alterra and RIVM	Alterra and RIVM	FHG Schmallenberg	EPA, Waterborn
Date of recent release	2000	2004	2002	2002
2. Documentation and system considerations				
2.1 User manual				
Availability	yes, process descriptions additionally available	yes	yes, but only for older versions	yes, but only for older versions
Language	English	yes	English/German	English
Clarity	sufficient	yes	not sufficient	not sufficient
Defines model limitations	yes	yes	not sufficient	yes
Includes conceptual model description	yes	yes	yes	yes
Includes mathematical model description	yes	yes	no	yes
Includes sensitivity analysis	yes	no	no	yes
Provides assistance in determining model parameters	partly	yes	partly	partly
Provides test examples	yes	yes	no	yes
Provides references	yes	yes	yes	yes
2.2 Other documentation considerations				
Tightness of version control	FOCUS version control	Strict version control according to protocol developed by Alterra and RIVM	FOCUS version control	FOCUS version control
Availability of source code	partly	no	partly	no

Model	FOCUS-PEARL	CONSENSUS-PEARL	PELMO	PRZM
2.3 System considerations				
Hardware requirements	standard PC	standard PC; operating systems WinNT, Win2000, Windows XP	standard PC	standard PC
Run time for standard scenario	several minutes	Several minutes for 26 year FOCUS run	several seconds/minutes	several seconds/minutes
Reliability	sufficient	sufficient	sufficient	sufficient
Clarity of error messages	sufficient	sufficient	mostly sufficient	mostly sufficient
2.4 Support				
Method of support	PEARL webpage	PEARL webpage	e-mail to author	not clear / FOCUS version control
availability of information about bugs, corrections, and new versions	FOCUS version control	PEARL webpage	FOCUS version control	FOCUS version control
Training for users	FOCUS gw training	no	FOCUS gw training	FOCUS gw training
2.5 Input				
Pre-processing, e.g. meteorological data	yes	yes	yes	yes
Meteorological input data	data base	meteo files	data base	data base
Digital maps: land use, emissions	no	no	no	no
Availability of needed data	partly	partly	partly	partly
Data range checking	yes	yes	partly	partly
User friendliness	sufficient	sufficient	sufficient	sufficient
Help Utility	yes	help utility in FOCUS-PEARL 2.2.2 can be used for common features	yes	yes
Sample input files	yes	yes	yes	yes
Database included	yes	no	yes	yes
Flexibility	sufficient	sufficient	sufficient	sufficient
2.6 Output				
Nature of output	table, graphic, ascii	ascii, graphics possible using XY software included in FOCUS PEARL	table, graphic, ascii	table, graphic, ascii
Clarity of output reports	sufficient	sufficient	sufficient	sufficient
Echo of input parameters	sufficient	yes	sufficient	sufficient
Post-processing	yes	no	yes	yes

Model	FOCUS-PEARL	CONSENSUS-PEARL	PELMO	PRZM
- User friendliness	sufficient	sufficient	sufficient	sufficient
- Help Utility	sufficient	-	sufficient	sufficient
- Sample output files	yes	no	yes	yes
- Flexibility	yes	yes	yes	yes
3. Model science				
3.1 Compartments considered				
- Air, Soil, Water, Plant, Benthic Sediment	soil, water, plant, air	soil, water, air, plant	soil, water, plant, air	soil, water, plant, air
- Dispersed phases: i.e. aerosols in air, particles in water droplets (treated as separate compartments or bulk compartments)	no	no	no	no
- Compartment segmentation (e.g. horizons in soil profile, layers in atmosphere)	can be defined	can be defined	can be defined	can be defined
3.2 Numerical technique				
- adequacy of algorithm	yes	yes	yes/limited	yes/limited
- definitions of boundary conditions	flexible	flexible	pre-defined	pre-defined
- stability	sufficient	sufficient	sufficient	sufficient
- numerical dispersion	suppressed	suppressed	pronounced	pronounced
- time step	variable	variable	fix - 1 day	fix - 1 day
- implicit/ explicit	explicit	explicit	implicit	implicit
- grid cell size	variable	variable	variable	variable
3.3 Processes considered				
- emission, transport in air, degradation in air	no	no	no	
- only emission	yes	yes	yes	
- only transport and degradation	no	no	no	
3.4 Emission model				
- type of emission: point, line or area source, single source or multiple sources (in time and space), source height	independent (point/area)	independent (point/area)	independent (point/area)	independent (point/area)
- type of emission: pulse or steady state	variable	variable	variable	variable
3.5 Atmospheric transport model				
- type: Gaussian plume, Lagrangian, Eulerian, trajectory or compartment model	n.a.	n.a	n.a.	n.a.

Model	FOCUS-PEARL	CONSENSUS-PEARL	PELMO	PRZM
spatial scale: 0-1 km, 1-1000 km, > 1000km (i.e. "local", "regional", "continental" and "global")	n.a.	n.a.	n.a.	n.a.
temporal scale (if dynamic): hour, month, year or steady state?	n.a.	n.a.	n.a.	n.a.
possibility to consider dynamic (decreasing) emission rates.	n.a.	n.a.	n.a.	n.a.
3.6 Deposition model				
wet deposition, dry deposition	n.a.	n.a.	n.a.	n.a.
3.7 Substance model				
emission: source surface (soil, plant, water), source strength, effect of environmental conditions on source strength	soil (plant)	soil (plant)	soil (plant)	soil (plant)
transformation: type of model, effect of environmental conditions, biotic or abiotic, compartments considered	n.a.	n.a.	n.a.	n.a.
distribution in air: dissolution in water droplets, sorption to air-borne particles	n.a.	n.a.	n.a.	n.a.
3.8 Degree of validation				
List of published validation tests. For each reference, the following items should be specified:	http://viso.ei.jrc.it/focus/gw/index.html	http://viso.ei.jrc.it/focus/gw/index.html	http://viso.ei.jrc.it/focus/gw/index.html	http://viso.ei.jrc.it/focus/gw/index.html
The names of the chemicals	many pesticides	many pesticides	many pesticides	many pesticides
The name and version of the model	FOCUS-PEARL 1.1.1	CONSENSUS-PEARL 2.1.1	PELMO 2.1 - FOCUS-PELMO 3.3.2	PRZM 3.0 - FOCUS-PRZM 2.4.1
Area and sources considered in model test				
Meteo data set used	yes	yes	yes	yes
Temporal and spatial scale and resolution	variable time steps	meteo data, soil water and pesticide fluxes and output on daily or hourly basis	1 day temporal resolution	1 day temporal resolution
All input independently derived from experiments or observations in the environment (Yes/No)	yes	yes	yes	yes

Table A4 – 2 Step 2 Evaluation of emission models (continued)

Model	IDEFICS	PEM	EXAMS
1. General information			
Name of model	IDEFICS	PEM (Pesticide emission model)	EXAMS
Name or number of most recent release	v3.2	PEM 1.1	EXAMS 2.98.04
Intended use of the model	Spray drift from conventional boom sprayers for field crops	Emission from soil and plants	Emission from water (behaviour in surface water)
Model developers	Holterman H.J. et al.	Scholtz M. T.	Lawrence A. Burns
Sponsoring institution	IMAG, The Netherlands	Canadian Ortech Environmental Inc.	US-EPA
Date of recent release	Feb 2002	2002/2003	Apr-03
2. Documentation and system considerations			
2.1 User manual			
Availability	in preparation	Yes	yes
Language	English	English	english
Clarity	good	Limited	sufficient
Defines model limitations	yes	no	yes
Includes conceptual model description	yes	no	yes
Includes mathematical model description	yes	no	yes
Includes sensitivity analysis	yes	no	no
Provides assistance in determining model parameters	yes	some	yes
Provides test examples	yes	no	yes
Provides references	yes	no	yes
2.2 Other documentation considerations			
Tightness of version control	good		several months
Availability of source code	no	restricted free trial licence	yes
2.3 System considerations			
Hardware requirements	min: MSDOS/386; recommended: P4; memory usage ~2MB	UNIX Fortran 77	PC
Run time for standard scenario	12 hours (P4)	approximately 30 minutes/per year of simulation	Seconds
Reliability	good	robust	sufficient
Clarity of error messages	unknown	average	mostly sufficient

Model	IDEFICS	PEM	EXAMS
2.4 Support			
Method of support	not applic	may be fee based	mail to ceam epa
Availability of information about bugs, corrections, and new versions	not applic	could be provided	Release notes available
Training for users	not applic	may be available for a fee	training courses
2.5 Input			
Pre-processing, e.g. meteorological data	drop size spectra	required for met.	scenario database
Meteorological input data	wind speed, RH, turbulence intensity	climate station data or NWP data	scenario database
Digital maps: land use, emissions	not applic	user	no
Availability of needed data	drop size spectra measured at our own institute; at present not distributed	user (some defaults provided)	partly
Data range checking	partly	some	yes
User friendliness	limited	average (no GUI)	not sufficient
Help Utility	limited	none	yes
Sample input files	input parameters have standard value at start-up	can be provided	yes
Database included	no	no	yes
Flexibility	good	some	sufficient
2.6 Output			
Nature of output	text files (mostly tables)	hourly emissions	ascii files, DOS graphics
Clarity of output reports	limited	message file	sufficient
Echo of input parameters	yes	yes	yes
Post-processing	additional software required from 'IDEFICS family'	user	partly
User friendliness	limited	no GUI	not sufficient
Help Utility	no	no	yes
Sample output files	no	can be provided	yes
Flexibility	no	no	sufficient
3. Model science			
3.1 Compartments considered			
Air, Soil, Water, Plant, Benthic Sediment	air, (+ surfaces of soil and water)	soil, plant	Air, Soil, Water, Plant, Benthic Sediment

Model	IDEFICS	PEM	EXAMS
- Dispersed phases: i.e. aerosols in air, particles in water droplets (treated as separate compartments or bulk compartments)	water droplets containing solid components; droplets are released into air	soil water, air and solids	no
- Compartment segmentation (e.g. horizons in soil profile, layers in atmosphere)	air is one compartment, limited by a downwind boundary (vertical; adjustable)	unsaturated soil zone and atmospheric surface boundary layer	
3.2 Numerical technique			
- adequacy of algorithm	good (based on physics, applied to practice)	published	?
- definitions of boundary conditions	yes	published	
- stability	good	robust	sufficient
- numerical dispersion	?		?
- time step	not applic	1200 seconds	?
- implicit/ explicit	?	semi-implicit	
- grid cell size	not applic	point model	variable
3.3 Processes considered			
- emission, transport, degradation	transport of droplets in air; droplets may evaporate gradually; no degradation of solid components		
- only emission		1-D transport of heat, moisture and solute in the soil and atmospheric surface layer.	
- only transport and degradation			
3.4 Emission model			
- type of emission: point, line or area source, single source or multiple sources (in time and space), source height	multiple point sources in space (various spray nozzles moving linearly)	point model	
- type of emission: pulse or steady state	pulse (instantaneous)	pulse	
3.5 Atmospheric transport model			
- type: Gaussian plume, Lagrangian, Eulerian, trajectory or compartment model	droplet trajectories (stepwise); air turbulence Eulerian	Atmospheric surface layer only	n.a.
- spatial scale: 0-1 km, 1-1000 km, > 1000km (ie. "local", "regional", "continental" and "global")	local (typically 0-20m at present)		n.a.

Model	IDEFICS	PEM	EXAMS
temporal scale (if dynamic): hour, month, year or steady state?	not applic	hourly	n.a.
possibility to consider dynamic (decreasing) emission rates.	no	yes - included	n.a.
3.6 Deposition model			
wet deposition, dry deposition	not applic	dry deposition in future version	n.a.
3.7 Substance model			
emission: source surface (soil, plant, water), source strength, effect of environmental conditions on source strength	source: spray nozzles; strength depends on nozzle type, liquid pressure and driving speed	soil and plant sources	surface water
transformation: type of model, effect of environmental conditions, biotic or abiotic, compartments considered	not applic	soil and air degradation half-life	n.a.
distribution in air: dissolution in water droplets, sorption to air-borne particles	solid components dispersed directly in water drops; no re-emission after deposition	no	n.a.
3.8 Degree of validation			
List of published validation tests. For each reference, the following items should be specified:	Computers and Electronics in Agriculture 19 (1997): 1-22		included in manual
The names of the chemicals	not applic	Emission of spray applied triallate and trifluralin from bare soil	
The name and version of the model	IDEFICS v2.1		
Area and sources considered in model test	conventional field sprayers with arable crops	experimental farm field in Ottawa, Ontario, Canada.	
Meteo data set used	average wind speed, RH, turbulence	field observations	
Temporal and spatial scale and resolution	spatial resolution 0.25m (0-10m); temporal: not applic	hourly	
All input independently derived from experiments or observations in the environment (Yes/No)	yes	yes	

APPENDIX 5: STEP 2 EVALUATION OF TRANSPORT AND DEPOSITION MODELS

Table A5 – 1 Step 2 Evaluation of Transport and deposition models

Model	PESTDEP	EVA 1.1	EVA 2.0	ISCST
1. General information				
Name of model	PESTDEP	EVA (exposure via air)		ISCST
Name or number of most recent release	PESTDEP 3.1	EVA 1.1 e	EVA 2.0	ISCST3
Intended use of the model	2-dimensional SRT of pesticides to surface water	SRT of pesticides	deposition after SRT	SRT of pesticides
Model developers	Willem A.H. Asman	R. Winkler, W. Koch		EPA
Sponsoring institution	Danish EPA, Danish Parliament, Global Environmental Consultancy, DIAS	German UBA		EPA
Date of recent release	26/12/2002	May 2003	November 2004	2002
2. Documentation and system considerations				
2.1 User manual				
Availability	yes	yes	yes	yes
Language	English	English	English	English
Clarity	sufficient	sufficient	sufficient	sufficient
Defines model limitations	yes	partially	partially	partially
Includes conceptual model description	yes	yes	yes	partially
Includes mathematical model description	yes	yes	yes	yes
Includes sensitivity analysis	in report	no	no	no
Provides assistance in determining model parameters	yes	?	?	yes
Provides test examples	in report	no	no	yes
Provides references	yes, and also in report	yes	yes	yes
2.2 Other documentation considerations				
Tightness of version control	several months	several months	several months	approx. annual
Availability of source code	no	yes	yes	yes
2.3 System considerations				
Hardware requirements	PC	PC		PC
Run time for standard scenario	depends on area to be modelled, < 1 min.	no runtime	no runtime	short

Model	PESTDEP	EVA 1.1	EVA 2.0	ISCST
Reliability	good	yes	good	good
Clarity of error messages	Error messages are given, but can only be read in DOS version!	EXCEL message	EXCEL message	sufficient
2.4 Support				
Method of support	e-mail to author	contact by e-mail	contact by e-mail	e-mail
Availability of information about bugs, corrections, and new versions	on request by to author	uba-internet page	uba-internet page	epa - web - page
Training for users	on request possible	when requested	when requested	yes, different organizers
2.5 Input				
Pre-processing, e.g. meteorological data	no	no	no	yes
Meteorological input data	yes	yes	no	yes
Digital maps: land use, emissions	no	no	no	no
Availability of needed data	yes, apart from some information on the temperature dependence of vapour pressure, Henry's law coefficient	yes	yes	yes
Data range checking	to some extent	no		?
User friendliness	medium	yes	yes	generally low but shell available
Help Utility	no	no	no	no
Sample input files	1 sample input file	yes	yes	yes
Database included	no	no	no	no
Flexibility	sufficient	?	?	sufficient
2.6 Output				
Nature of output	file	EXCEL result sheets	EXCEL result sheets	ASCII file
Clarity of output reports	sufficient	yes	yes	sufficient
Echo of input parameters	no	EXCEL input sheet	EXCEL input sheet	no
Post-processing	no	no	no	no
User friendliness	medium	yes	yes	low
Help Utility	no	no	no	no
Sample output files	1 sample output file	yes	yes	yes
Flexibility	1 type of output	?	?	yes

Model	PESTDEP	EVA 1.1	EVA 2.0	ISCST
3. Model science				
3.1 Compartments considered				
- Air, Soil, Water, Plant, Benthic Sediment	air, soil, water, plant	Air, water, soil, plant	water, soil, plant	air
- Dispersed phases: i.e. aerosols in air, particles in water droplets (treated as separate compartments or bulk compartments)	no	aerosols, drift	aerosols, drift	no
- Compartment segmentation (e.g. horizons in soil profile, layers in atmosphere)	in principle more layers in the atmosphere and 1 layer in crops, soil and water	no	no	no
3.2 Numerical technique				
- adequacy of algorithm	yes	Analytical solution used	Empirical relationship	yes
- definitions of boundary conditions	yes	yes	yes	yes
- stability	stable	yes	yes	stable
- numerical dispersion	small	Not relevant	Not relevant	?
- time step	variable, depending on input parameters	not relevant (1 day)	not relevant output in hourly resolution	variable
- implicit/ explicit	finite difference method	not relevant	not relevant	?
- grid cell size	flexible	not relevant	not relevant	?
3.3 Processes considered		"		
- emission, transport, degradation	emission, transport, dry deposition, not degradation	yes	no	no
- only emission	no	no	no	no
- only transport and degradation	no	no	no	yes
3.4 Emission model				
- type of emission: point, line or area source, single source or multiple sources (in time and space), source height	area source	single source, virtual point source	not relevant	point/area source
- type of emission: pulse or steady state	steady state	steady state	not relevant	steady state
3.5 Atmospheric transport model				
- type: Gaussian plume, Lagrangian, Eulerian, trajectory or compartment model	Gaussian plume (Lagrangian)	Gaussian plume	not relevant	Gaussian plume (Lagrangian)
- spatial scale: 0-1 km, 1-1000 km, > 1000km (ie. "local", "regional", "continental" and "global")	1-10 km	local	not relevant	Short Term

Model	PESTDEP	EVA 1.1	EVA 2.0	ISCST
temporal scale (if dynamic): hour, month, year or steady state?	steady state	steady state	not relevant	steady state
possibility to consider dynamic (decreasing) emission rates.	not in current version, but possible to simulate that with more runs	no	not relevant	yes
3.6 Deposition model				
wet deposition, dry deposition	dry deposition	dry deposition	dry deposition	dry and wet
3.7 Substance model				
emission: source surface (soil, plant, water), source strength, effect of environmental conditions on source strength	soil, plant, effect of some environmental factors on source strength, but not of the meteorological factors	soil, plant	soil, plant	no
transformation: type of model, effect of environmental conditions, biotic or abiotic, compartments considered	no, but fast transformation in water can be dealt with	abiotic	not relevant	
distribution in air: dissolution in water droplets, sorption to air-borne particles	no	sorption to aerosols	no	no
3.8 Degree of validation				
List of published validation tests. For each reference, the following items should be specified:	subprocesses are tested against measurements, but not necessarily for pesticides	none (in progress)	empirical model validated with windtunnel and field data	not available
The names of the chemicals	emission is only based on experimental data	different pesticides	different pesticides	
The name and version of the model	PESDEP 3.1	EVA 1.1	EVA 2.0	
Area and sources considered in model test	no	?	yes	
Meteo data set used	dispersion is tested (compared with Prairie Grass data)	no	no	
Temporal and spatial scale and resolution	spatial resolution is defined by the user	local	local	
All input independently derived from experiments or observations in the environment (Yes/No)	yes	yes	yes	yes

Table A5 – 1 Step 2 Evaluation of Transport and deposition models (continued)

Model	OPS	EUTREND	EUROS
1. General information			
Name of model	OPS	EUTREND	EUROS
Name or number of most recent release	OPS-PRO 4.1	EUTR1.17	5.2
Intended use of the model	transport and deposition of atmospheric pollutants	transport and deposition of atmospheric pollutants	chemical transport model (air), ozone, PM, POP's
Model developers	J.A. van Jaarsveld	J.A. van Jaarsveld	J. Matthijsen, F.Sauter, L. de Waal, A. van Pul
Sponsoring institution	RIVM	RIVM	RIVM, The Netherlands
Date of recent release	last quarter 2003	1998	1/May/2003
2. Documentation and system considerations			
2.1 User manual			
Availability	yes (on line)	brief user manual	good
Language	english	english	English
Clarity	adequate		moderate - good
Defines model limitations	yes	no	some
Includes conceptual model description	yes	no	yes
Includes mathematical model description	yes	no	yes
Includes sensitivity analysis	gives references	no	partial
Provides assistance in determining model parameters	to some extend	no	poor
Provides test examples	no	no	yes
Provides references	yes	yes	yes
2.2 Other documentation considerations			
Tightness of version control	moderate	not very tight	moderate
Availability of source code	not available	not available	not available
2.3 System considerations			
Hardware requirements	normal PC	normal PC	UNIX workstation, PC
Run time for standard scenario	variable, depends mainly on spatial detail	variable, depends mainly on spatial detail	5 hours UNIX HP 9000
Reliability			good
Clarity of error messages	sufficient		moderate - good

Model	OPS	EUTREND	EUROS
2.4 Support			
- Method of support	no support	no support	limited assistance
- Availability of information about bugs, corrections, and new versions	web site	not available	not available
- Training for users	not foreseen	not available	no
2.5 Input			
- Pre-processing, e.g. meteorological data	with special pre-processor. At the moment not available for users	with special pre-processor. At the moment not operational	data files (ASCII or HDF format)
- Meteorological input data	standard (hourly) observations at weather stations	standard synoptical observations at weather stations in Europe	wind, temperature, relative humidity, precipitation, cloud cover, sea temperature
- Digital maps: land use, emissions	land use is available, emissions should be provided by the user	land use is available, emissions should be provided by the user	land use, roughness length, emissions
- Availability of needed data	meteorological and other data are available for the Netherlands and included	meteorological data are only available for 1989 and 1990	meteo via ECMWF
- Data range checking	yes	no support	partial
- User friendliness	sufficient		poor
- Help Utility	yes	no	no
- Sample input files	no	no	yes
- Database included	meteo data for the Netherlands 1981-2003	only 1989 and 1990 met data	no
- Flexibility	moderate		poor
2.6 Output			
- Nature of output	concentration and deposition in the form of grids or as records per location	concentration and deposition in the form of grids or as records per location	concentrations, depositions (grid files)
- Clarity of output reports	sufficient		moderate - good
- Echo of input parameters	yes	no	yes
- Post-processing	yes, displaying maps	no	contour plots, time graphs
- User friendliness	sufficient		moderate
- Help Utility	yes	no	no

Model	OPS	EUTREND	EUROS
- Sample output files	no	no	yes
- Flexibility	?		moderate
3. Model science			
3.1 Compartments considered			
- Air, Soil, Water, Plant, Benthic Sediment	air	air	air, soil, vegetation module present, not yet implemented
- Dispersed phases: i.e. aerosols in air, particles in water droplets (treated as separate compartments or bulk compartments)	gas and/or aerosol in air	gas and/or aerosol in air	gas and aerosols, gas, water, solid fraction on soil and water concentration in sea and large inland water bodies
- Compartment segmentation (e.g. horizons in soil profile, layers in atmosphere)	n.a.	n.a.	4 layers in atmosphere, 5 layers in soil
3.2 Numerical technique	n.a.	n.a.	
- adequacy of algorithm			good
- definitions of boundary conditions			via ASCII files, monthly & latitudinal profiles
- stability			good
- numerical dispersion			depends on grid size
- time step			1/2 hour
- implicit/ explicit			explicit
- grid cell size			variable (7.5 - 60 km)
3.3 Processes considered			
- emission, transport, degradation	emission (some aspects), dispersion, transport, chemical conversion, deposition	emission (some aspects), dispersion, transport, chemical conversion, deposition	yes
- only emission			
- only transport and degradation			
3.4 Emission model			
- type of emission: point, line or area source, single source or multiple sources (in time and space), source height	multiple point and area sources	multiple point and area sources	point or area, source height for point sources
- type of emission: pulse or steady state	steady state	steady state	time dependent (year, week, day profiles)

Model	OPS	EUTREND	EUROS
3.5 Atmospheric transport model			
- type: Gaussian plume, Lagrangian, Eulerian, trajectory or compartment model	combination of Gaussian and trajectory model	combination of Gaussian and trajectory model	Eulerian
- spatial scale: 0-1 km, 1-1000 km, > 1000km (ie. "local", "regional", "continental" and "global")	variable, local to regional scale	variable, regional to continental scale	regional
- temporal scale (if dynamic): hour, month, year or steady state?	month, year or long term	year	hour
- possibility to consider dynamic (decreasing) emission rates.	no	no	per year
3.6 Deposition model			
- wet deposition, dry deposition	wet and dry	wet and dry	both
3.7 Substance model			
- emission: source surface (soil, plant, water), source strength, effect of environmental conditions on source strength	partly supported	partly supported	rate of emissions to air dependent on season
- transformation: type of model, effect of environmental conditions, biotic or abiotic, compartments considered	depends on substance, the generic approach considers first order degradation only	depends on substance, the generic approach considers first order degradation only	fixed degradation on air, water, soil compartment
- distribution in air: dissolution in water droplets, sorption to air-borne particles	both	both	substance in gas phase, aerosol surface, rain water
3.8 Degree of validation			
- List of published validation tests. For each reference, the following items should be specified:	1) Van Jaarsveld J. A. and Schutter M. A. A. (1993). Chemosphere, 27, 131-139; 2) Van Jaarsveld J. A. and de Leeuw F. A. A. M. (1993). Environmental Software, 8, 91-100; 3) 8. Van Jaarsveld J.A.(2003). Inside the OPS model. RIVM Report 500037xxx. In preparation.	1) Van Jaarsveld J.A. (1994). Air Pollution Modelling and its application X, Gryning and Millán (Eds), p 143-157; 2) Van Jaarsveld J.A., van Pul W.A.J., de Leeuw F.A.A.M. (1997). Atmospheric Environment, 31, 1011-1024	none, only internal test reports available. Detailed analyses of lindane distribution over Europe in air, water, soil compartment in Jacobs and Van Pul, 1996.
- The names of the chemicals			
- The name and version of the model			
- Area and sources considered in model test			

Model	OPS	EUTREND	EUROS
- Meteo data set used			
- Temporal and spatial scale and resolution			
- All input independently derived from experiments or observations in the environment (Yes/No)			

Table A5 – 1 Step 2 Evaluation of Transport and deposition models (continued)

Model	RAMS	HYPACT	PlumePlus
1. General information			
Name of model	RAMS	HYPACT	PlumePlus
Name or number of most recent release	v4.4	v1.20	3.2
Intended use of the model	mesoscale atmospheric analysis and weatherforecasting	dispersion of air pollutants in 3-D, mesoscale, time dependent wind and turbulence fields	dispersion calculation hour by hour method
Model developers	Colorado State University, Duke University, ATMET		Boersen
Sponsoring institution			TNO MEP Apeldoorn
Date of recent release			Sep-03
2. Documentation and system considerations			
2.1 User manual			
Availability	technical manual;user manual; namelist description	technical manual;user manual; namelist description	yes
Language	english	english	Dutch
Clarity	good	good	good
Defines model limitations	yes: user manual	yes: user manual	distance source receptor < 25 KM
Includes conceptual model description	yes: technical manual	yes: technical manual	no; see report TNO-MEP, 1998, Nieuw Nationaal Model, 292 pp.
Includes mathematical model description	yes: technical manual	yes: technical manual	no; see report TNO-MEP, 1998, Nieuw Nationaal Model, 292 pp.
Includes sensitivity analysis	no	no	yes
Provides assistance in determining model parameters	yes: user manual and namelist description	yes: user manual and namelist description	
Provides test examples	yes	yes	yes
Provides references	yes	yes	yes
2.2 Other documentation considerations			
Tightness of version control	OK	OK	moderate

Model	RAMS	HYPACT	PlumePlus
Availability of source code	under licence yes	under licence yes	no
2.3 System considerations			
Hardware requirements	anything from PC to clusters to supercomputers; under UNIX and MSWindows; parallel using MPI	anything from PC to clusters to supercomputers; under UNIX and MSWindows; parallel using MPI	PC windows/w95/98/200/ME and XP
Run time for standard scenario	system dependent	system dependent	system dependent
Reliability	OK	OK	OK
Clarity of error messages	poor	poor	sufficient
2.4 Support			
Method of support	very good through user group (mailing list) and ATMET support, and occasional dedicated workshops	very good through user group (mailing list) and ATMET support, and occasional dedicated workshops	helpdesk - workshop-
Availability of information about bugs, corrections, and new versions	good	good	via infomil website http://www.infomil.nl/
Training for users	custom made on demand only	custom made on demand only	available
2.5 Input			
Pre-processing, e.g. meteorological data	yes	yes	yes
Meteorological input data	ECMWF, NCEP analyses'	RAMS output	yearly upgrades from 1995 to 2002
Digital maps: land use, emissions	global datasets landuse; topography; sst available; NOT emissions	global datasets landuse; topography; sst available; NOT emissions	land use data not available; emission data should be specified by user
Availability of needed data	very good	very good	metedata yearly updated for 2 locations
Data range checking	moderate	moderate	yes
User friendliness	moderate	moderate	high
Help Utility	no	no	helpdesk
Sample input files	yes	yes	available
Database included	yes	yes	database available as external file
Flexibility	very good	very good	no because model is consensus model

Model	RAMS	HYPACT	PlumePlus
2.6 Output			
- Nature of output	user specified subsets of 4D fields of nearly all modelvariables	user specified subsets of 4D fields of nearly all modelvariables	excel text files
- Clarity of output reports	OK	OK	very clear
- Echo of input parameters	yes	yes	yes
- Post-processing	yes into formats for various visualisation software (GrADS, Vis5D, etc)	yes into formats for various visualisation software (GrADS, Vis5D, etc)	excel matrix
- User friendliness	moderate	moderate	high
- Help Utility	no	no	implemented
- Sample output files	yes	yes	available
- Flexibility	very good	very good	file/printer/plot
3. Model science			
3.1 Compartments considered			
- Air, Soil, Water, Plant, Benthic Sediment	Air, Soil, Plant	air	air
- Dispersed phases: i.e. aerosols in air, particles in water droplets (treated as separate compartments or bulk compartments)	aerosols yes		aerosols in air
- Compartment segmentation (e.g. horizons in soil profile, layers in atmosphere)	user specified; basically unlimited for soil and atmosphere		no
3.2 Numerical technique			
- adequacy of algorithm	very good		
- definitions of boundary conditions	several options		no boundary conditions
- stability	good		
- numerical dispersion			
- time step			
- implicit/ explicit	explicit		both used
- grid cell size	user specified; from ~100m to 100km		not relevant
3.3 Processes considered			
- emission, transport, degradation	emission transport	emission, transport, degradation	yes

Model	RAMS	HYPACT	PlumePlus
- only emission	emissionfields user specified		yes
- only transport and degradation	only transport; degradationin principle easy to implement		yes
3.4 Emission model			
- type of emission: point, line or area source, single source or multiple sources (in time and space), source height	all	all	point and surface
- type of emission: pulse or steady state	any	all	pulse
3.5 Atmospheric transport model			
- type: Gaussian plume, Lagrangian, Eulerian, trajectory or compartment model	Eulerian	hybrid: Langrangian near field;Eulerian far field	Gaussian
- spatial scale: 0-1 km, 1-1000 km, > 1000km (ie. "local", "regional", "continental" and "global")	regional to global	regional to global	10- 25000 mtr
- temporal scale (if dynamic): hour, month, year or steady state?	hour to few years depending on computer resources	hour to few years depending on computer resources	hour
- possibility to consider dynamic (decreasing) emission rates.	yes	yes	
3.6 Deposition model			
- wet deposition, dry deposition	n/a	dry deposition	both dry and wet deposition
3.7 Substance model			
- emission: source surface (soil, plant, water), source strength, effect of environmental conditions on source strength	n/a	n/a	area source can be any area
- transformation: type of model, effect of environmental conditions, biotic or abiotic, compartments considered	n/a		only transformation of NO to NO2
- distribution in air: dissolution in water droplets, sorption to air-borne particles	n/a		sorption to air-borne particles
3.8 Degree of validation			
- List of published validation tests. For each reference, the following items should be specified:	many		benchmark

Model	RAMS	HYPACT	PlumePlus
- The names of the chemicals	n/a		optional, unlimited
- The name and version of the model	n/a		
- Area and sources considered in model test	n/a		yes
- Meteo data set used	n/a		1995 till 2002 KNMI Netherlands
- Temporal and spatial scale and resolution	n/a		
- All input independently derived from experiments or observations in the environment (Yes/No)	n/a		yes

Table A5 – 1 Step 2 Evaluation of Transport and deposition models (continued)

Model	IFDM	ASDM
1. General information		
Name of model	IFDM (Immission Frequency Distribution Model)	ADMS
Name or number of most recent release	IFDM-PC (Commercial, with user interface), IFDM_Mother (For R&D and specific non-routine applications)	3.1
Intended use of the model	Local scale dispersion of pollutants (point sources and area sources), IFDM-PC: permit granting; IFDM_Mother: reverse modelling, special source configuration, ..	calculation dispersion and deposition of air pollutants
Model developers	Meteorological: Bultynck & Mallet Area's of application: Jan Kretzschmar; Current software: Guido Cosemans	CERC (Cambridge Environmental Research Consultants
Sponsoring institution	Vito since 1990. Model developed and maintained at the Mol Nuclear Energy Research Center, Belgium, from 1968 till 1990	
Date of recent release	Commercial PC-version: 1993 (MS-DOS - Windows 95- Windows NT-Windows 2000) and 2002 (X-Windows) IFDM-Mother: 2003 Since 2002, a set of Windows programs are available for graphical investigation of the model results. (The 1993 version provided MS-DOS graphics only)	2001
2. Documentation and system considerations		
2.1 User manual		
Availability	Yes	licence
Language	Dutch and English	English
Clarity	Seems to be good, over 40 license holders had no problem with it (or did not need it given the 'intuitive' user interface	good
Defines model limitations	Up to 20 km from source	yes
Includes conceptual model description	yes	yes
Includes mathematical model description	yes	yes

Model	IFDM	ASDM
- Includes sensitivity analysis	yes (copies of some relevant publications since 1968)	?
- Provides assistance in determining model parameters	yes	yes
- Provides test examples	yes	yes
- Provides references	yes	yes
2.2 Other documentation considerations		
- Tightness of version control	OK. IBM mainframe version unchanged from 1984 till 1993, IFDM-PC unchanged from 1993 till 2002, X-windows necessitated recompilation with recent Fortran compiler.	
- Availability of source code	Property of Vito	
2.3 System considerations		
- Hardware requirements	IBM-compatible PC, Windows. (The program and user interface are written in languages and tools for which Linux-versions are available, however, it is not our intention to make it available on Unix unless some one should bewailing to pay for this conversion.	Windows NT, Windows 95 and later versions, Pentium 266 MHz Pc with 64 MB of RAM and 1 GB hard disk space
- Run time for standard scenario	Milliseconds. The IBM-mainframe version of 1984 was called IFDM-super fast because it ran 100 times faster than the straight-forward implementation of the bi-Gaussian equations in the 1972 IFDM-mainframe version. For example: in 1996, for 200 sources, 160 receptors, 8760 hours of meteorological data, computations took 10 minutes on 66 MHz 486-IBM-compatible PC (IFDM-PC). Today, PC's are about 40 times faster.	flat terrain, 1 year period of met. Data, 31 mins (333 Mhz Pentium II with 128 MB of Ram and 8 GB hard disk space)
- Reliability	Excellent up to now. Only one scientist is responsible for it. He has a masters degree in computer engineering and software, and works in atmospheric dispersion on the local scale since 1975. The program was designed so that no matter what keyboard input is entered, it should remain working.	
- Clarity of error messages	Fool-proof. Most common problem till some years ago, was lack of space on the hard disk. (usually because they did calculations for a receptor grid of 1000 x 1000 receptors, or something very large.)	

Model	IFDM	ASDM
2.4 Support		
Method of support	Telephone, e-mail,	helpdesk
Availability of information about bugs, corrections, and new versions		yes
Training for users	yes, a one day course on atmospheric dispersion in general, with a demonstration of IFDM-PC at the end is organized about once a year. A License includes the right to come with a PC to Vito, have the software installed, and to go through some typical calculations.	yes, annual user group meetings
2.5 Input		
Pre-processing, e.g. meteorological data	Is provided. For routine calculations for permit granting , the models comes with 3 years of preprocessed meteorological data from the Mol 114 m high meteorological data, thought to be representative for Belgium.	yes
Meteorological input data	Time series (half) hourly data on wind and stability (+ rainfall)	by hand, from a prepared example file, data files created by the user, hourly sequential data obtained from a supplier
Digital maps: land use, emissions	no	
Availability of needed data	good. Note that Vito has models for scales different from the local scale.	
Data range checking	yes. Most items can be selected from drop down menus.	
User friendliness	Excellent, I hope. For instance, the source emissions can be specified in units for mass ranging from monograms till tons, and for time from one second to one year.	
Help Utility	Is not implemented, and no user has asked for it - up to now.	
Sample input files	Yes	
Database included	Yes, 3 years meteorological data.	
Flexibility	IFDM-PC is up to the needs of most users. IFDM-Mother offers all the flexibility a model developer can write in Fortran.	

Model	IFDM	ASDM
2.6 Output		
Nature of output	ASCII tables with average concentrations, percentiles and maxima. Input data are echo-ed in the header lines of the result data. Can be exported to Excel or graphical packages. Graphical representations possible with IFDM Windows graphical post processor.	numerical data in MSExcel, x-y plots (gridded Cartesian, gridded polar, specified points), connections with Surfer (contour plotting), Arcview and MapInfo
Clarity of output reports	Very good	
Echo of input parameters	Yes	
Post-processing	Yes	
User friendliness	Excellent	
Help Utility	The Windows graphical postprocessor comes with an online manual.	
Sample output files	Yes - in online manual	
Flexibility	Good to very good.	
3. Model science		
3.1 Compartments considered		
Air, Soil, Water, Plant, Benthic Sediment	Air	air
Dispersed phases: i.e. aerosols in air, particles in water droplets (treated as separate compartments or bulk compartments)	no	
Compartment segmentation (e.g. horizons in soil profile, layers in atmosphere)	Vertical (and horizontal) dispersion in the atmosphere	
3.2 Numerical technique		
adequacy of algorithm	bi-Gaussian dispersion formula	
definitions of boundary conditions	no - implicit in stability	
stability	Dispersion parameters based on a Bulk Richardson Number, originally defined over the temperature difference between 114 m and 8 m above the ground, and the square of the wind speed at 69 m. For places where such meteorological tower data is not available, an algorithm to estimate the stability based on solar altitude, cloud cover and wind speed is available.	

Model	IFDM	ASDM
- numerical dispersion	bi-Gaussian	
- time step	steady state during 30 or 60 minutes	
- implicit/ explicit		
- grid cell size		variable, maximum of 100 points in each direction (x or y; 100 x 100) + z value for height above ground
3.3 Processes considered		
- emission, transport, degradation	yes. Degradation is not implemented in the current versions, but (nuclear) decay was present in the pre-1984 versions of IFDM.	emission and transport, chemical reactions between nitric oxide, nitrogen dioxide and ozone
- only emission	Limited in IFDM-PC (see later).	
- only transport and degradation		
3.4 Emission model		
- type of emission: point, line or area source, single source or multiple sources (in time and space), source height	IFDM-PC: point, area, Multiple source urban, rural, industrial. Time variability (several weekly cycles for industry, temperature dependency for residential heating, daily cycle for traffic and area sources . IFDM_Mother: point, area, line; time variability by ON/OFF cycle, wind speed dependency of source strength (wind erosion at old lead smelters) and so on.	point, line area, volume, jet, single and multiple
- type of emission: pulse or steady state	Both possible	pulse and steady
3.5 Atmospheric transport model		
- type: Gaussian plume, Lagrangian, Eulerian, trajectory or compartment model	Gaussian plume	Gaussian plume
- spatial scale: 0-1 km, 1-1000 km, > 1000km (ie. "local", "regional", "continental" and "global")	0-20 km	0-100
- temporal scale (if dynamic): hour, month, year or steady state?	hour	hour, day, year
- possibility to consider dynamic (decreasing) emission rates.	Yes, in IFDM-Mother	yes, fluctuations

Model	IFDM	ASDM
3.6 Deposition model		
- wet deposition, dry deposition	yes. Wet deposition by a removal rate per hour depending on rain intensity, dry deposition by a dry deposition speed (one value in IFDM-PC, Sehmel-Hodgon model in IFDM_Mother)	yes
3.7 Substance model		
- emission: source surface (soil, plant, water), source strength, effect of environmental conditions on source strength	In IFDM-PC, source strength for house heating depends on outside temperature. In IFDM_Mother, emission by wind-erosion has been modelled. In principle, in IFDM-Mother, any modulation factor on the emission could be programmed.	source strength
- transformation: type of model, effect of environmental conditions, biotic or abiotic, compartments considered	Only removal by rain or dry deposition are currently modelled.	
- distribution in air: dissolution in water droplets, sorption to air-borne particles	No	no
3.8 Degree of validation		
- List of published validation tests. For each reference, the following items should be specified:	SEE ATTACHED WORD DOCUMENT.	
- The names of the chemicals		predefined: SO ₂ , NO ₂ , NO _x CO, PM ₁ , odour. Up to 10 pollutants may be defined.
- The name and version of the model	No changes in physics underlying the model.	3.1
- Area and sources considered in model test		flat terrain, line, area and volume sources, dry deposition, buildings, complex terrain, No _x chemistry, fluctuations, visible plumes
- Meteo data set used		
- Temporal and spatial scale and resolution	usually one year for SO ₂ , heavy metals. The duration of the monitoring campaigns for SF ₆	
- All input independently derived from experiments or observations in the environment (Yes/No)	YES	yes

APPENDIX 6: STEP 2 EVALUATION OF MULTIMEDIA MODELS

Table A6 – 1 Step 2 Evaluation of Multimedia Models

Model	CEMC Lev. III (TaPL3)	SimpleBox EUSES	CalTOX
1. General information			
Name of model	CEMC Level III (aka TaPL3)	SimpleBox	CalTOX
Name or number of most recent release	2,1	3,0+	2,3
Intended use of the model	Calculates air transport potential	Calculates air transport potential	Calculates air transport potential
Model developers	Mackay, D.	van de Meent, D.	McKone, T.
Sponsoring institution	CEMC, Trent University	RIVM, Bilthoven, The Netherlands	University of California at Berkeley and Ernest Orlando Lawrence Berkeley National Laboratory
Date of recent release	Jun-00	Aug-03	Mar-97
2. Documentation and system considerations			
2.1 User manual			
Availability	In help files and scientific publications	Detailed RIVM reports order from web	Yes from web
Language	English	English	English
Clarity	Moderate	Clear	Clear
Defines model limitations	Yes	Yes	Yes
Includes conceptual model description	Yes	Yes	Yes
Includes mathematical model description	Yes	Yes	Yes
Includes sensitivity analysis	No	No	Yes
Provides assistance in determining model parameters	No	No	No
Provides test examples	Yes	Yes	Yes
Provides references	Yes	Yes	Yes
2.2 Other documentation considerations			
Tightness of version control	Excellent	Good	Good
Availability of source code	Yes	Yes	Yes

Model	CEMC Lev. III (TaPL3)	SimpleBox EUSES	CalTOX
2.3 System considerations			
- Hardware requirements	PC	PC	PC
- Run time for standard scenario	<1 second per chemical	<1 second per chemical	<1 second per chemical
- Reliability	Good	Good	Good
- Clarity of error messages	Poor	Poor	Poor
2.4 Support			
- Method of support	Through web	Through web	Through web
- Availability of information about bugs, corrections, and new versions	Website	Website	Website
- Training for users	Not formalised	Not formalised	Not formalised
2.5 Input			
- Pre-processing, e.g. meteorological data	No	No	No
- Meteorological input data	No	No	No
- Digital maps: land use, emissions	No	No	No
- Availability of needed data	Physical-chemical properties usually available	Physical-chemical properties usually available	Physical-chemical properties usually available
- Data range checking			
- User friendliness	Excellent	Good	Excellent
- Help Utility	Yes	No	No
- Sample input files	Yes	Yes	No
- Database included	Yes	Yes	No
- Flexibility	Poor, no batch mode	Good	Good
2.6 Output			
- Nature of output	On-screen and output files	Spreadsheet	Spreadsheet
- Clarity of output reports	Excellent	Good	Good
- Echo of input parameters	Yes	Yes	Yes
- Post-processing	Yes	Yes	Yes
- User friendliness	Excellent	Good	Good
- Help Utility	Yes	No	No
- Sample output files	No	No	No
- Flexibility	Poor	Good	Good

Model	CEMC Lev. III (TaPL3)	SimpleBox EUSES	CalTOX
3. Model science			
3.1 Compartments considered			
- Air, Soil, Water, Plant, Benthic Sediment	All except plant	All	All
- Dispersed phases: i.e. aerosols in air, particles in water droplets (treated as separate compartments or bulk compartments)	Bulk	Bulk	Bulk
- Compartment segmentation (e.g. horizons in soil profile, layers in atmosphere)	None	Soil segmentation	Soil segmentation
3.2 Numerical technique			
- adequacy of algorithm	ok	ok	ok
- definitions of boundary conditions	ok	ok	ok
- stability	ok	ok	ok
- numerical dispersion	ok	ok	ok
- time step	ok	ok	ok
- implicit/ explicit	ok	ok	ok
- grid cell size	ok	ok	ok
3.3 Processes considered			
- emission, transport, degradation	All	All	All
- only emission			
- only transport and degradation			
3.4 Emission model			
- type of emission: point, line or area source, single source or multiple sources (in time and space), source height	Area source	Area source	Area source
- type of emission: pulse or steady state	steady state	steady state	steady state
3.5 Atmospheric transport model			
- type: Gaussian plume, Lagrangian, Eulerian, trajectory or compartment model	Eulerian/compartment model	Eulerian/compartment model	Eulerian/compartment model
- spatial scale: 0-1 km, 1-1000 km, > 1000km (ie. "local", "regional", "continental" and "global")	regional	regional	regional
- temporal scale (if dynamic): hour, month, year or steady state?	steady state	steady state	steady state
- possibility to consider dynamic (decreasing) emission rates.	No	No	No

Model	CEMC Lev. III (TaPL3)	SimpleBox EUSES	CalTOX
3.6 Deposition model			
- wet deposition, dry deposition	Both	Both	Both
3.7 Substance model			
- emission: source surface (soil, plant, water), source strength, effect of environmental conditions on source strength	Medium specific	Medium specific	Medium specific
- transformation: type of model, effect of environmental conditions, biotic or abiotic, compartments considered	Half-lives not temperature dependent	Half-lives not temperature dependent	Half-lives not temperature dependent
- distribution in air: dissolution in water droplets, sorption to air-borne particles	Speciation estimated in air	Speciation estimated in air	Speciation estimated in air
3.8 Degree of validation			
- List of published validation tests. For each reference, the following items should be specified:	These are evaluative models for estimating travel potential and cannot be validated. An intercomparison exercise showed that all 6 models give similar rankings for CTDs for >600 chemicals	These are evaluative models for estimating travel potential and cannot be validated. An intercomparison exercise showed that all 6 models give similar rankings for CTDs for >600 chemicals	These are evaluative models for estimating travel potential and cannot be validated. An intercomparison exercise showed that all 6 models give similar rankings for CTDs for >600 chemicals
- The names of the chemicals			
- The name and version of the model			
- Area and sources considered in model test			
- Meteo data set used			
- Temporal and spatial scale and resolution			
- All input independently derived from experiments or observations in the environment (Yes/No)			

Table A6 – 1 Step 2 Evaluation of Multimedia Models (continued)

Model	ChemRANGE	ELPOS (CemoS)	IMPACT2002
1. General information			
Name of model	ChemRANGE	ELPOS	IMPACT 2002
Name or number of most recent release	2.1	1.0.1	1.1
Intended use of the model	Calculates air transport potential	Calculates air transport potential	Calculates PECs on a European regional level
Model developers	Scheringer, M.	Beyer, A. and Matthies, M.	Jolliet O, Margni M, Charles R, Humbert S, Payet J, Rebitzer G, Rosenbaum R
Sponsoring institution	Swiss Federal Institute of Technology, Zurich	University of Osnabrueck, Germany	L'Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland
Date of recent release	Jun-02	Sep-01	2003
2. Documentation and system considerations			
2.1 User manual			
Availability	Documented in scientific papers	Detailed report downloadable from web	Reports and papers downloadable from web
Language	English	English	English
Clarity	Moderate	Moderate	Moderate
Defines model limitations	Yes	Yes	Yes
Includes conceptual model description	Yes	Yes	Yes
Includes mathematical model description	Yes	Yes	Yes
Includes sensitivity analysis	No	No	Yes
Provides assistance in determining model parameters	No	Yes	No
Provides test examples	No	Yes	Yes
Provides references	Yes	Yes	Yes
2.2 Other documentation considerations			
Tightness of version control	Good	Good	Unknown
Availability of source code	Yes	Yes	No

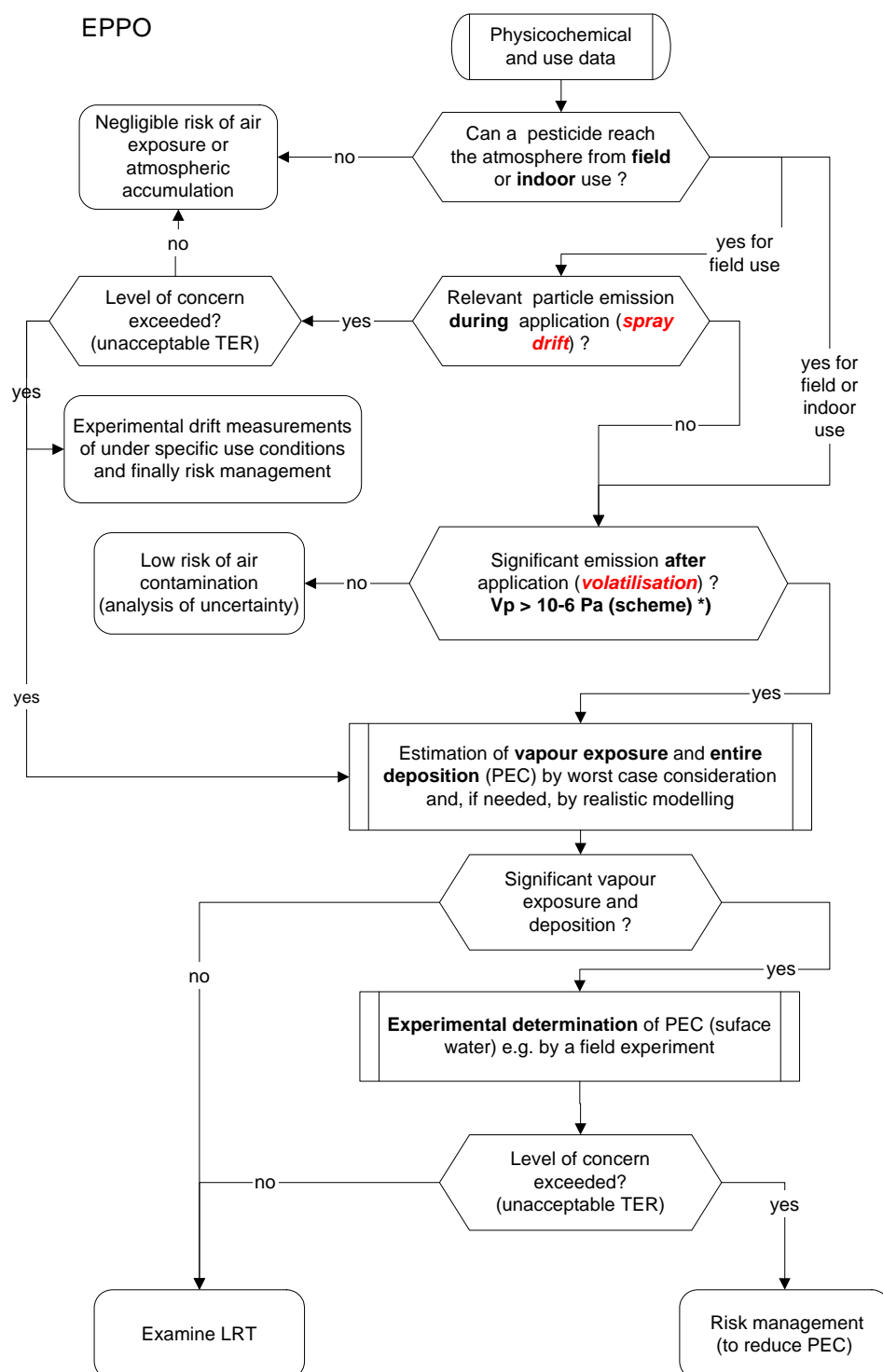
Model	ChemRANGE	ELPOS (CemoS)	IMPACT2002
2.3 System considerations			
- Hardware requirements	PC	PC	PC
- Run time for standard scenario	<1 second per chemical	<1 second per chemical	A few seconds per chemical
- Reliability	Good	Good	Good
- Clarity of error messages	Poor	Poor	Poor
2.4 Support			
- Method of support	Through web	Through web	Through web/EPFL
- Availability of information about bugs, corrections, and new versions	Website	Website	Website
- Training for users	Not formalised	Not formalised	Not formalised
2.5 Input			
- Pre-processing, e.g. meteorological data	No	No	No
- Meteorological input data	No	No	No
- Digital maps: land use, emissions	No	No	No
- Availability of needed data	Physical-chemical properties usually available	Physical-chemical properties usually available	Physical-chemical properties usually available
- Data range checking			
- User friendliness	Good	Excellent	Satisfactory
- Help Utility	No	No	No
- Sample input files	No	Yes	No
- Database included	No	Yes	No
- Flexibility	Good	Good	Satisfactory
2.6 Output			
- Nature of output	Spreadsheet	Spreadsheet	Excel spreadsheet
- Clarity of output reports	Good	Excellent	Poor
- Echo of input parameters	Yes	Yes	Yes
- Post-processing	Yes	Yes	Yes
- User friendliness	Good	Excellent	Poor
- Help Utility	No	No	No
- Sample output files	No	No	No
- Flexibility	Good	Good	Poor

Model	ChemRANGE	ELPOS (CemoS)	IMPACT2002
3. Model science			
3.1 Compartments considered			
- Air, Soil, Water, Plant, Benthic Sediment	All except plant, sediments	All except plant	All
- Dispersed phases: i.e. aerosols in air, particles in water droplets (treated as separate compartments or bulk compartments)	Bulk	Bulk	Bulk
- Compartment segmentation (e.g. horizons in soil profile, layers in atmosphere)	None	None	None
3.2 Numerical technique			
- adequacy of algorithm	ok	ok	ok
- definitions of boundary conditions	ok	ok	ok
- stability	ok	ok	ok
- numerical dispersion	ok	ok	ok
- time step	ok	ok	ok
- implicit/ explicit	ok	ok	ok
- grid cell size	ok	ok	ok
3.3 Processes considered			
- emission, transport, degradation	All	All	All
- only emission			
- only transport and degradation			
3.4 Emission model			
- type of emission: point, line or area source, single source or multiple sources (in time and space), source height	Area source	Area source	Area source
- type of emission: pulse or steady state	steady state	steady state	steady state and dynamic
3.5 Atmospheric transport model			
- type: Gaussian plume, Lagrangian, Eulerian, trajectory or compartment model	Eulerian/compartment model	Eulerian/compartment model	Eulerian/compartment model
- spatial scale: 0-1 km, 1-1000 km, > 1000km (ie. "local", "regional", "continental" and "global")	regional	regional	Regional and European continental
- temporal scale (if dynamic): hour, month, year or steady state?	steady state	steady state	steady state

Model	ChemRANGE	ELPOS (CemoS)	IMPACT2002
- possibility to consider dynamic (decreasing) emission rates.	No	No	Yes
3.6 Deposition model			
- wet deposition, dry deposition	Both	Both	Both
3.7 Substance model			
- emission: source surface (soil, plant, water), source strength, effect of environmental conditions on source strength	Medium specific	Medium specific	Medium specific
- transformation: type of model, effect of environmental conditions, biotic or abiotic, compartments considered	Half-lives not temperature dependent	Half-lives, temperature dependence estimated	Half-lives
- distribution in air: dissolution in water droplets, sorption to air-borne particles	Speciation estimated in air	Speciation estimated in air	Speciation estimated in air
3.8 Degree of validation			
- List of published validation tests. For each reference, the following items should be specified:	These are evaluative models for estimating travel potential and cannot be validated. An intercomparison exercise showed that all 6 models give similar rankings for CTDs for >600 chemicals	These are evaluative models for estimating travel potential and cannot be validated. An intercomparison exercise showed that all 6 models give similar rankings for CTDs for >600 chemicals	Some limited evaluating of the spatial model against monitoring data Margini et al. (2004)
- The names of the chemicals			Polychlorinated dibenzo-p-dioxins and furans
- The name and version of the model			1,1
- Area and sources considered in model test			Yes
- Meteo data set used			Unknown
- Temporal and spatial scale and resolution			Yes
- All input independently derived from experiments or observations in the environment (Yes/No)			Yes

APPENDIX 7: EPPO AIR SCHEME

FIGURE A7-1: THE EPPO AIR SCHEME

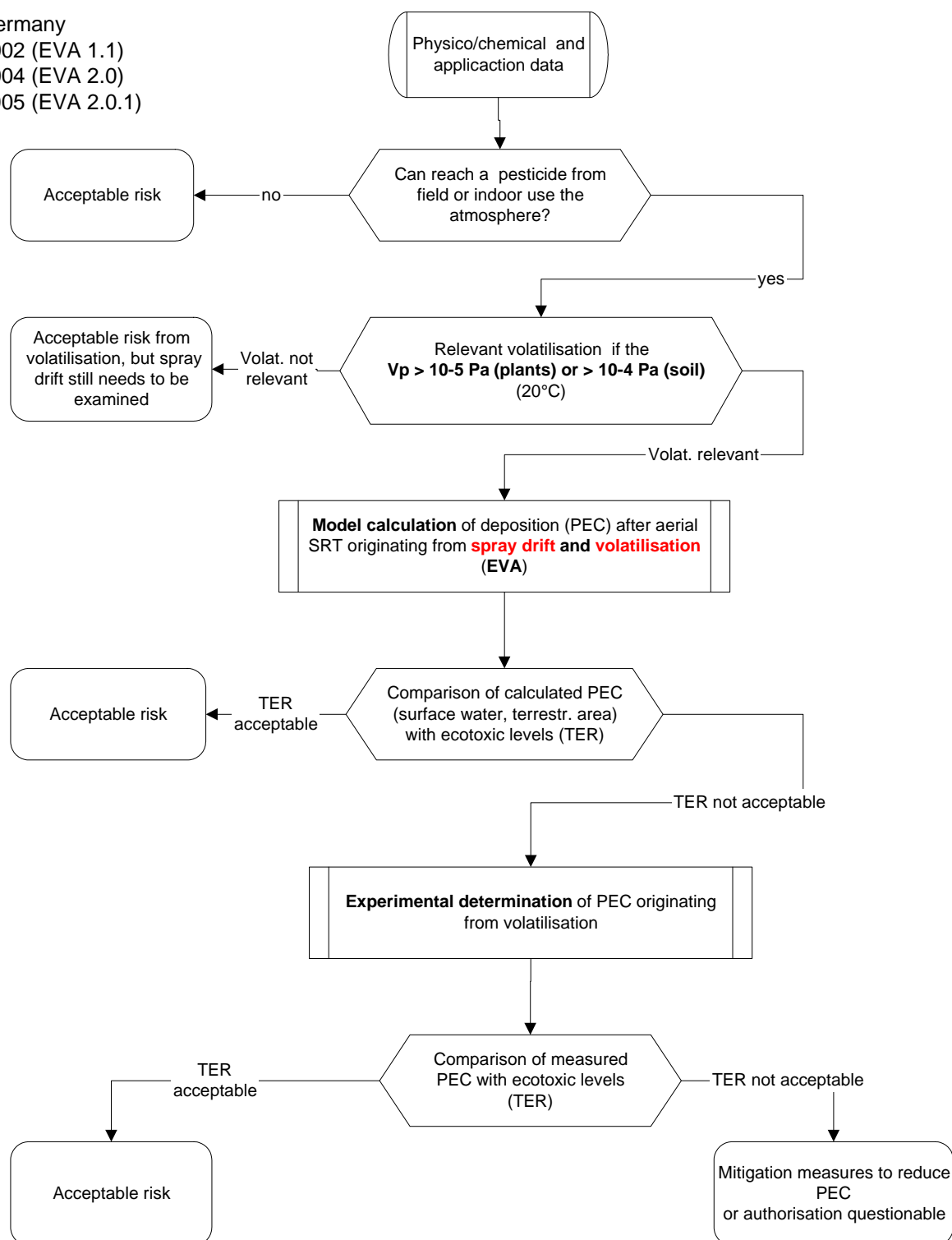


*) Low emission is expected at vapour pressures below 10-3 Pa (soil) and 10-5 Pa (plants) according to Tables 5 (2003) or 3.5 (2000)

APPENDIX 8: GERMAN SHORT RANGE ASSESSMENT SCHEME

Figure A8-1: The German Short-Range Assessment Scheme

Germany
2002 (EVA 1.1)
2004 (EVA 2.0)
2005 (EVA 2.0.1)



APPENDIX 9: MEDRICE PEC CALCULATION

The Med Rice report proposes in the first step a paddy field with a depth of 10 cm and drainage canals (surface waters) for providing and/or drainage of the paddy water with a depth of 1 m (MED-RICE, 2003). The barrier between paddy field and canal is assumed to amount to 1 m in width.

The concentration of a pesticide applied to the paddy field can then be calculated as

$$C_{pw} = \text{application rate} \times (1 - \text{interception by the plants}) / 10 \text{ cm}$$

The concentration in the canal resulting from spray drift (2.77 % loss of the application rate) and outflow can be calculated as

$$C_{sw} = (\text{application rate} \times 2.77 \%) / 1 \text{ m} + (C_{pw} / \text{dilution factor})$$

The dilution factor is derived from the ratio of depths. In this example it is 10.

Numerical example

Assumptions: Application rate 1000 g a.s./ha; Interception by plants: 50 %

Calculations:

$$C_{pw} = 1000 \text{ g / ha} \times (1 - 0.5) / 10 \text{ cm} = 1 \text{ mg / dm}^2 \times 0.5 / 1 \text{ dm}$$

$$= 0.50 \text{ mg / L} = 500 \text{ } \mu\text{g / L}$$

$$C_{sw} \text{ resulting from outflow} = C_{pw} / 10 = 50 \text{ } \mu\text{g / L}$$

$$C_{sw} \text{ resulting from spray drift} = 1000 \text{ g/ha} \times 0.0277 / 1 \text{ m}$$

$$= 2.77 \text{ mg / m}^2 / 1 \text{ m}$$

$$= 2.77 \text{ } \mu\text{g / L}$$

Result and Discussion

The spray drift exposure to the canal (surface water) accounts for $2.77 / 50 \times 100 = 5.5 \%$ of the exposure caused by outflow in this typical example. As shown in Chapter 5.4.1 the deposition after volatilisation at a short distance (1 m) is low if compared to the spray drift. This is also expected for the deposition after volatilisation from a paddy water.

Consequently, the exposure caused by volatilisation and subsequent deposition to an canal at a short distance would be very low when compared to the entire exposure caused by direct outflow of the paddy water and spray drift.

APPENDIX 10: EXPOSURE ASSESSMENT ACCORDING TO FOCUS SURFACE WATER

Figure A10–1: Tiered Assessment Scheme in FOCUS Surface Water Scheme

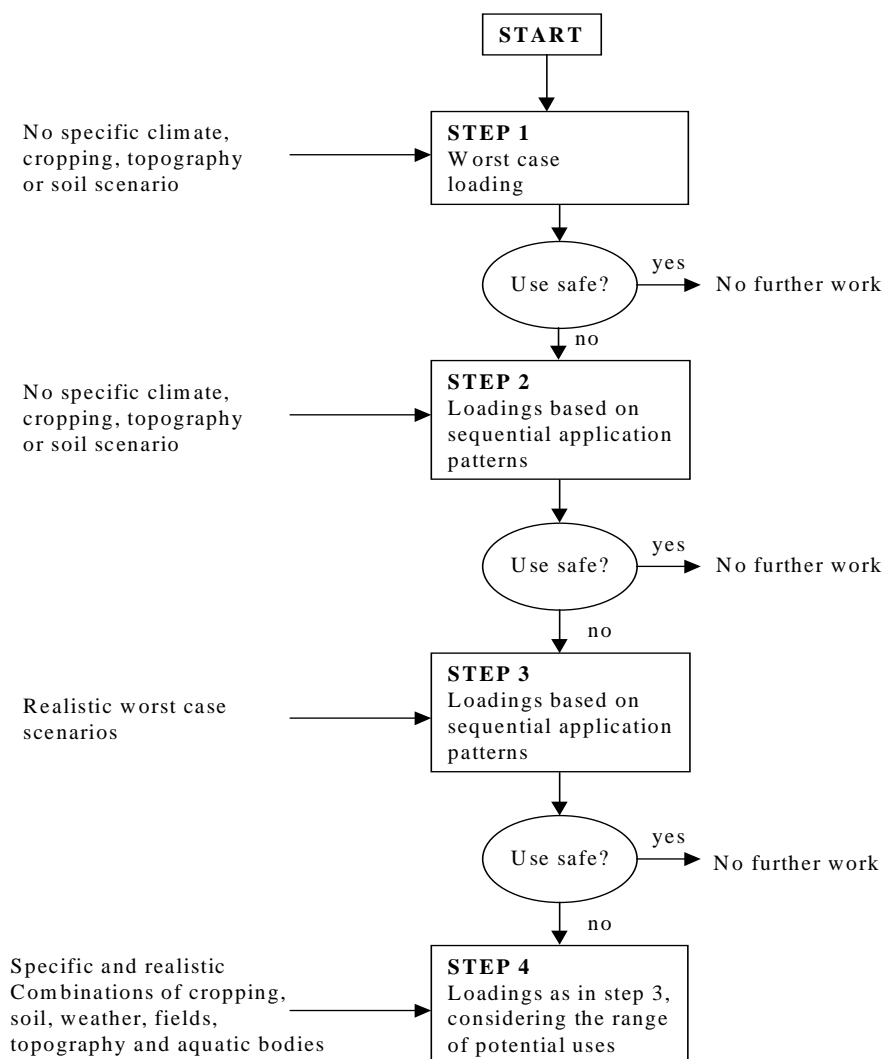


Table A10 – 1: Spray Drift Inputs For FOCUS Steps 1 and 2

Crop / technique	Distance to water (m)	Number of application per season							
		1	2	3	4	5	6	7	>7
cereals, spring	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
cereals, winter	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
citrus	3	15.7	12.1	11.0	10.1	9.7	9.2	9.1	8.7
cotton	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
field beans	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
grass / alfalfa	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
hops	3	19.3	17.7	15.9	15.4	15.1	14.9	14.6	13.5
legumes	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
maize	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
oil seed rape, spring	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
oil seed rape, winter	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
olives	3	15.7	12.1	11.0	10.1	9.7	9.2	9.1	8.7
pome / stone fruit, (early)	3	29.2	25.5	24.0	23.6	23.1	22.8	22.7	22.2
pome / stone fruit (late)	3	15.7	12.1	11.0	10.1	9.7	9.2	9.1	8.7
potatoes	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
soybeans	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
sugar beet	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
sunflower	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
tobacco	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
vegetables, bulb	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
vegetables, fruiting	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
vegetables, leafy	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
vegetables, root	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5

Crop / technique	Distance to water	Number of application per season							
vines, early applications	3	2.7	2.5	2.5	2.5	2.4	2.3	2.3	2.3
vines, late applications	3	8.0	7.1	6.9	6.6	6.6	6.4	6.2	6.2
application, aerial	3	33.2	33.2	33.2	33.2	33.2	33.2	33.2	33.2
application, hand (crop < 50 cm)	1	2.8	2.4	2.0	1.9	1.8	1.6	1.6	1.5
application, hand (crop > 50 cm)	3	8.0	7.1	6.9	6.6	6.6	6.4	6.2	6.2
no drift (incorporation, granular or seed treatment)	1	0	0	0	0	0	0	0	0

* NOTE: for the distinction between early and late references is made to the BBCH-codes as mentioned in Table 2.4.2-1.

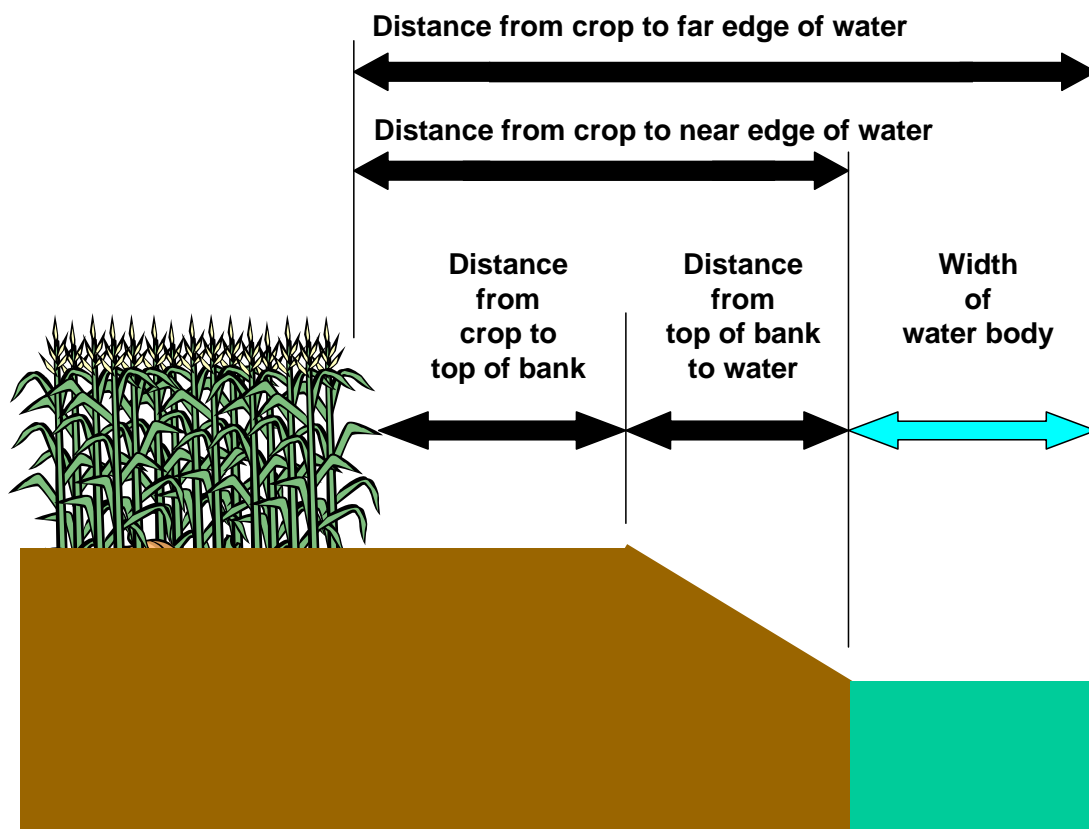
Table A10 – 2: Waterbody characteristics and distances from crop to waterbody used in FOCUS Step 3

Crop grouping or Application Method	Distance from edge of field to top of bank (m)	Water Body Type	Distance from top of bank to edge of water body (m)	Total Distance From Edge of Field to Water Body (m)
cereals, spring	0.5	Ditch	0.5	1.0
cereals, winter				
grass / alfalfa				
oil seed rape, spring				
oil seed rape, winter		Stream	1.0	1.5
vegetables, bulb				
vegetables, fruiting		Pond	3.0	3.5
vegetables, leafy				
vegetables, root				
application, hand (crop < 50 cm)				
potatoes	0.8	Ditch	0.5	1.3
soybeans				
sugar beet		Stream	1.0	1.8
sunflower				
cotton				
field beans				
legumes		Pond	3.0	3.8
maize				
tobacco	1.0	Ditch	0.5	1.5
		Stream	1.0	2.0
		Pond	3.0	4.0
citrus	3.0	Ditch	0.5	3.5
hops				
olives		Stream	1.0	4.0

Crop grouping or Application Method	Distance from edge of field to top of bank (m)	Water Body Type	Distance from top of bank to edge of water body (m)	Total Distance From Edge of Field to Water Body (m)
pome/stone fruit, early applications				
vines, late applications		Pond	3.0	6.0
application, hand (crop > 50 cm)				
application, aerial	5.0	Ditch	0.5	5.5
		Stream	1.0	6.0
		Pond	3.0	8.0

Explanation of the column headers is given in Figure A10 – 2

Figure A10 – 2: Schematic of distances used in FOCUS Step 3 exposure estimation.



Opinion of the Scientific Panel on Plant protection products and their Residues on a request from EFSA on the Final Report of the FOCUS Air Working Group on Pesticides in Air: Consideration for exposure assessment. (SANCO/10553/2006 draft 1 (13 July 2006)).

(Question N° EFSA-Q-2007-047)

adopted 03 July 2007

SUMMARY OF OPINION

After application of plant protection products the chemicals in the product may volatilise from the surface of the treated plants, soil or water. These airborne residues are transported downwind, transformed, and may be deposited at short range or in remote regions. This emission is caused by processes other than spray drift, drainage, or run-off from soil. Deposition of these airborne residues may then coincide with the exposure at the edge of field already assessed in the existing risk assessment schemes, but may also result in an unassessed exposure of the terrestrial or aquatic environment, either nearby or in remote areas.

The FOCUS Air group was formed to develop guidance for applicants and Member States on appropriate methods for calculating exposure concentrations resulting from emission to air of plant protection products. The FOCUS Air group has produced a Report containing a proposal for exposure assessment for plant protection products in air. The Report considered that the contribution from the deposition of volatilised residues was quantitatively less important than spray drift at the edge of field. The relative importance of deposition after volatilisation increases if spray drift mitigation is required (e.g. buffers zones, drift reducing nozzles). The short-range transport (SRT) assessment scheme uses a vapour pressure trigger to identify substances of potential concern. The trigger in the Report is 10^{-5} Pa (at 20 °C) if a substance is applied to plants and 10^{-4} Pa (at 20 °C) if the substance is applied directly to soil. Substances that exceed these triggers, and require drift mitigation in order to pass the terrestrial or aquatic risk assessment, need to have deposition following volatilisation quantified and added to deposition from spray drift. The Report recommends quantification by modelling with the EVA2.0 model, if safety cannot be demonstrated by this means then further experimental data are required. The Report also recommends a trigger of a DT50 in air of 2 days to identify substances of potential concern for long-range transport (LRT). Substances having a longer DT50 require further evaluation to assess their potential impact upon the environment; recommendations on how such an evaluation may be done are presented in the FOCUS Air Group Report.

The Scientific Panel on Plant Protection Products and their Residues was asked for a critical opinion on the scientific review and practical recommendations made by the FOCUS Air group on the exposure assessment for plant protection products in air. As a specific point the Panel was asked to consider whether the vapour pressure cut off values for not assessing short range transport are appropriate, in the context of the tiered risk assessment scheme outlined.

The PPR Panel acknowledges the tremendous efforts which have gone into the preparation of the Report. The PPR Panel appreciates the broad view of the Report and the magnitude of the work completed.

However, the PPR Panel concludes that the FOCUS Air Report does not reflect the state of the art of science in the field of atmospheric transport and deposition of pesticides.

The PPR Panel is of the opinion that the exposure assessment scheme needs more clarification regarding its applicability for the various possible methods of pesticide application, as well as for introducing refinements.

The PPR Panel recommends that the trigger values for volatilisation as proposed by the Report (10^{-5} Pa for plants and 10^{-4} Pa for soil) are not used to eliminate the need for a risk assessment at the short range.

The PPR Panel is of the opinion that the Report's recommendations regarding the use of the EVA2.0 model for short range exposure assessment are scientifically not robust enough. The PPR Panel has investigated whether the proposed methodology for short range transport generates realistic worst case estimates of exposure, which are required for risk assessment. The PPR Panel has come to the conclusion that the recommended model does not give realistic worst case exposure estimates.

The PPR Panel considers the Report's conclusion that the DT50 trigger of 2 days is suitable to assess the need for exposure assessment of long range transport, to be appropriate for practical reasons.

The main recommendations of the PPR Panel are:

1. The PPR Panel recommends the chapters on atmospheric transport and modelling be reconsidered. The PPR Panel recommends that the sections on atmospheric deposition and monitoring include a process description of dry and wet deposition. The PPR Panel recommends that transformation products in the atmosphere be considered, as is currently required by the Directive 91/414/EEC. The PPR Panel recommends that the Report should summarise the key properties of the useful models and provide further guidance for the practical use of these transport models. It should be stated whether these models have been validated for regularly measured air-pollution compounds.
2. The PPR Panel recommends that in the SRT modelling the contribution of volatilisation to the exposure should be accounted for over a longer period of time than 24 hours. The PPR Panel recommends that for short range exposure in the field the Report should define realistic worst-case scenarios for field size and atmospheric conditions.
3. The PPR Panel recommends a more thorough analysis of the uncertainty in the calculated exposure concentrations be carried out.
4. The PPR Panel recommends the Report should provide guidance on how and when hazardous properties to the atmosphere should be assessed, and should consider the issue of solvent emissions as a potential problem.

Key words: Aerial transport, Atmospheric, Emission, Deposition, Long Range Transport, Pesticides, Short Range Transport, Transformation, Trigger, Vapour Pressure, Volatilisation

ACKNOWLEDGEMENTS

The Scientific Panel on Plant protection products and their Residues wishes to thank Laura McConnell, Addo van Pul, Carole Bedos, Willem Asman and the PRAPeR-team for their contributions to this opinion.

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BACKGROUND

The FOCUS Steering Committee, established under DG SANCO of the Commission, identified the need to develop guidance on exposure from aerial transport of pesticides. A working group was established to review potential approaches for calculating exposure concentrations for EU-dossiers for plant protection products. As for other FOCUS groups it was formed by members coming from the MS regulatory authorities, Academia and the Industry.

The remit of this group was to review the current state-of-the-art, where possible recommending approaches that could be implemented forthwith. The working group considered approaches suitable for supporting listing of active substances in Annex I of dir. 91/414/EEC, but also those that could be applied in risk assessments to support national registration.

In July 2006, the FOCUS Air group presented the final document (SANCO/10553/2006 draft 1 13 July 2006), hereafter referred to as the “Report”, containing its main conclusions and proposals.

The intention of the Commission and Member States is that the exposure assessments as outlined in the Report should be the guidance that is used to address the data requirements 7.2.2 (annex II) and 9.3 (annex III) of Directive 91/414/EEC as laid out in Directive 95/36/EC (the current data requirements).

The formation and main work of the group preceded the sharing of responsibility for risk assessment and risk management between the European Food Safety Authority (EFSA) and the European Commission DG-SANCO.

Before incorporating this guidance document into the current procedure of risk assessment of pesticide active substances, the PRAPeR unit in EFSA therefore requested the independent Opinion of the PPR Panel.

TERMS OF REFERENCE

The Scientific Panel on Plant Protection Products and their Residues (PPR Panel) of EFSA is asked for an opinion on the document “Pesticides in Air: Considerations for Exposure Assessment (SANCO/10553/2006, draft 1.0 (13 July 2006))” the final report of the FOCUS Working Group on pesticides in air, paying particular attention to whether the recommendations are:

- consistent with the state of the art of the science in this scientific field;
- scientifically robust enough for the intended use and presented in a way that facilitates communication of the risk assessment procedures and hazard characterisation proposed.

As a specific point the Panel are asked to consider whether the vapour pressure cut off values for not assessing short range transport are appropriate, in the context of the tiered risk assessment scheme outlined.

1. Introduction to the evaluation of the Report

The topic of pesticides in air comprises many fields of knowledge: emission, transformation, atmospheric transport, deposition, impact on air quality, and exposure for terrestrial and aquatic risk assessment. The topic should cover different spatial scales and the results should be applicable for the authorisation of plant protection products under the EU legislation. The PPR Panel acknowledges the tremendous efforts which have gone into the preparation of the Report.

The FOCUS Working Group took the proceedings of a workshop held in the Netherlands in 1998 (van Dijk *et al.*, 1999) as the state of knowledge on pesticides in air up to that date and reviewed literature starting from the date of this workshop. The PPR Panel notes the conclusions and recommendations of the mentioned workshop, especially the following issues:

- Initial screening criteria should consider the potential to become airborne during application, which depends on method of application and the formulation applied. It concerns a highly variable and uncertain event; with little data available.
- Initial screening criteria should also consider the volatilisation potential after the substance reaches the (non-)target surface. It was considered scientifically feasible to set numerical values
- The transport potential to discriminate between short-range and long-range can be based on the calculated atmospheric residence time.
- Transport modelling was considered feasible; the qualitative estimate of uncertainty was 30-50% based on modelling concepts and meteorological variability.
- Deposition and re-emission are events considered to be rather uncertain. For deposition the uncertainty was estimated (based on expert judgement) to be a factor of 3-4.
- PEC calculations would have to be based on scenarios. The uncertainty was estimated to be a factor of 10.
- Short range modelling could be based on dispersion models, while long range modelling might be done using Lagrangian models. For the long-range transport assessment the temperature dependency of physico-chemical properties and degradation should be carefully assessed.
- to account for vulnerable habitats, an extra safety factor in the effect assessment should be considered.
- More research, both in the field and in the laboratory, was considered necessary, in particular:
 - to validate and improve emission, transport, and deposition modelling,
 - to gain more reliable estimates of the physico-chemical properties of pesticides,
 - to validate the applicability of current ecotoxicological standards for vulnerable habitats in regions that are reached only after long range transport.

The objective of this PPR Panel opinion is to give a critical review of the Report intended to help the understanding, implementation and communication of the Report. In order to assess the merits of the science used in and the proposals made by the Report, the following general questions and criteria have been used:

- Is the science used applicable and useful for the purpose? Have the critical issues and uncertainties identified in the Netherlands Health Council Workshop been addressed?
- The applicability of the proposals to the authorisation process under Directive 91/414/EEC should be outlined (i.e. types of products, treatment and application techniques; routes of exposure; geographical applicability).
- Are all key scientific uncertainties highlighted? Has any indication been given about the degree of uncertainty or consensus involved?
- Are significant gaps in the current evidence base identified?
- The work should be based on a critical review of state of the art. If data sources have been judged, the criteria used should be provided.
- The objective of triggers should be stated and the criteria for the choice of a trigger value should be clear.
- The value of a trigger should be validated against the purpose in the risk assessment model and the scientific evidence for such a value. This validation should include the uncertainty around the values and its impact on the conclusions.

2. General remarks on the Report

2.1 APPLICABILITY OF THE PROPOSED APPROACH FOR EXPOSURE ASSESSMENT OF PLANT PROTECTION PRODUCTS

The PPR Panel notes that the remit of this FOCUS group was to review the current state-of-the-art of exposure assessment, where possible recommending approaches that could be implemented forthwith.

The PPR Panel supports the decision in the Report to focus on short range transport (SRT) and long range transport (LRT).

The intensive model search resulted in a selection of seven models for short range transport (SRT) in the Report. All models in principle can be used for calculations for outdoor applications. However, the Report further stated that none of the models fulfilled the requirements for regulatory use for reasons of lack of validation and for the non-existence of scenarios that cover worst case conditions. The PPR Panel has two remarks on that statement:

- 1) Normally scenarios are only defined by modellers or model users if necessary. The fact that for these models scenarios were not present *a priori* does not mean that they could not be easily defined. At this point a further analysis of the models, their uncertainty and definitions of (realistic) worst case scenarios could have been carried out.
- 2) The recommended EVA2.0 model is only a tool with one scenario implicitly present in the model. It is not a model with which different scenarios can be run. This is an important drawback. It is not clear from the Report whether this built-in scenario of

EVA2.0 is worst case for all applications in all circumstances in all EU-member states. It is not possible to investigate these variations in (worst case) scenarios using the model.

2.2. ENVIRONMENTAL AND HUMAN EXPOSURE

The exposure assessment via air is a cross-cutting issue between environmental fate and worker, bystander and residential safety. The Report concluded that worst-case human exposure by air was covered in the EUROPOEM II report (2002), and hence the issue was not further dealt with in the Report. The PPR Panel agrees not to look at these human exposures to airborne pesticides within the Report because it involves additional issues, such as the person's activity and clothing.

2.3. TREATMENT OF UNCERTAINTY

It is the opinion of the PPR Panel that the Report has not dealt adequately with characterising the uncertainty involved in the proposed exposure assessments. As a general principle, characterising uncertainty should be a fundamental part of risk assessment, and this applies to both deterministic and probabilistic assessments. The communication about the uncertainties that surround the proposed methodology is confusing in the current Report. The nature of the uncertainty should always be described at least qualitatively and its impact on the conclusions and recommendations should be discussed.

3. Specific comments

The specific remarks by the PPR Panel follow the Chapters of the Report.

3.1 INTRODUCTION (CHAPTER 1)

The introduction is clear about the background and the remit of the FOCUS Air Group. The output presented in the Report is summarised as follows:

- A review of the current state of knowledge and regulatory approaches to pesticides in air.
- A Tiered risk assessment scheme for the deposition of volatilised residues at a distance <1 km from the source of application (short-range). Guidance is given on how this exposure scheme fits into the existing schemes for exposure assessment under 91/414/EEC.
- A trigger to identify substances that are unlikely to show significant long-range transport (defined as >1000 km from the source) behaviour and guidance on how to evaluate substances that are identified as being of potential concern.
- An inventory of suitable models to estimate exposure from long- and short-range transport of pesticides in air.
- Recommendations on how to assess whether a pesticide presents a risk to air quality

Below the comments of the PPR Panel on this output are presented. The comments follow the chapters of the Report:

Chapter 2. Current level of knowledge about emission

This chapter summarises the existing knowledge of the emission of pesticides to the air and discusses approaches to identify volatile substances.

Chapter 3. Current level of knowledge about atmospheric transport, transformation and deposition

The intention of this chapter is to provide a clear, concise and up to date overview of the major processes relating to the fate of a pesticide once it reaches the atmosphere (either by losses at the time of application or by subsequent volatilisation losses from plant or soil surfaces).

Chapter 4. Inventory of appropriate mathematical models

The transfer of pesticides from target to non-target areas can be split into three dominant processes: (i) emission to air (ii) transport and transformation in air (iii) deposition from air. These processes are distinct and require different modelling approaches. This chapter provides an evaluation of the available models.

Chapter 5. Exposure assessment of pesticides applying to short-range transport via air

The intention of the FOCUS Air group was to determine which pesticides do not volatilise significantly and could therefore be excluded from further consideration; the short-range trigger was established to identify these substances. For pesticides exceeding the short-range trigger, guidance would be provided on how to calculate exposure resulting from volatilisation, and how it should be included into the existing exposure assessment.

Chapter 6. Long range transport potential

In the absence of clear risk assessment guidance, the aim of the FOCUS Air group was to firstly provide a simple means to screen out substances that are of no concern for long-range transport; and secondly, to provide generic guidance on how to evaluate those substances identified as having the potential for long-range transport.

Chapter 7. Adverse effects to the atmosphere

This chapter investigates the potential for pesticides to adversely affect the atmospheric environment, the following topics are addressed: global warming, ozone depletion, photochemical smog formation, acidification and eutrophication.

3.2. CURRENT LEVEL OF KNOWLEDGE ABOUT EMISSION (CHAPTER 2)

The PPR Panel has noted that the literature review is extensive but that some recent references can be added:

- On emission during application: (Gil & Sinfort, 2005; Gil *et al.*, 2006; Ravier *et al.*, 2005)
- on emission by volatilization from soil (measurements): (Pattey *et al.*, 1995), (Briand *et al.*, 2003) and (Bedos *et al.*, 2006)
- on volatilisation from plants (measurements): Leistra *et al.*, (2006) who compared different direct methods of measurements. Majewski (1999) details this level of uncertainty of direct measurements.
- on emission by volatilization from paddy fields: (Ferrari *et al.*, 2005)
- Prueger *et al.*, (2005) also support the effect of atmospheric humidity and soil moisture on volatilization from soils.

These additional papers bring some new information but do not change the conclusions of FOCUS report on these topics.

The PPR Panel is of the opinion that with respect to two topics more existing information should be provided.

- The first topic is the duration of volatilisation. For example the study carried out by Briand *et al.*, (2003) provides information that the duration of volatilisation is not sufficiently taken into account in the Report's recommended approach for short term exposure: some pesticides (with lower Vapour Pressure (V_p)) may show volatilisation during more than 24hrs. The PPR Panel recommends that in the SRT modelling as addressed in chapter 5, the contribution of volatilisation to the exposure is accounted for over a longer period of time than 24 hours.
- The second topic is the emission from greenhouses. The PPR Panel agrees that there are very few measurements of aerial pesticide concentrations in the vicinity of greenhouses that are useful for the risk assessment. However, greenhouse density in the landscape has great influence on the outdoor environmental exposure (Glass *et al.*, 2002; Baas & Huygen, 1992). In the Report, the variety in greenhouse constructions in the EU has not been elaborated upon. Greenhouse size and construction characteristics influence the pesticide volatilisation that might be expected to result in a large variation in air concentrations in the vicinity of greenhouses. More information on emission needs to be generated in order to improve on the exposure assessment for greenhouses.

The PPR Panel recommends that clear definitions are included of the processes of drift and volatilisation, and any other processes that should be identified as critical in describing pesticide movement into the air during and after application. Perhaps a conceptual diagram would be helpful to clarify these different processes.

The PPR Panel recommends more research on the effect of the formulation on losses during application, bearing in mind that the hazard of co-formulants to air should be assessed as well.

The Report is not clear about the need for an assessment of treated seed or of granules. The text in pages 127 and 146 suggests that these applications may need no assessment. The Report should address this issue in a clear and concise way. Also the assessment schemes should differentiate between the emission during actual applications and the volatilisation from soil after application. The PPR Panel wishes to refer to the Panel's opinion on estimating exposure by non-spray applications for risk assessment in aquatic ecotoxicology (EFSA PPR, 2004).

The PPR Panel has noted that the emission to air following several types of applications have not been dealt with, e.g. amenity use (hard surfaces), and gassing of commodities and of storage rooms. Furthermore, volatilisation following application to inundated land, like rice paddies has not been considered. The diversity in greenhouses across Europe has not been considered. Finally, the potential exposure through wind erosion of dry bare soil (during ploughing or at other times) has not been fully explored. More agricultural practises and emission routes could have been covered.

At the end of chapter 2, the Report does not explain why the trigger on vapour pressure is chosen at 10% volatilisation (cumulative over 24 h). In the opinion of the Panel the proposal of a trigger value for volatilisation of 10% emission is not justified because volatilisation is not a risk assessment aim in itself. It can be a source of exposure in environmental compartments such as surface water and soil. E.g. volatilisation of 5% of a high dose of a pesticide that is highly toxic to organisms may lead to a high risk whereas 15% volatilisation of a low dose of a non-toxic pesticide may be no problem. Therefore the use of only exposure (or emission) values as trigger value is not sufficient for risk characterisation. For this reason the PPR Panel considers this trigger to be inappropriate and recommends that the exposure from volatilisation always should be combined with the other routes of entry into the environmental compartment of concern, for example dust drift and drainage as discussed further in EFSA PPR (2004), FOCUS (2001) and SANCO (2002).

The PPR Panel does agree to a designated exposure assessment for compounds with vapour pressures above 10^{-2} Pa.

3.3. CURRENT LEVEL OF KNOWLEDGE ABOUT ATMOSPHERIC TRANSPORT, TRANSFORMATION AND DEPOSITION (CHAPTER 3)

3.3.1. Comments on 3.1 Introduction

This chapter 3 is well constructed and clearly states the scale boundaries for short-, mid- and long-range transport. The distances associated with these three scales are adequately justified.

3.3.2. Comments on 3.2 Transport

The description in section 3.2, which perhaps should be renamed atmospheric transport, is largely based on the pesticide literature. This is, however, an indirect

source. With regard to meteorological processes this part should refer to the meteorological literature. The PPR Panel recommends this section be reconsidered with regard to atmospheric diffusion and dry deposition processes.

3.3.3 Comments on 3.3 Transformation

The section on transformation is clearly written, providing the rationale and limitations of the current state of our ability to predict gas phase degradation reaction rates. In this section photochemical reactions are seen as a means to remove pesticides from the atmosphere. The PPR-Panel agrees to this approach but recommends also to evaluate the reaction products of the pesticides. In theory they could be more harmful than the pesticides themselves. If the reaction products also are harmful, they should be taken into account in the evaluation procedure of the pesticide.

3.3.4 Comments on 3.4 Deposition

In the opinion of the PPR Panel it is important to give more information about the dry and wet deposition mechanisms, e.g. about the different resistances and which resistance under which conditions is limiting for the dry deposition. This should be the framework in which the measurements should be presented. The description should also take the possibility of some saturation into account. This information can be used later to come to estimates of the maximum amount that can be deposited as a function of the downwind distance to the field where the pesticide is applied. The dry deposition velocity is a function of the properties of the component (diffusivity, i.e. the ability to diffuse in air), the properties of the surface (different for different plants, water, soil, etc) and the meteorological conditions. For that reason it is also useful to mention the meteorological conditions when dry deposition measurements are presented. It is possible to make estimates of the maximum dry deposition of whatever gas as a function of downwind distance. These estimates are only a function of the upwind size of the field, the meteorology and the molecular weight of the pesticide. This should be done to get a worst case estimate. Appendix 1 contains an example of this.

3.3.5 Comments on 3.5 Monitoring data for wet deposition and atmospheric concentrations

The PPR Panel is of the opinion that processes for dry and wet deposition should be defined and the interpretation of the field data should be done within this framework.

In support of the review, data from Asman *et al.* (2005) could be added. This paper gives also information on the minimum transport distances for some pesticides.

The PPR Panel would welcome some considerations in the Report on the accumulation of pesticides in media where degradation is slow, like water bodies and snow/ice.

The PPR Panel in general agrees with the conclusions of this chapter in the sense that there is a need for guidance on how to assess the quality of existing monitoring studies. The PPR Panel would like to bring to the attention of the FOCUS Working Group a guidance document provided by the EU funded project NORMAN (NORMAN 2007) that indicates three different validation levels: at the research laboratory, at the reference laboratory and at the routine laboratory level. A protocol at research laboratory level already exists for sampling and measuring the atmospheric deposition of organochlorine pesticides and other persistent organic pollutants. Several monitoring

studies have been carried out under the frame of the EU-funded projects¹ EMERGE, MOLAR and AL:PE that report a detailed sampling plan integrated into a validated analytical method. The PPR Panel considers that monitoring programmes could well benefit from using this hierarchical approach.

3.3.6 Comments on 3.6 Re-emission issues following deposition

The PPR Panel considers that the persistence of the pesticide in soil and water in the section on re-emission and the influence on the re-volatilisation should be addressed.

3.4. INVENTORY OF APPROPRIATE MATHEMATICAL MODELS (CHAPTER 4)

The PPR Panel agrees with the approach taken in chapter 4, discerning important processes, the description and review of the empirical, mechanistic, and numerical approaches to model emission, and the description of the possible approaches to the transport and deposition models. The PPR Panel appreciates the extensive inventory of models (listing 86 models) and the criteria applied to consider the suitability of the models for the exposure assessment.

In general the models were screened for the important processes. However, in the opinion of the PPR Panel the model selection was not up to date. Particularly the modelling efforts of the Meteorological Synthesizing Centre East of UN-ECE EMEP² is omitted. This is nowadays one of the leading groups in modelling transport and deposition of persistent organic pollutants (POPs) for medium range and long range transport.

The PPR Panel recommends that the section on transport should first define which scale has to be modelled and then what processes should be described for every scale. This will help to identify which models are appropriate. It is not necessary to describe all models that have ever been used. A more focused inventory of the families of models that calculate POPs and pesticides would have been sufficient.

All processes that determine the levels of pesticides in air or deposition are discussed. However, only very limited information was given on the deposition processes (dry and wet). Approaches exist to estimate *a priori* the deposition velocities on the basis of physico-chemical properties. These considerations, relevant to the conclusions on whether deposition modelling is feasible, are missing from this chapter.

In section 4.2.3 it should be mentioned somewhere that the volatilisation rate is a function of the wind speed/turbulence as well. Volatilisation models should have been included in this section.

In Section 4.3.1 there seems to be a misunderstanding about models. The PPR Panel recommends the description of the models be corrected. A Lagrangian model is a model where the calculations are done while following the air parcel. An Eulerian model is a model that describes what is happening within a fixed (not moving) volume, where air is transported through. A Gaussian plume model is in fact a Lagrangian model. On page 83 it is said that deposition and transformation are taken into account roughly in Gaussian types of model. However, many models, for example OPS model of Van Jaarsveld, do this in a very detailed fashion.

The PPR panel recommends that the Report should summarise the key properties of the useful models and provide further guidance for the practical use of these transport

¹ See <http://www.mountain-lakes.org/emerge/> for further information

² www.msceast.org

models. It should be included if these models have been validated for regularly measured air-pollution compounds.

On page 116 the Report states that 'several of the multi-media models have been recommended for use in this Chapter'. The Report only mentioned what models passed the Step 1 evaluation, but not what models are left after further consideration. The PPR Panel recommends that the Report clarifies this aspect, and also how these multi-media models should be used in the assessment scheme.

The PPR Panel recommends adding a bullet point on page 120 that 'emission is a factor not fully understood' (since this conclusion was reached on page 109).

The PPR Panel does not agree with the conclusion on the validation status of LRT models given on page 121. Although more work could be done on validation, however, some experience with these models already exist. The difficulty certainly does not lie in the modelling of the air movements, but in the availability and reliability of data on use and emission, and even physicochemical properties, from which all models suffer. Moreover, the uncertainty in the models should be seen in the light of the uncertainty in the total risk assessment.

3.4.2 Specific comments on the recommended model for SRT

The EVA2.0-model is recommended in the Report for SRT and some features of the model are given. However, it is not possible to judge the merits of the model on the basis of the information in the Report. Furthermore, the model is not readily available from the cited website in the Report.

The PPR Panel has attempted to review the EVA 2.0 model, using both the Report, the software for the EVA2.0.1 model kindly provided by the authors³, and underlying literature, and has the following remarks.

1) Presentation of additional information is required in the Report on the following points:

- Calculation of the emission: No information is given in the Report on the way emission is calculated in the model. The Report briefly states that 5 vapour pressure classes are distinguished in EVA 1.1, but does not mention that this emission module is maintained in EVA 2.0. This should be described, together with the temporal dynamics depending on vapour pressure classes. From the data of Kördel *et al.* (1999) it is clear that the emission data consist of estimates for (half)-hourly intervals up to 24h. These estimates for three vapour pressure classes in turn are based on a very small dataset (2 substances, measurements up to only 6 hours). The estimates are stated to be in fair agreement to other data; but they are clearly not in agreement with the measured volatilisation of lindane from sugar beet crop that is reported also (Kördel *et al.*, 1999).
- Volatilisation/deposition from plants compared to soil: On page 104, it is noted that "The EVA 2.0 model uses the assumption that deposition after volatilisation from soil is one third of the deposition after volatilisation from plants. The justification for this assumption comes from Kördel *et al.*, (1999) who used the same value." This assumption is rather strong. However, the Report does not present the arguments that lead to this assumption. Also Kördel *et al.* (1999) only state that one can assume, based on the research of Walter *et al.* (1996),

³ The EVA2.0.1 model is a draft version of the updated EVA2.0 model that was made available to the PPR Panel. The EVA2.0.1 version is in concept identical to the EVA2.0 model described in the Report.

that this ratio is 3, without any further clarification. The PPR panel recommends that the data from the primary source be presented and discussed.

- Emission from orchards, vine and hops compared to field crops: On page 106, it is noted that: "deposition after volatilisation from orchards, vines and hops is twice that of field crops." Information explaining this statement is lacking. Few studies are available on volatilisation from these kinds of crops so it is difficult to evaluate the relevance of this statement.

2) Some hypotheses formulated in the report are questionable:

- Deposition on water: on page 104 it is stated: "The deposition data in EVA 2.0 relate to the deposition onto water. These data can be used as a first rough approximation to estimate deposition onto soil." However, there are no data presented to underpin this hypothesis. The less soluble compounds can show higher deposition on grass than on water (e.g., a modelling study was performed with FIDES -Flux Interpretation by Dispersion and Exchange over Short-range- to calculate the concentrations and the deposition fluxes under field conditions and different scenarios with varying canopy resistances, and surface roughness) (Loubet *et al.*, 2006). So this assumption may lead to an underestimation of the deposition on ecosystems.
- Vapour pressure as the most important parameter influencing deposition: On page 104 it is stated: "The wind tunnel results (Fent 2004) and field experiments (Siebers *et al.*, 2003b; Gottesbüren *et al.*, 2003) show that vapour pressure is the most important parameter influencing deposition." The PPR Panel has noted that this dependence is only linked with the effect of Vp on volatilisation from plants and it is not obvious that Vp may be the major parameter having an effect on deposition. Also, already on page 52, the Report noted the work of Duyzer *et al.* (1997) on parameterisation of dry deposition velocity as a function of Henry's law constant and other phase coefficients. Moreover, Gottesbüren *et al.* (2003) studied only two pesticides (pendimethalin and lindane). Siebers *et al.* (2003b) studied the deposition of only 3 different pesticides (lindane, pirimicarb and parathion) with not very different vapour pressures (a factor of 10). So the two field experiments cannot be used to discuss the effect of vapour pressure on deposition (the authors themselves noted that further studies are required with other compounds with different vapour pressure).
- The PPR Panel is of the opinion that the risk assessment should not be based on fixed deposition rates depending on classes (be it vapour pressure or other properties).

3) The conservativeness of the EVA 2.0 model is not clear.

- On page 103: it is stated that "the results of the wind-tunnel study were used to establish an empirical model that calculates realistic, worst-case deposition derived from the wind-tunnel data." The PPR panel agrees to qualify EVA2.0 as an empirical model.
- The conclusion given on page 106 "Although 15 experiments were carried out to further verify the worst-case nature of the proposed exposure assessment" indicates that the FOCUS Air group is aware of the limitations of the EVA2.0 model. EVA2.0 model has one scenario implicitly present and it is not clear whether this built-in scenario of EVA2.0 is worst case for all applications in all circumstances in all EU-member states. With EVA2.0 it is not possible to investigate these variations in (worst case) scenarios.
- The PPR Panel is not confident that EVA2.0 is conservative in the sense that it represents a realistic worst-case:

- the wind tunnel data are only a small set of events of what is possible in reality. It is not shown or proven that the wind tunnel experiments resemble the worst case or even a realistic worst case.
- The worst case in EVA2.0 has been chosen to be "the 90th percentile deposition for the substance having the highest deposition in each vapour pressure class" (page 104 in the Report) but the number of pesticides tested in each class is limited, and the choice of 90th percentile is arbitrary.
- EVA2.0 does not take into account the size of the treated field, as an empirical relation derived from experiments carried out in wind tunnels are used.
- The model does not take into account the effect of atmospheric stability and the diffusivity in air.
- To evaluate the worst case identified in EVA2.0, the PPR Panel has made indicative calculations to shed some light on EVA2.0 applicability (condition description and results are described in Appendix 1). Main conclusions are:
 - deposition is a strong function of field size: The maximum dry deposition at 1 m downwind distance for an upwind field length of 300 m is about 33 times as much as that EVA2.0.1 gives for a 25 m field, in the case that volatilisation is 100%. In order to give the same maximum deposition as EVA2.0.1 the volatilisation should be $100/33 = 3\%$. It is certain that for many pesticides the volatilisation is larger than 3% and for that reason it can be concluded that EVA2.0.1 under predicts the maximum dry deposition that is possible.
 - the calculated maximum deposition at 1 m is also clearly lower (a factor of 14) in EVA2.0.1 than for a 25 meters field size in the case the volatilization is 100%.

On page 108 the Report states that in the validation of PESTDEP (Asman *et al.*, 2002) in the wind tunnel experiments, it was noted that it was difficult to parameterise the model to reproduce the conditions of the wind tunnel, especially the wind profile and the effect of the wind tunnel wall on dispersion. Similar remarks have been made in the validation of the model CONSENSUS-PEARL (for which the reference was lacking in the Report). Also in the review of the models in this chapter, availability of suitable emission data have been highlighted as a limitation for testing of transport models. The Report does not discuss the limitations of tunnel tests on the usefulness of their results for risk assessment or model validation. As a result, the extent to which the EVA2.0 model is suitable for its purpose remains unclear; also the purpose of wind tunnels for higher tier assessments is not clear.

3.5 EXPOSURE ASSESSMENT OF PESTICIDES APPLYING TO SHORT-RANGE TRANSPORT VIA AIR (CHAPTER 5)

On the use of trigger values and the recommended model for short range exposure assessment the reader is referred to section 3.2 and 3.4.2. In view of the findings the PPR Panel does not support the approach taken in the Report that exposure *via* air should only be assessed in situations where spray drift mitigation measures are required.

The PPR Panel recommends to include in Figure 5.4-3 and 5.4-4 a box for compounds with a $V_p > 10^{-2}$ Pa. The Report states that the SRT assessment cannot be used for fumigants or pesticides with vapour pressures $> 10^{-2}$ Pa. Fumigant losses due to volatilization are often $> 50\%$, and toxicity to humans and wildlife are a serious concern

for some products. How will risk from these chemicals be addressed in this assessment scheme?

The PPR Panel recommends that the Report clarifies how the additional assessment of the impact of degradation on or penetration into leaf surfaces, for example using CONSENSUS-PEARL, connects to the EVA 2.0 input/output. The PPR Panel recommends including in Figure 5.4-3 and 5.4-4 a box for this refinement option.

The PPR Panel recommends that Section 5.5 is not presented as dealing with 'special cases'. Instead, the PPR Panel recommends that the assessment schemes clarify what types of pesticide application are to be covered under the Directive 91/414/EEC, which are addressed in the schemes, and which are not. Amongst others amenity use, wind erosion, and gassing of warehouses and commodities should be addressed in the Report.

3.6 LONG RANGE TRANSPORT POTENTIAL (CHAPTER 6)

The PPR Panel is of the opinion that the way LRT models are discussed is insufficient in view of the state of art of science and of the remit of FOCUS Air. The PPR Panel recommends a more thorough analysis of the uncertainty in the calculated exposure concentrations by the models, which could result in another conclusion.

On page 116 the Report proposed that multi-media models should be used to rank substances and compare them to substances like lindane and PCBs. However, this proposal is not further mentioned nor considered for (long range) assessment. The PPR Panel recommends clarifying this recommendation in Chapter 6.

The PPR Panel considers that the analysis that the DT50 trigger of 2 days is suitable to assess the need for exposure assessment of long range transport, is appropriate for practical reasons since it is also consistent with other assessment schemes (e.g. in UNECE (1998)). The PPR Panel notes that applying this trigger value does not guarantee that a substance with a shorter DT50 will not end up in media far (>1000 km) from the application.

The PPR Panel is concerned whether the Guidance provided is useful for risk assessment. Indeed the chapter addresses a lot of items of which it is not always clear what is meant and what could be done in a risk assessment concerning long range transport.

In an attempt to focus on the conclusions of the chapter, the following questions and remarks need further consideration:

- the idea of assessing substances that fit certain criteria for entering an exposure assessment based on 1) their evaporation potential, 2) the transport and deposition behaviour and 3) the potential impact is good. However, it is not elaborated further. This conclusion should be clarified.
- the issue of persistence in media (e.g. soil, water) is not addressed.
- For an appropriate interpretation of measurements of long range transport spatially and temporally distributed emission inventories for each pesticide are needed.
- to state that the in-field and edge-field scale scenarios of the guidance documents for supporting the assessments under Directive 91/414/EEC could be used, is not sufficient. The crux is essentially in the safety factors that would have to be included. This is not elaborated at all in the Report.

- the conclusion on models is meagre compared to the conclusions of the Health Council Report. In the last years a lot of effort has been put into modelling. A further consideration of the possibilities and uncertainties in the models could lead to a more positive conclusion.

3.7 ADVERSE EFFECTS TO THE ATMOSPHERE (CHAPTER 7)

The PPR Panel recommends that the chapter be improved in the following way:

- The conclusion on page 163 of the Report should be backed up with an analysis of pesticide properties.
- The Chapter should give clear guidance on how and when potential hazardous properties of a pesticide to the atmospheric environment should be assessed.
- Pesticides sold as liquid formulations and fumigants often contain volatile and reactive co-formulants and active ingredients which may contribute to ground-level ozone formation in the presence of NO_x. The issues of co-formulant emissions and reactivity should be addressed especially in regions with reduced air quality.
- The PPR Panel suggests clarifying whether the Global Warming Potential is determined relative to CFC-11 or relative to CO₂.

4. Conclusions and Recommendations

The Scientific Panel on Plant Protection Products and their Residues acknowledges the tremendous efforts which have gone into the preparation of the Report. Broad issues like emission, transport, transformation and deposition are included and discussed. The PPR Panel appreciates the broad view of the *Report* and the magnitude of the work completed.

The PPR Panel concludes that the FOCUS Air Report does not reflect the state of the art of science in the field of atmospheric transport and deposition.

The PPR Panel is of the opinion that the Report's recommendations regarding the trigger values and the use of the model EVA2.0 for short range exposure assessment is scientifically not robust enough.

The PPR Panel is of the opinion that the exposure assessment scheme needs more clarification regarding its applicability for the various possible methods of pesticide application, as well as for introducing refinements.

The PPR Panel recommends that the trigger values for volatilisation as proposed by the Report (10^{-5} Pa for plants and 10^{-4} Pa for soil) are not used to eliminate the need for a risk assessment at the short range.

The PPR Panel considers the conclusion that the DT50 trigger of 2 days is suitable to assess the need for exposure assessment of long range transport, to be appropriate for practical reasons.

The main recommendations of the Panel are:

1. The PPR Panel recommends the Chapter on atmospheric transport (Chapter 3) be reconsidered with more emphasis on atmospheric diffusion and dry deposition processes.

2. The PPR Panel recommends that the sections on atmospheric deposition and monitoring should include a process description of the dry and wet deposition.
3. The PPR Panel recommends that transformation products in the atmosphere need to be considered, as is currently required by the Directive 91/414/EEC.
4. The PPR Panel recommends the description of the models in Chapter 4 be corrected and complemented with more focus on atmospheric science. The PPR panel recommends that the Report should summarise the key properties of the useful models and provide further guidance for the practical use of these transport models. It should be included if these models have been validated for regularly measured air-pollution compounds.
5. The PPR Panel recommends that in the SRT modelling as addressed in Chapter 5, the contribution of volatilisation to the exposure is accounted for over a longer period of time than 24 hours.
6. The PPR Panel recommends that for short range exposure in the field the Report defines in Chapter 5 realistic worst-case scenarios for field size and atmospheric conditions.
7. The PPR Panel recommends a more thorough analysis of the uncertainty in the calculated exposure concentrations be carried out.
8. The PPR Panel recommends the guidance on hazardous properties to the atmosphere in Chapter 7 be improved by supporting the conclusion of the Report with an analysis of pesticide properties, providing clear guidance on how and when potential hazardous properties should be assessed, and consider the issue of solvent emissions as a potential problem.

DOCUMENTATION PROVIDED TO EFSA

FOCUS (2006). Pesticides in air: Considerations for exposure assessment (SANCO/10553/2006 draft 1 (13th July 2006).

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GLOSSARY / ABBREVIATIONS

µg	Microgram
µg/L	Microgram per litre
µg/m ³	Microgram per cubic metre
AF	Assessment factor
Diffusivity	The ability to diffuse in air
DT ₅₀	Half-life for transformation
EC	European Commission
EC ₅₀	Effect Concentration at which 50 % of effect occurred
EEC	European Economic Community
EU	European Union
EUROPOEM	European Predictive Operator Exposure Model
Extrapolation	Extrapolation occurs when measurements for one set of species or conditions are used to represent or estimate values for other species or conditions.
EVA	A model to calculate <u>Exposure Via Air</u>
FOCUS	Forum for the Co-ordination of pesticide fate models and their Use
GAP	Good Agricultural Practice
GD	Guidance Document
MS	Member State
NSA	Non-Spray Applications
Pa	Pascal, unit for Vapour Pressure
PEARL	Pesticide <u>E</u> mission <u>A</u> ssessment at <u>R</u> egional and <u>L</u> ocal scales
PEC	Predicted Environmental Concentration
PESTDEP	A model to calculate <u>P</u> esticide <u>D</u> eposition <u>v</u> ia air to water
POP	Persistent Organic Pollutant
PPP	Plant protection products
PPR Panel	Scientific Panel on Plant Protection products and their Residues
RA	Risk Assessment
SANCO	European Commission Health and Consumer Protection Directorate General
MRT	Medium Range Transport
SRT	Short range transport
LRT	Long range transport
TER	Toxicity-Exposure Ratio
TOXSWA	<u>T</u> oxic <u>s</u> ubstances in surface <u>w</u> aters; describes the exchange flux between water and atmosphere by the film model of two laminar layers at an interface.
Uncertainty	Uncertainty results from limitations in knowledge, for example if the measurements are subject to experimental error or if the extrapolation is approximate.
Uniform Principles	Annex VI of Directive 91/414/EEC: establishing common criteria for evaluating products at a national level were published on 27 September 1997 (OJ L265, p.87).
US EPA	United States Environmental Protection Agency
Vp	Vapour pressure

APPENDIX 1. MAXIMUM POSSIBLE DOWNWIND DRY DEPOSITION OF PESTICIDES

Introduction

The purpose of this appendix is:

- To evaluate if the maximum downwind dry deposition modelled with the EVA2.0.1 model is the realistically possible maximum downwind dry deposition.
- To evaluate if EVA2.0.1 does take into account all important factors that influence the maximum possible downwind dry deposition.

In section 1 a model is described, which is used to evaluate EVA2.0.1. In section 2 the situation to be modelled is described and the assumptions that are made. In section 3 the model's results are presented. In section 4 a comparison is made with EVA2.0.1 and conclusions are drawn.

1. Description of an atmospheric transport and deposition model used to evaluate EVA2.0.1

The maximum possible dry deposition of pesticides as a function of the downwind distance is calculated with the atmospheric transport and dry deposition model that is part of PESTDEP. The model is a 2-dimensional steady state K-model for stationary meteorological conditions (Asman, 1998).

Under steady-state conditions, taking x in the wind direction, neglecting diffusion in the x direction and using first-order closure:

$$u(z) \frac{\partial c(z)}{\partial x} = \frac{\partial}{\partial z} \left[K_z(z) \frac{\partial c(z)}{\partial z} \right] + Q + R$$

where

$u(z)$	=	horizontal wind speed (m s^{-1})
$c(z)$	=	concentration at height z (kg m^{-2}) (note: not kg m^{-3} as the model is two dimensional)
x	=	coordinate along wind direction (m)
z	=	coordinate vertical direction (m)
$K_z(z)$	=	eddy diffusivity in the z direction ($\text{m}^2 \text{s}^{-1}$)
Q	=	source strength ($\text{kg s}^{-1} \text{m}^{-2}$)
R	=	rate by which compound is formed by reaction (positive value) or rate at which the compound decreases by reaction (negative value) ($\text{kg s}^{-1} \text{m}^{-2}$).

In case the field is indefinitely wide in the cross-wind direction (y direction) the numerical results of the 2-dimensional model per m of cross-wind distance are equal to the results of a 3-dimensional model, because there is no net diffusion in the cross-wind direction in such a situation (the amount of material in diffusing in one direction cross-wind is then equal to the amount diffusing in the opposite direction). In that case all units in the above equation for the 2-dimensional model have to be divided by the dimension m to give the results for a 3-dimensional model.

The equation is integrated using the finite-difference method. In order to model the vertical exchange correctly the model contains many vertical layers.

The wind speed is a function of the height in the model. For neutral atmospheric conditions this relation is:

$$u(z) = \frac{u_*}{\kappa} \ln \left(\frac{z-d}{z_{0m}} \right)$$

$u(z)$	=	wind speed at height z (m s^{-1})
u_*	=	friction velocity (m s^{-1}); this is a measure of turbulence. The larger u_* , the larger the turbulence
κ	=	von Karman's constant (0.4; dimensionless)
z	=	height (m)
z_{0m}	=	surface roughness length for momentum (m); this is a measure of the surface roughness and is set to 1/10 of the height of obstacles (e.g. crop)
d	=	displacement height (m). It is set to 0.67 times the height of the obstacles

In case of stable or unstable atmospheric conditions corrections are made to this equation. The stability of the atmosphere is characterized by the Monin-Obukhov length (Araya, 1988).

It should be noted that when the wind speed increases with a factor of two (same stability), the concentrations will decrease with a factor of two, as the same emitted amount is diluted more.

The exchange of material (gases, particles) between two adjacent layers in a K-model is described by the eddy diffusivity K_H ($\text{m}^2 \text{s}^{-1}$), which has given its name to this type of model. The value of K_H for neutral atmospheric conditions is:

$$K_H(z) = 1.67 \kappa u_* z$$

The factor of 1.67 is recommended based on Flesch *et al.* (2002), and accounts for the fact that material and heat are not transported at the same speed as momentum.

The dry deposition in the model is described by a common resistance model (Hicks *et al.*, 1987) and describes that the dry deposition depends on three subsequent resistances.

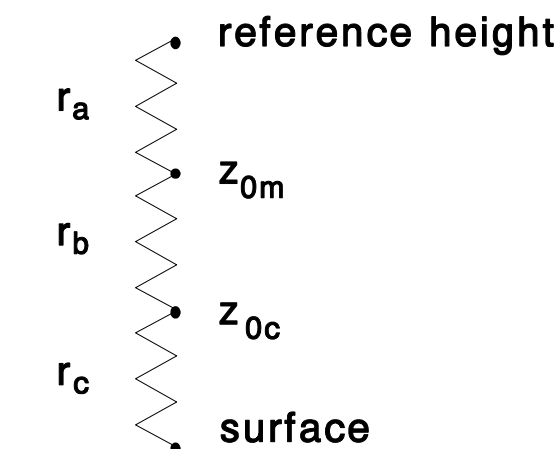


Figure 1. Model for resistance to exchange between the atmosphere and a surface (soil, vegetation, water body).

The cross-wind integrated dry deposition flux F ($\text{kg m}^{-1} \text{s}^{-1}$) in the 2-dimensional model is given by:

$$F = \frac{c(z)}{r_a(z) + r_b + r_c}$$

where:

c = the cross-wind integrated concentration (kg m^{-2}) at height z .

In this model r_a is the atmospheric resistance (s m^{-1}), which is a measure for the resistance for vertical turbulent transport in the air. It has the same value for all gases:

$$r_a(z) = \frac{1}{\kappa u_*} \ln \left(\frac{z-d}{z_{0m}} \right)$$

From the equation it can be seen that when the wind speed increases with a factor of two (and so does u_*), r_a decreases with a factor of two.

The laminar boundary layer resistance r_b (s m^{-1}) depends not only on the properties of the gas/particle, but also on the properties of the surface. The value of r_b for gases for vegetation is given by (Hicks *et al.*, 1987):

$$r_b = \frac{2 \left(\frac{\text{Sc}_g}{\text{Pr}} \right)^{\frac{2}{3}}}{\kappa u_*}$$

where:

Pr = the Prandtl number (dimensionless; value: 0.72)

Sc_g = the Schmidt number in the gas phase

Sc_g is defined by:

$$\text{Sc}_g = \frac{\nu_a}{D_g}$$

where:

ν_a = kinematic viscosity of the air ($\text{m}^2 \text{s}^{-1}$)

D_g = molecular diffusivity of the gas in the gas phase ($\text{m}^2 \text{s}^{-1}$);

Both ν_a and D_g are a function of the temperature, but in much the same fashion. This means that Sc_g is almost independent of the temperature.

The molecular diffusivity of pesticides in air at 25 °C can be approximated by the following equation (Asman *et al.*, 2003):

$$D_g(25) = k_1 \frac{1.42 \times 10^{-4}}{M^{0.589}}$$

where:

M = the molecular mass in g mol^{-1} ,

k_1 = a constant necessary to obtain the right dimensions.

The value of M is 1.0 and its dimension is given by:

$$\frac{m^2 g^{0.589}}{s mol^{0.589}}$$

Its parameterization is based on the results of the Fuller, Schettler and Giddings model for pesticides with different molecular weights (Lyman *et al.*, 1990).

From the equation for r_b it can be seen that if the wind speed increases with a factor of two (and so does u^*), r_b decreases with a factor of two.

The surface resistance r_c is a measure for the uptake of the component by the surface. It depends on the properties of the surface as well as on the properties of the component. In order to get the maximum dry deposition velocity that is possible r_c is set to 0 in all calculations presented here.

The dilution by the diffusion part of the model was tested against a data set for measurements from a low source for sulphur dioxide (the “Prairie grass experiment”, see e.g. Van Ulden, 1978). This was done for a distance of 50 m, the shortest distance to a source for which data are available. Figure 2 shows that the model is able to simulate the dilution (cross-wind integrated concentration in the air/source strength) reasonably well. For this comparison, short-time measurements are used, which always will show some natural variation. The figure contains all 58 measurements. The model is able to calculate concentrations within 30% of the measured concentrations for 54 measurements. When leaving out 4 outliers the correlation coefficient is 0.97. These outliers represent cases with a very stable atmosphere and very low wind speed, i.e. conditions for which the flow might be determined by other processes than the wind higher up in the atmosphere, such as local differences in heating/cooling due to differences in surface properties. Atmospheric diffusion models cannot handle these situations. For that reason the maximum dry deposition presented in section 2 is calculated for a moderately stable situation.

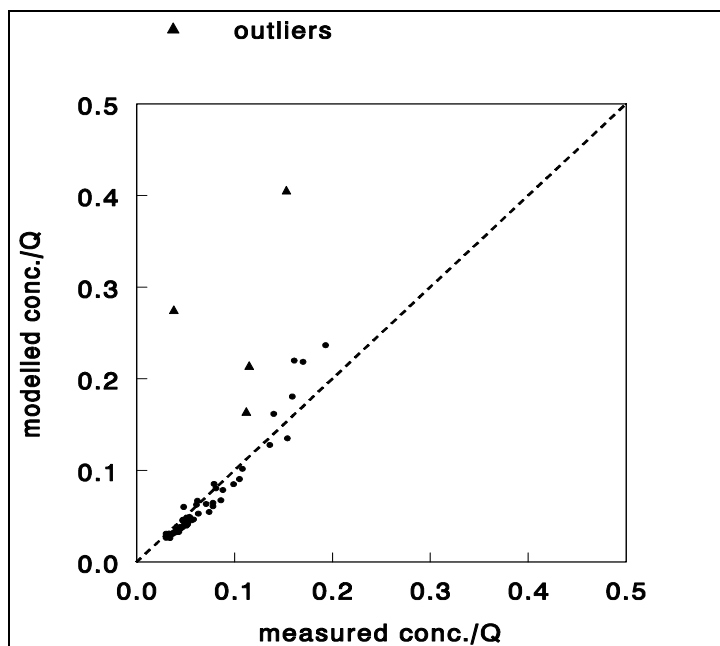


Figure 2. Modelled vs. measured cross-wind integrated dilution (cross-wind integrated concentration/source strength) for a distance of 50 m from the source. The dashed line indicates the curve that would be obtained if the modelled dilutions were equal to the measured dilutions.

The maximum possible downwind deposition of pesticides does not depend on the properties of the pesticides, apart from the molecular diffusivity D_g that plays a role in the laminar boundary layer resistance r_b .

If the wind speed increases by a factor of two, the concentration in the air and r_a and r_b will decrease by a factor of two. From the equation for F it can then be seen that the flux F does not change as a function of the wind speed (see also Asman, 1998). This holds only for the maximum dry deposition velocity, i.e. if r_c is 0.

The maximum deposition given by EVA2.0.1 expressed as a fraction of the applied rate is given by Fent (2004):

$$F_{EVA}(x) = 1.56 \times 10^{-2} \exp(-0.05446(x-1))$$

where:

x = the downwind distance in m

2. Modelled situations

If the maximum possible dry deposition has to be modelled the parameters have to be chosen, so that they are likely to give the highest dry deposition, but that they still are in the range of what is physically possible.

The dry deposition downwind of a field onto which pesticides are applied is a function of the upwind length of the field (Asman *et al.*, 2003). An upwind field length of 300 m was chosen as basis for the calculations. If the width of the field also would be 300 m, the field size is 9 ha, which is large but not uncommon. For reasons of comparison results are also given for two other upwind field lengths: 25 m (used in the wind tunnel experiments that are used to derive the parameterization in EVA2.0.1) and 100 m.

At stable conditions the vertical diffusion of material is somewhat limited. For that reason the concentrations and thereby the dry deposition would be larger during such conditions. It was at therefore decided to take a Monin-Obukhov length of 20 m to characterize the stability.

It was assumed that the height of the crop, i.e. the height of emission, was 1.0 m. The concentration was also calculated at this height, as this gives the highest values. It should be noted that the model is unable to calculate concentrations at much lower heights.

It was assumed that the pesticide cannot be dry deposited to the field onto which it was applied, i.e. that dry deposition first takes place downwind of the field onto which the pesticide was applied. This gives somewhat higher dry deposition downwind than would be the case otherwise.

It was assumed that the pesticide is not subject to any chemical reaction.

As mentioned in the previous section, the results do not depend on the wind speed.

In reality the field is not indefinitely long in the cross-wind direction (y direction) as was assumed. As a result at some downwind distance from the field, the concentrations, especially at the boundaries will become lower than predicted with this model. The distance at which that will be the case depends on the cross-wind width of the field and to some extent also on the upwind field length as well. For a field of a size of 300x300 m², this will first be of importance a few times 300 m downwind.

3. Model results

Table 1 shows the model results for upwind field lengths of 300, 100 and 25 m (situation in the wind tunnel for which the results are used to parameterize EVA2.0.1), if it is assumed that 100% of the applied pesticide volatilizes. In practice, however, this is not the case and only a fraction of the applied amount volatilises. To get the dry deposition in this case the numbers in the table (apart from those for EVA2.0.1) have to be multiplied by this fraction.

It is also assumed that the meteorological conditions are constant during the period.

The model results reflect the maximum dry deposition for the period for which volatilisation is assumed to take place. So if the volatilisation has occurred over a 5-day period, the maximum dry downwind deposition reflects a period of 5 days. If the volatilisation has taken place over 24 hours, the maximum downwind deposition reflects a period of 24 hours (Figure 3).

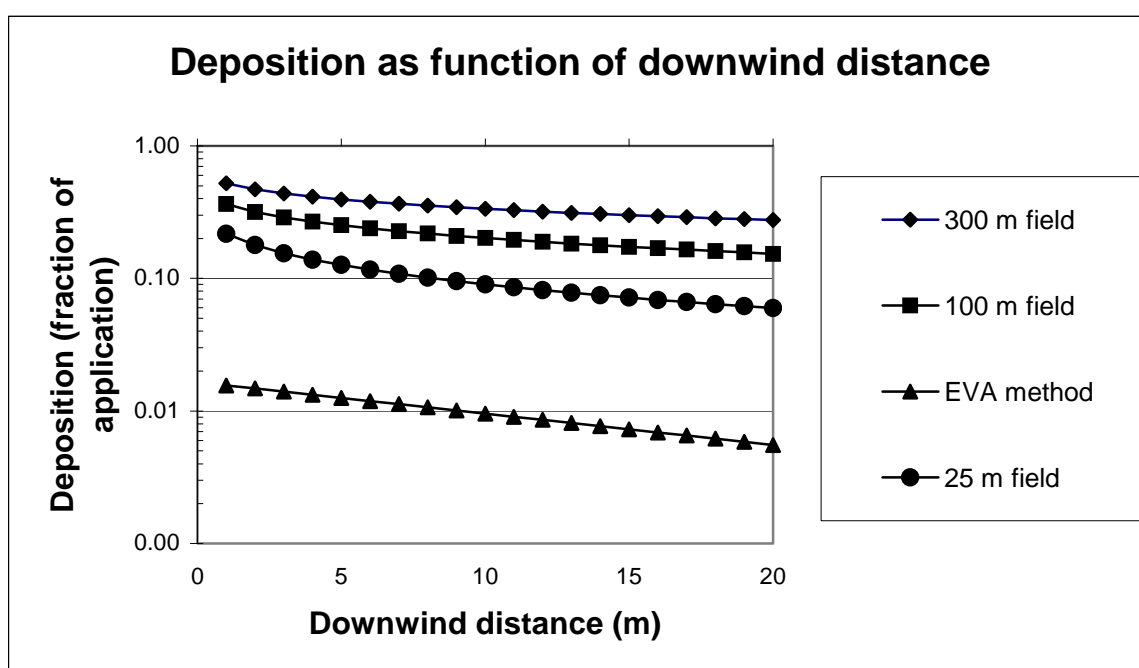


Figure 3. Maximum dry deposition at 1 m downwind distance from a field onto which a pesticide is applied. One model result is from the EVA2.0.1 method (triangles). The other results are from the calculations derived from PESTDEP, assuming that 100% of the pesticide has volatilized for a stable atmosphere (Monin-Obukhov length: 20 m). The results from the calculations derived from PESTDEP are for different upwind lengths of the field onto which the pesticide is applied (25m (like in EVA2.0.1), 100m and 300 m).

Table 1. Maximum dry deposition of pesticides, assuming that 100% of the applied pesticide volatilizes, and results from the EVA2.0.1 model (last column).

	Upwind size: 300 m	Upwind size: 100 m	Upwind size: 25 m (Simulation of EVA)	EVA2.0.1
Downwind distance (m)	Deposition (fraction of emission)	Deposition (fraction of emission)	Deposition (fraction of emission)	Deposition (fraction of emission)
0	0.0000	0.0000	0.0000	0.0000
1	0.5220	0.3630	0.2173	0.0156
2	0.4690	0.3170	0.1781	0.0148
3	0.4370	0.2880	0.1549	0.0140
4	0.4130	0.2680	0.1386	0.0132
5	0.3940	0.2520	0.1263	0.0125
6	0.3790	0.2380	0.1164	0.0119
7	0.3660	0.2270	0.1082	0.0113
8	0.3540	0.2180	0.1013	0.0107
9	0.3440	0.2090	0.0954	0.0101
10	0.3350	0.2020	0.0902	0.0096
11	0.3270	0.1950	0.0856	0.0090
12	0.3190	0.1890	0.0816	0.0086
13	0.3120	0.1830	0.0779	0.0081
14	0.3060	0.1780	0.0746	0.0077
15	0.3000	0.1730	0.0716	0.0073
16	0.2940	0.1690	0.0688	0.0069
17	0.2890	0.1650	0.0663	0.0065
18	0.2840	0.1610	0.0640	0.0062
19	0.2800	0.1570	0.0618	0.0059
20	0.2750	0.1530	0.0598	0.0055
40	0.2160	0.1100	0.0369	
60	0.1830	0.0870	0.0270	
80	0.1600	0.0728	0.0214	
100	0.1440	0.0628	0.0178	
120	0.1310	0.0554	0.0153	
140	0.1200	0.0496	0.0134	
160	0.1110	0.0450	0.0119	
180	0.1040	0.0412	0.0108	
200	0.0973	0.0380	0.0098	
300	0.0747	0.0276	0.0069	
400	0.0610	0.0217	0.0053	
600	0.0449	0.0153	0.0036	
800	0.0356	0.0119	0.0028	
1000	0.0295	0.0097	0.0023	

4. Conclusions

All conclusions are based on the results presented in Table 1 and Figure 3.

- The simulation with the calculations derived from PESTDEP shows that the maximum dry deposition downwind of a field onto which a pesticide is applied does depend on the upwind length of this field, on the diffusivity of the gaseous

pesticide in air and on the atmospheric stability, characterized by the Monin-Obukhov length. It does not depend on the wind speed.

- The results of EVA2.0.1 do not depend on the upwind length of the field, which is a very important factor. Moreover, they are not a function of the atmospheric stability or the diffusivity of the gaseous pesticide in air, which also influence the maximum dry deposition downwind of the field onto which a pesticide is applied.
- The maximum dry deposition at 1 m downwind distance given by the calculations derived from PESTDEP for an upwind field length of 300 m is about 33 times as much as that EVA2.0.1 gives for the same situation, in the case the volatilisation is 100%. In order to give the same maximum deposition as EVA2.0.1 the volatilisation should be $100/33 = 3\%$. It is certain that for many pesticides the volatilisation is larger than 3% and for that reason it can be concluded that EVA2.0.1 under predicts the maximum dry deposition that is possible, even in case there is some uncertainty in the results of the calculations derived from PESTDEP for specific situations as illustrated by Figure 2.
- When using the same upwind length of the field as in EVA2.0.1 (25 m) the result from the calculations derived from PESTDEP at a downwind distance of 1 m is about 14 times higher than EVA2.0.1 gives for the same situation, in case the volatilisation is 100%. In order to give the same maximum deposition as EVA2.0.1 the volatilization should be $100/14 = 7\%$. So even in the case of the very short upwind length of the field the EVA2.0.1 model under predicts the maximum dry deposition that is possible.
- The maximum dry deposition is also important at distances larger than 20 m, the maximum distance for which EVA2.0.1 is able to give results.

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Comment Number	EFSA Comment	FOCUS Air Group Response	Changes to the Report
1	The PPR Panel concludes that the FOCUS Air Report does not reflect the state of the art of science in the field of atmospheric transport and deposition.	We acknowledge that the report does not represent the state of the art with respect to atmospheric deposition but believe that this would not have changed the overall conclusions. The group have made changes to the report to reflect the PPR panel's comments.	Change Section 4.9.1 to read "further work is required to collate information on the basic processes involved in deposition after volatilisation. Once this has been done and once experimentally tested process-based models become available the SRT scheme requires re-evaluation."
2	The PPR Panel is of the opinion that the Report's recommendations regarding the trigger values and the use of the model EVA2.0 for short range exposure assessment is scientifically not robust enough.	We agree that the EVA 2.0 model has limitations and only propose the EVA 2.0 model as an interim solution (see response to Comments 10, 49, 50). Similarly the trigger values were set at levels at which little or no volatilisation can be expected, based upon the best data available to the Group, and we believe that these should stand.	For clarity change text in Section 4.9.1 "EVA model can be used... as an interim solution". Change text at bottom of P131 bottom line "As stated in Section 4.9.1 the EVA model can be used as an interim solution for the assessment of short-range deposition" Change 3 rd paragraph on p133 to read "in general FOCUS AIR proposes that EVA2.0 could be used in Tier II of the exposure assessment for volatilisation and short-range transport of pesticides in the air and subsequent deposition onto non-target areas as an interim solution. The proposed scheme should be revised as soon as a better, experimentally tested, model becomes available."
3	The PPR Panel is of the opinion that the exposure assessment scheme needs more clarification regarding its applicability for the various possible methods of pesticide application, as well as for introducing refinements.	The Group considered major agricultural use patterns and, due to time restraints, were unable to consider all possible application technologies (see responses to Comments 19 and 20). Extra information on how to assess deposition on highly volatile compounds have been added in response to PPR panel comments (see comment 53), and the assessment scheme has been kept open to allow refinements as necessary (e.g. see Comment 54).	See comments 19,20,53,54 Add sentence to 3 rd paragraph p133 "It should be noted that the use of EVA 2.0 for FOCUS AIR is limited to the estimation procedure of the deposition after spraying outdoor agricultural crops. Other functionalities of EVA 2.0 such as the calculation of predicted environmental concentrations, toxicity exposure ratios as well as emissions from indoor uses should not be used within the procedures proposed by FOCUS AIR. "
4	The PPR Panel recommends that the trigger values for volatilisation as proposed by the Report (10-5 Pa for plants and 10-4 Pa for soil) are not used to	The group reviewed the data available on volatilisation from plants and soil and still consider that the trigger values for volatilisation are appropriate. (see response to Comment 22)	None

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	eliminate the need for a risk assessment at the short range.		
5	The PPR Panel recommends the Chapter on atmospheric transport (Chapter 3) be reconsidered with more emphasis on atmospheric diffusion and dry deposition processes.	We agree that it would be helpful to have more information in dry and wet deposition processes, but do not believe that such information would significantly change the conclusions of the report (See response to Comment 25)	See response to Comment 25
6	The PPR Panel recommends that the sections on atmospheric deposition and monitoring should include a process description of the dry and wet deposition.	See above	See above
7	The PPR Panel recommends that transformation products in the atmosphere need to be considered, as is currently required by the Directive 91/414/EEC.	There is very little experimental literature on this point. Theoretical calculations to assess the degradation of substances in air have been part of the 91/414/EEC process since the start, however the Group is not aware that the metabolites arising from this theoretical process have ever been considered as worthy of further assessment. Consequently The FOCUS air report is primarily aimed at addressing the current MS concerns for exposure assessment of parent molecules	None
8	The PPR Panel recommends the description of the models in Chapter 4 be corrected and complemented with more focus on atmospheric science. The PPR panel recommends that the Report should summarise	The key properties of the models were identified during the screening phase. Use of the model with organic substances was a Step 1 screening criterion. Detailed consideration of the practical use of every model was beyond the scope of this group.	None

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	the key properties of the useful models and provide further guidance for the practical use of these transport models. It should be included if these models have been validated for regularly measured air-pollution compounds.		
9	The PPR Panel recommends that in the SRT modelling as addressed in Chapter 5, the contribution of volatilisation to the exposure is accounted for over a longer period of time than 24 hours.	We believe that the contribution of volatilisation should still be limited to 24 hours. See response to comment 16	None
10	The PPR Panel recommends that for short range exposure in the field the Report defines in Chapter 5 realistic worst-case scenarios for field size and atmospheric conditions.	We agree that it is unknown the extent to which the scenario implicit in the EVA 2.0 model is a worst-case for Europe (see response to Comment 48). However the proposed scheme is only put forward as an interim solution until a better model becomes available.	See response to comment 48
11	The PPR Panel recommends a more thorough analysis of the uncertainty in the calculated exposure concentrations be carried out.	We acknowledge that an analysis of uncertainty would be useful, but the group gave greater priority to other topics	add following text in Section 5.4.2: "Moreover, an analysis of the uncertainty in the input data for this model and their propagation to the calculated exposure concentrations would give valuable information on the reliability of these exposure concentrations. "
12	8. The PPR Panel recommends the guidance on hazardous properties to the atmosphere in Chapter 7 be improved by supporting the conclusion of the Report with an analysis of pesticide properties, providing clear guidance on how and when potential hazardous	The Report indicated it was unlikely that pesticides would have a hazardous effect upon the atmosphere and consequently believe that this would be of limited value. The group gave emissions of active ingredients the highest priority and considered emission of solvents to be of lesser importance.	None

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	properties should be assessed, and consider the issue of solvent emissions as a potential problem.		
13	<p>1) Normally scenarios are only defined by modellers or model users if necessary. The fact that for these models scenarios were not present <i>a priori</i> does not mean that they could not be easily defined. At this point a further analysis of the models, their uncertainty and definitions of (realistic) worst case scenarios could have been carried out</p> <p>2)The recommended EVA2.0 model is only a tool with one scenario implicitly present in the model. It is not a model with which different scenarios can be run. This is an important drawback. It is not clear from the Report whether this built-in scenario of EVA2.0 is worst case for all applications in all circumstances in all EU-member states. It is not possible to investigate these variations in (worst case) scenarios using the model.</p>	See response to Comment 10, 11 above and responses to comments (48, 49, 50).	See comment 48

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14	<p>It is the opinion of the PPR Panel that the Report has not dealt adequately with characterising the uncertainty involved in the proposed exposure assessments. As a general principle, characterising uncertainty should be a fundamental part of risk assessment, and this applies to both deterministic and probabilistic assessments. The communication about the uncertainties that surround the proposed methodology is confusing in the current Report. The nature of the uncertainty should always be described at least qualitatively and its impact on the conclusions and recommendations should be discussed</p>	<p>We agree that a consideration of uncertainty would be useful but gave greater priority to other topics</p>	<p>See response to Comment 11</p>

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15	<p>The PPR Panel has noted that the literature review is extensive but that some recent references can be added:</p> <ul style="list-style-type: none"> o On emission during application: (Gil & Sinfort, 2005; Gil <i>et al.</i>, 2006; Ravier <i>et al.</i>, 2005) o on emission by volatilization from soil (measurements): (Pattey <i>et al.</i>, 1995), (Briand <i>et al.</i>, 2003) and (Bedos <i>et al.</i>, 2006) o on volatilisation from plants (measurements): Leistra <i>et al.</i>, (2006) who compared different direct methods of measurements. Majewski (1999) details this level of uncertainty of direct measurements. o on emission by volatilization from paddy fields: (Ferrari <i>et al.</i>, 2005) o Prueger <i>et al.</i>, (2005) also support the effect of atmospheric humidity and soil moisture on volatilization from soils. 	<p>We agree with the panel that some references were omitted, however it should be noted that some appeared after the group reported and that, as the PPR panel itself noted, these new references do not affect the outcome of the report, consequently they have not been added to the main text. These additional references are included in the PPR panel opinion, which appears as an Appendix to this report.</p>	<p>The PPR panel opinion has been added to the report</p>

Comment Number	EFSA Comment	FOCUS Air Group Response	Changes to the Report
16	<p>The first topic is the duration of volatilisation. For example the study carried out by Briand et al., (2003) provides information that the duration of volatilisation is not sufficiently taken into account in the Report's recommended approach for short term exposure: some pesticides (with lower Vapour Pressure (Vp)) may show volatilisation during more than 24hrs. The PPR Panel recommends that in the SRT modelling as addressed in chapter 5, the contribution of volatilisation to the exposure is accounted for over a longer period of time than 24 hours</p>	<p>Briand et al (2003) concluded that cumulative volatilisation losses are very low (about 1% for alachlor and about 0.1% for atrazine within 4 days after spray application in the field). These data do not change the position of the group that 24 hours is an appropriate period over which to consider deposition.</p>	None
17	<p>The second topic is the emission from greenhouses. The PPR Panel agrees that there are very few measurements of aerial pesticide concentrations in the vicinity of greenhouses that are useful for the risk assessment. However, greenhouse density in the landscape has great influence on the outdoor environmental exposure (Glass <i>et al.</i>, 2002; Baas & Huygen, 1992). In the Report, the variety in greenhouse constructions in the EU has not been elaborated upon. Greenhouse size and</p>	<p>To the group's knowledge, there is little literature dealing with the relationship between greenhouse construction and size with outdoor concentrations of pesticides. We agree with the panel that more information on emission, greenhouse construction and density within the EU, needs to be generated in order to improve on the exposure assessment for greenhouses.</p>	None

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	construction characteristics influence the pesticide volatilisation that might be expected to result in a large variation in air concentrations in the vicinity of greenhouses. More information on emission needs to be generated in order to improve on the exposure assessment for greenhouses		
18	The PPR Panel recommends that clear definitions are included of the processes of drift and volatilisation, and any other processes that should be identified as critical in describing pesticide movement into the air during and after application. Perhaps a conceptual diagram would be helpful to clarify these different processes	Add a definition of spray drift, volatilisation and emission during application to the Glossary	Definitions of spray drift, volatilisation and emission have been added to the Glossary.
19	The PPR Panel recommends more research on the effect of the formulation on losses during application, bearing in mind that the hazard of co-formulants to air should be assessed as well.	We agree that the effect of formulation should be further investigated, but such work is beyond the scope of this Group. However we do not agree that assessment of the hazard of co-formulants is appropriate under 91/414/EEC	Comment added to Further Work Chapter to include effect of formulation on volatilisation during application.

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20	<p>The Report is not clear about the need for an assessment of treated seed or of granules. The text in pages 127 and 146 suggests that these applications may need no assessment. The Report should address this issue in a clear and concise way. Also the assessment schemes should differentiate between the emission during actual applications and the volatilisation from soil after application. The PPR Panel wishes to refer to the Panel's opinion on estimating exposure by non-spray applications for risk assessment in aquatic ecotoxicology (EFSA PPR, 2004)</p>	<p>It is the Group's opinion that any assessment by the notifier should be on a case-by-case basis taking into account all relevant information such as the Panel's opinion on estimating exposure by non-spray applications (EFSA PPR(2004)). Note that the PPR panel's opinion was published after the Group had reviewed emission pathways.</p>	None
21	<p>The PPR Panel has noted that the emission to air following several types of applications have not been dealt with, e.g. amenity use (hard surfaces), and gassing of commodities and of storage rooms. Furthermore, volatilisation following application to inundated land, like rice paddies has not been considered. The diversity in greenhouses across Europe has not been considered. Finally, the potential exposure through wind erosion of dry bare soil (during ploughing or at other</p>	<p>The Group considered major agricultural use patterns and, due to time restraints, were unable to consider all possible application technologies. This is consistent with other exposure schemes under 91/414/EEC such as FOCUS SW</p>	None

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	times) has not been fully explored. More agricultural practises and emission routes could have been covered		
22	<p>At the end of chapter 2, the Report does not explain why the trigger on vapour pressure is chosen at 10% volatilisation (cumulative over 24 h). In the opinion of the Panel the proposal of a trigger value for volatilisation of 10% emission is not justified because volatilisation is not a risk assessment aim in itself. It can be a source of exposure in environmental compartments such as surface water and soil. E.g. volatilisation of 5% of a high dose of a pesticide that is highly toxic to organisms may lead to a high risk whereas 15% volatilisation of a low dose of a non-toxic pesticide may be no problem. Therefore the use of only exposure (or emission) values as trigger value is not sufficient for risk characterisation. For this reason the PPR Panel considers this</p>	<p>The 10% emission value was not used as a trigger but rather as an indication of when total volatilisation is likely to be insignificant, given the uncertainty in measurement of this quantity. The trigger values for the vapour pressure were set at one order of magnitude less than the vapour pressure beneath which volatilisation was less than 10% in order to set a conservative trigger level.</p>	<p>Units have been added to the trigger values on P38 of the report</p>

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	<p>trigger to be inappropriate and recommends that the exposure from volatilisation always should be combined with the other routes of entry into the environmental compartment of concern, for example dust drift and drainage as discussed further in EFSA PPR (2004), FOCUS (2001) and SANCO (2002).</p>		
23	<p>The description in section 3.2, which perhaps should be renamed atmospheric transport, is largely based on the pesticide literature. This is, however, an source. With regard to meteorological processes this part should refer to the meteorological literature. The PPR Panel recommends this section be reconsidered with regard to atmospheric diffusion and dry deposition processes</p>	<p>Section renamed to Atmospheric Transport of Pesticides. The Introduction to this Chapter specifically stated that it was not the intention of the group to investigate the literature on meteorology.</p>	<p>Rename Section Atmospheric Transport of Pesticides</p>

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24	<p>In this section photochemical reactions are seen as a means to remove pesticides from the atmosphere. The PPR-Panel agrees to this approach but recommends also to evaluate the reaction products of the pesticides. In theory they could be more harmful than the pesticides themselves. If the reaction products also are harmful, they should be taken into account in the evaluation procedure of the pesticide.</p>	<p>There is very little experimental literature on this point. Theoretical calculations to assess the degradation of substances in air have been part of the 91/414/EEC process since the start, however the Group is not aware that the metabolites arising from this theoretical process have ever been considered as worthy of further assessment. Consequently The FOCUS air report is primarily aimed at addressing the current MS concerns for exposure assessment of parent molecules</p>	None
25	<p>In the opinion of the PPR Panel it is important to give more information about the dry and wet deposition mechanisms, e.g. about the different resistances and which resistance under which conditions is limiting for the dry deposition. This should be the framework in which the measurements should be presented. The description should also take the possibility of some saturation into account. This information can be used later to come to estimates of the maximum amount that can be deposited as a function of the downwind distance to the field where the pesticide is applied. The dry deposition velocity is a function of the properties of the</p>	<p>We acknowledge that further information on wet and dry deposition would be useful, but do not believe that this would substantially alter the conclusions of the report. The Section on Further Work has been enhanced to take into account the PPR Panel's opinions.</p>	Chapter 9: Further work has been enhanced to take account of PPR panel's comments

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	<p>component (diffusivity, i.e. the ability to diffuse in air), the properties of the surface (different for different plants, water, soil, etc) and the meteorological conditions. For that reason it is also useful to mention the meteorological conditions when dry deposition measurements are presented. It is possible to make estimates of the maximum dry deposition of whatever gas as a function of downwind distance. These estimates are only a function of the upwind size of the field, the meteorology and the molecular weight of the pesticide. This should be done to get a worst case estimate. Appendix 1 contains an example of this.</p>		
26	<p>The PPR Panel is of the opinion that processes for dry and wet deposition should be defined and the interpretation of the field data should be done within this framework</p>	<p>In gathering together the available literature, the group attempted to present factual summaries of the information provided. We do not consider it appropriate to interpret the field data provided by other authors</p>	<p>None</p>
27	<p>In support of the review, data from Asman <i>et al.</i> (2005) could be added. This paper gives also information on the minimum transport distances for some pesticides</p>	<p>These data were published after the group reported and would require further evaluation by the group. These data are referenced in the PPR panel report which appears in an Appendix.</p>	<p>PPR panel opinion included as an Appendix to the Report.</p>

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28	<p>The PPR Panel would welcome some considerations in the Report on the accumulation of pesticides in media where degradation is slow, like water bodies and snow/ice</p>	<p>The accumulation of pesticides in snow and ice was not part of the remit of the group. The aim was to look at behaviour in air and how the exposure via air could be incorporated into the existing risk assessments for soil and surface water</p>	None
29	<p>The PPR Panel would like to bring to the attention of the FOCUS Working Group a guidance document provided by the EU funded project NORMAN (NORMAN 2007) that indicates three different validation levels: at the research laboratory, at the reference laboratory and at the routine laboratory level. A protocol at research laboratory level already exists for sampling and measuring the atmospheric deposition of organochlorine pesticides and other persistent organic pollutants. Several monitoring studies have been carried out under the frame of the EU-funded projects¹ EMERGE, MOLAR and AL:PE that report a detailed sampling plan integrated into a validated analytical method. The PPR Panel considers that monitoring programmes could well benefit from using this hierarchical approach</p>	<p>This document was published after the Group had reported; a reference to this document appears in the PPR panel opinion appended to the FOCUS Air report.</p>	PPR panel opinion included as an Appendix to the Report.

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30	The PPR Panel considers that the persistence of the pesticide in soil and water in the section on re-emission and the influence on the re-volatilisation should be addressed.	See response to Comment 28	None
31	The modelling efforts of the Meteorological Synthesizing Centre East of UN-ECE EMEP2 is omitted. This is nowadays one of the leading groups in modelling transport and deposition of persistent organic pollutants (POPs) for medium range and long range transport.	An inventory of models which are appropriate to simulate transport of organic substances in air was carried out by the Group. The EMEP MSC POP model from the Meteorological Synthesizing Centre East of EMEP did not pass screening phase because it was not available to users outside of EMEP MSC East and thus it was not possible to assess its suitability. Nevertheless the work of this group shows how transport models can be used to assess long-range transport, examples of this work can be found at http://www.msceast.org	None
32	The PPR Panel recommends that the section on transport should first define which scale has to be modelled and then what processes should be described for every scale. This will help to identify which models are appropriate. It is not necessary to describe all models that have ever been used. A more focused inventory of the families of models that calculate POPs and pesticides would have been sufficient.	The first screening criterion for the categorisation of the models was the scale at which the model operates. Therefore the inventory was divided in short-range and long-range transport models. It was further defined which processes are important to be modelled at each scale. The processes that should be described by the different types of models are given in the list of screening criteria in Section 4.5. Thus, it was for instance found that wet deposition is not an important process for deposition after short range transport since due to GAP it can be assumed that no precipitation occurs during and a few days (volatilisation relevant time) after application.	None

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33	<p>All processes that determine the levels of pesticides in air or deposition are discussed. However, only very limited information was given on the deposition processes (dry and wet). Approaches exist to estimate <i>a priori</i> the deposition velocities on the basis of physico-chemical properties. These considerations, relevant to the conclusions on whether deposition modelling is feasible, are missing from this chapter.</p>	<p>Deposition is the most complex process in the context of pesticide transport in air. Physico-chemical properties of substances are only one contributing factor. The atmospheric conditions and the surface where the substance is deposited also have a significant influence on this process. There exist completely different approaches to model dry and wet deposition. We agree with the panel that further work on the driving factors for dry and wet deposition should receive consideration.</p>	<p>Add recommendation in Chapter 9 for further work on the driving factors affecting dry and wet deposition.</p>
34	<p>In section 4.2.3 it should be mentioned somewhere that the volatilisation rate is a function of the wind speed/turbulence as well. Volatilisation models should have been included in this section.</p>	<p>In chapter 4.2.3 the processes implemented in existing models are described.. The general processes and factors influencing volatilisation are listed in Chapter 2: "Current level of knowledge about emission". In Section 2.3 (page 16) it is written that volatilisation of pesticides is amongst other factors dependent on wind and turbulence. In Section 2.4 (page 23) influencing factors for volatilisation from plants are mentioned, amongst them wind speed. The text could be changed in "Wind speed and turbulence are important ...". Volatilisation models (e.g. PEM) are listed under 4.7.1.</p>	<p>The text in Section 2.4 (page 23) changed to "Wind speed and turbulence are important ...".</p>

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35	<p>In Section 4.3.1 there seems to be a misunderstanding about models. The PPR Panel recommends the description of the models be corrected. A Lagrangian model is a model where the calculations are done while following the air parcel. An Eulerian model is a model that describes what is happening within a fixed (not moving) volume, where air is transported through. A Gaussian plume model is in fact a Lagrangian model. On page 83 it is said that deposition and transformation are taken into account roughly in Gaussian types of model. However, many models, for example OPS model of Van Jaarsveld, do this in a very detailed fashion.</p>	<p>The FOCUS air group is aware of the differences between Lagrangian and Eulerian type models. Whereas a Gaussian type model is in fact a Lagrangian model this statement is not reversible. But the FOCUS air group agrees with the PPR panel that there are Gaussian type models where deposition and transformation are described in great detail. The corresponding sentence in the report will be adjusted accordingly.</p>	<p>New text for page 82 after heading 4.3.1.1 Gaussian type models: Although the Gaussian type models are in fact Lagrangian models they are discussed separately due to the broad use of such models.</p> <p>In Equation 4.3-1 removal processes such as deposition and transformation are not taken into account. It is possible however to include these processes in the Gaussian model in a very detailed manner (e.g. Van Jaarsveld, 1995). The difficulty in the Gaussian plume concept is to derive correct ...</p>
36	<p>The PPR panel recommends that the Report should summarise the key properties of the useful models and provide further guidance for the practical use of these transport models. It should be included if these models have been validated for regularly measured air-pollution compounds.</p>	<p>The key properties of the models were identified during the screening phase. Use of the model with organic substances was a Step 1 screening criterion. Detailed consideration of the practical use of every model was beyond the scope of this group.</p>	<p>None</p>

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37	On page 116 the Report states that 'several of the multi-media models have been recommended for use in this Chapter'. The Report only mentioned what models passed the Step 1 evaluation, but not what models are left after further consideration. The PPR Panel recommends that the Report clarifies this aspect, and also how these multimedia models should be used in the assessment scheme.	A Step 2 evaluation of the multi-media models was carried out and listed in Appendix 6. In Section 4.9.2 it is stated that 6 multi-media models passed Step 2 screening criteria and are principally acceptable for modelling long-range transport. Amongst those models there are two evaluative models (Chemrange and Elpos). However, the possibility and limitations of the evaluative models have been clearly described in Section 4.7.3.2 and 4.7.3.3. A short note and a reference will be added to Section 4.7.3.	Change Section 4.7.3 accordingly
38	The PPR Panel recommends adding a bullet point on page 120 that 'emission is a factor not fully understood' (since this conclusion was reached on page 109).	We agree	Add extra bullet on p120
39	The PPR Panel does not agree with the conclusion on the validation status of LRT models given on page 121. Although more work could be done on validation, however, some experience with these models already exist. The difficulty certainly does not lie in the modelling of the air movements, but in the availability and reliability of data on use and emission, and even physicochemical properties, from which all models suffer. Moreover, the uncertainty in the	The group consider that LRT models have not be evaluated to a large degree and certainly hardly at all for pesticides (except lindane). Understanding of transport processes e.g. surface-air exchange and particle transport still needs to be improved. We agree however that the difficulty with these models does not lie with modelling air movements but with obtaining data on use and emissions.	Change Report to reflect that data on use and emissions are difficult to obtain

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	models should be seen in the light of the uncertainty in the total risk assessment.		
40	The EVA2.0-model is recommended in the Report for SRT and some features of the model are given. However, it is not possible to judge the merits of the model on the basis of the information in the Report. Furthermore, the model is not readily available from the cited website in the Report.	We believe that we have been clear regarding the merits of EVA2.0 i.e. That it is an empirical model, based upon experimental data (see Comment 41) and that it is proposed only as an interim solution until a better, experimentally-validated model becomes available (see comment 2). The website link will be updated	Following link to EVA 2.0 website added http://www.bvl.bund.de/chn_027/nn_496790/DE/04_Pflanzenschutzmittel/00_doks_downloads/zul_umwelt__eva20__prog-EN.html__nnn=true

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41	<p>1) Presentation of additional information is required in the Report on the following points: Calculation of the emission: No information is given in the Report on the way emission is calculated in the model. The Report briefly states that 5 vapour pressure classes are distinguished in EVA 1.1, but does not mention that this emission module is maintained in EVA 2.0. This should be described, together with the temporal dynamics depending on vapour pressure classes. From the data of Kördel et al. (1999) it is clear that the emission data consist of estimates for (half)-hourly intervals up to 24h. These estimates for three vapour pressure classes in turn are based on a very small dataset (2 substances, measurements up to only 6 hours). The estimates are stated to be in fair agreement to other data; but they are clearly not in agreement with the measured volatilisation of lindane from sugar beet crop that is reported also (Kördel et al., 1999).</p>	<p>It seems to be a misunderstanding with the EVA 1.1 and EVA 2.0 versions. These versions are completely different modelling approaches. EVA 1.1 was a processed based approach with the three basic processes: volatilization, transport with and diffusion in the air and finally deposition. However, its experimental validation in outdoor windtunnel trials failed. The predicted correlation between deposition after volatilization and windspeed as well as the influence of the temperature could not verified experimentally.</p> <p>As a consequence, a completely empirical version, EVA 2.0, was developed based on the measured deposition data of substances volatilized in an outdoor windtunnel. In EVA 2.0 merely the vapour pressure and the deposition after volatilization was correlated. As a confirmation of its conservatism, EVA 2.0 provides a higher prediction for deposited pesticides than measured in two available field volatilization trials. Lindane was used to define a worst-case deposition scenario since significantly higher lindane deposits were observed than expected from the series of vapour pressures of substances involved in the windtunnel trials.</p>	<p>Report has been changed for clarity. on p103 section 4.7.2.1 para starting in the absence. Change last sentence to: This approach forms the basis of a new model termed EVA2.0, which is an empirical model in which the individual processes of emission, transport and deposition are not described separately. As a consequence, a completely empirical version, EVA 2.0, was developed based on the measured deposition data of substances volatilized in an outdoor windtunnel. In EVA 2.0 only the vapour pressure and the deposition after volatilization was correlated. As a confirmation of its conservatism, EVA 2.0 provides a higher prediction for deposited pesticides than measured in two available field volatilization trials. Lindane was used to define a worst-case deposition scenario since significantly higher lindane deposits were observed than expected from the series of vapour pressures of substances involved in the windtunnel trials.</p>

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42	<ul style="list-style-type: none"> Volatilisation/deposition from plants compared to soil: On page 104, it is noted that "The EVA 2.0 model uses the assumption that deposition after volatilisation from soil is one third of the deposition after volatilisation from plants. The justification for this assumption comes from Kördel et al., (1999) who used the same value." This assumption is rather strong. However, the Report does not present the arguments that lead to this assumption. Also Kördel et al. (1999) only state that one can assume, based on the research of Walter et al. (1996), that this ratio is 3, without any further clarification. The PPR panel recommends that the data from the primary source be presented and discussed 	<p>We agree with the PPR panel that more information is needed. The original publication of Walter et al. (1996) reports the results of an inter-laboratory study on volatilization of pesticides from plants and soil involving 18 different laboratories and three radiolabelled substances. Although the emission ratio "plant-versus-soil" is not directly mentioned in the publication of Walter et al. the given 24h cumulative portions volatilized from plants (French beans) or from soil (mostly sandy soil, OC: 0.5-1.5%) can be derived from the individual results for each laboratory that participated. For two substances with a vapour pressure >10-4 Pa (20°C) the volatilization ratio was approximately 3 (2.9 +/- 0.8 with n = 11). Data from the third substance with a very low vapour pressure (2 x 10-6 Pa, 20°C) could not be used due to too low volatilization rates.</p>	<p>report changed to add clarity. p.104, 3rd paragraph: The EVA 2.0 model uses the assumption that deposition after volatilisation from soil is one third of deposition after volatilisation from plants. The justification for this assumption comes from Kördel et al. (1999) who derived this value from measured volatilization data of an inter-laboratory study with two substances and 11 different comparisons reported by Walter et al. (1996).</p>
43	<ul style="list-style-type: none"> Emission from orchards, vine and hops compared to field crops: On page 106, it is noted that: "deposition after volatilisation from orchards, vines and hops is twice that of field crops." Information explaining this statement is lacking. Few studies are available on volatilisation from these kinds of crops so it is difficult to evaluate the relevance of this statement. 	<p>We agree that this is an assumption made because no data were available and that this is a weakness of the model. The PPR are directed towards a publication by Fent (2007) which measures the deposition after volatilisation from vineyards.</p>	None

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44	<p>Deposition on water: on page 104 it is stated: "The deposition data in EVA 2.0 relate to the deposition onto water. These data can be used as a first rough approximation to estimate deposition onto soil." However, there are no data presented to underpin this hypothesis. The less soluble compounds can show higher deposition on grass than on water (e.g., a modelling study was performed with FIDES -Flux Interpretation by Dispersion and Exchange over Short-range- to calculate the concentrations and the deposition fluxes under field conditions and different scenarios with varying canopy resistances, and surface roughness) (Loubet <i>et al.</i>, 2006). So this assumption may lead to an underestimation of the deposition on ecosystems.</p>	<p>We agree that this is an assumption made in the absence of data. As data become available this assumption needs to be revisited. The Chapter on Further Work has been enhanced to take account of this comment - see response to Comment 25</p>	<p>Chapter 9 changed to reflect comments Change second paragraph on p132 to read "Nonetheless in the current absence of direct knowledge regarding deposition to terrestrial surfaces, EVA2.0 could also be used for this exposure route as an interim solution"</p>

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45	<p>Vapour pressure as the most important parameter influencing deposition: On page 104 it is stated: "The wind tunnel results (Fent 2004) and field experiments (Siebers <i>et al.</i>, 2003b; Gottesbüren <i>et al.</i>, 2003) show that vapour pressure is the most important parameter influencing deposition." The PPR Panel has noted that this dependence is only linked with the effect of Vp on volatilisation from plants and it is not obvious that Vp may be the major parameter having an effect on deposition. Also, already on page 52, the Report noted the work of Duyzer <i>et al.</i> (1997) on parameterisation of dry deposition velocity as a function of Henry's law constant and other phase coefficients. Moreover, Gottesbüren <i>et al.</i> (2003) studied only two pesticides (pendimethalin and lindane). Siebers <i>et al.</i> (2003b) studied the deposition of only 3 different pesticides (lindane, pirimicarb and parathion) with not very different vapour pressures (a factor of 10). So the two field experiments cannot be used to discuss the effect of vapour pressure on deposition (the authors themselves noted</p>	<p>We agree with the PPR panel that this statement needs to be clarified.</p>	<p>Change report to: In these experiments vapour pressure was found to be the most important parameter influencing environmental exposure via air.</p>

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	that further studies are required with other compounds with different vapour pressure).		
46	The PPR Panel is of the opinion that the risk assessment should not be based on fixed deposition rates depending on classes (be it vapour pressure or other properties).	The Group proposed the EVA 2.0 model as an interim solution for estimate environmental exposure; if other models and scenarios become available this framework may be changed (see comment number 2).	Report has been changed to reflect the recommendation that EVA 2.0 is proposed as an interim solution.
47	On page 103: it is stated that “the results of the wind-tunnel study were used to establish an empirical model that calculates realistic, worst-case deposition derived from the wind-tunnel data.” The PPR panel agrees to qualify EVA2.0 as an empirical model.		None required

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48	<ul style="list-style-type: none"> The conclusion given on page 106 "Although 15 experiments were carried out. to further verify the worst-case nature of the proposed exposure assessment" indicates that the FOCUS Air group is aware of the limitations of the EVA2.0 model. EVA2.0 model has one scenario implicitly present and it is not clear whether this built-in scenario of EVA2.0 is worst case for all applications in all circumstances in all EU-member states. With EVA2.0 it is not possible to investigate these variations in (worst case) scenarios. 	<p>We agree that there is only one scenario implicit within EVA 2.0 and it cannot be determined at the moment whether this model is worst-case in all scenarios in all Member States.</p>	<p>Text changed in Section 5.4.2 It should be noted that EVA 2.0 contains only one built-in scenario and it cannot be determined at the moment whether this model is worst-case in all scenarios in all EU Member States.</p>
49	<ul style="list-style-type: none"> The PPR Panel is not confident that EVA2.0 is conservative in the sense that it represents a realistic worst-case: <ul style="list-style-type: none"> the wind tunnel data are only a small set of events of what is possible in reality. It is not shown or proven that the wind tunnel experiments resemble the worst case or even a realistic worst case. The worst case in EVA2.0 has been chosen to be "the 90th percentile deposition for the substance having the highest deposition in each vapour pressure class" (page 104 in the 	<p>As mentioned in comment number 48 the workgroup is aware that EVA 2.0 does not cover every scenario of pesticide use occurring in agricultural practice. However, deposition expectations by EVA 2.0 are more conservative than measured in the windtunnel (with the limitation of volatilization from arable crops). The workgroup admits that the number of substance tested in each volatility class is limited, but larger data sets measured under reproducible conditions are not available. The workgroup is also aware that atmospheric stability and the variable size of a treated field are not taken in account. EVA 2.0 has been calibrated with a fixed 25m sprayed field under constant wind conditions, however windtunnel results are consistent with field trials using larger field</p>	None

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	<p>Report) but the number of pesticides tested in each class is limited, and the choice of 90th percentile is arbitrary.</p> <ul style="list-style-type: none"> o EVA2.0 does not take into account the size of the treated field, as an empirical relation derived from experiments carried out in wind tunnels are used. o The model does not take into account the effect of atmospheric stability and the diffusivity in air. 	<p>sizes (Gottesburen and Siebers).</p>	

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50	<p>To evaluate the worst case identified in EVA2.0, the PPR Panel has made indicative calculations to shed some light on EVA2.0 applicability (condition description and results are described in Appendix 1). Main conclusions are:</p> <ul style="list-style-type: none"> o deposition is a strong function of field size: The maximum dry deposition at 1 m downwind distance for an upwind field length of 300 m is about 33 times as much as that EVA2.0.1 gives for a 25 m field, in the case that volatilisation is 100%. In order to give the same maximum deposition as EVA2.0.1 the volatilisation should be $100/33 = 3\%$. It is certain that for many pesticides the volatilisation is larger than 3% and for that reason it can be concluded that EVA2.0.1 under predicts the maximum dry deposition that is possible. o the calculated maximum deposition at 1 m is also clearly lower (a factor of 14) in EVA2.0.1 than for a 25 meters field size in the case the volatilization is 100%. 	<p>EVA 2.0 is based upon the environmental exposure measured using the best data available to the workgroup including field data of greater size than windtunnels. We acknowledge that the conservatism of these estimates in the context of the EU is unknown. It is difficult to evaluate the theoretical calculations provided by the PPR panel. Models should be able to reproduce the data from the windtunnel and field studies if they are to be used for extrapolation.</p>	None

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51	The Report does not discuss the limitations of tunnel tests on the usefulness of their results for risk assessment or model validation. As a result, the extent to which the EVA2.0 model is suitable for its purpose remains unclear; also the purpose of wind tunnels for higher tier assessments is not clear.	We acknowledge that the wind-tunnel tests and consequently EVA 2.0 have uncertainties, however we believe these data are the best that are currently available and they are consistent with the (albeit limited) amount of field data available. The group would welcome the provision of further field data to improve the estimates of environmental exposure via air. The purpose of wind-tunnel data would be to generate experimental data on environmental exposure of a specific pesticide in the case that the first Tier modelling data showed unacceptable risk.	Add to Further Work Chapter to reflect that more experimental data on deposition are needed.
52	On the use of trigger values and the recommended model for short range exposure assessment the reader is referred to section 3.2 and 3.4.2. In view of the findings the PPR Panel does not support the approach taken in the Report that exposure via air should only be assessed in situations where spray drift mitigation measures are required.	We have addressed the comments in Sections 3.2 and 3.4.2 and believe that the original proposal for including deposition after volatilisation only when spray drift mitigation is required should still stand.	None
53	The PPR Panel recommends to include in Figure 5.4-3 and 5.4-4 a box for compounds with a $V_p > 10\text{-}2\text{ Pa}$. The Report states that the SRT assessment cannot be used for fumigants or pesticides with vapour pressures $> 10\text{-}2\text{ Pa}$. Fumigant losses due to volatilization are often $> 50\%$, and toxicity to	We agree	Change Figures 5.4-3 and 5.4-4 to include box for high VP compounds "Study to determine air concentration and deposition"

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	humans and wildlife are a serious concern for some products. How will risk from these chemicals be addressed in this assessment scheme?		
54	The PPR Panel recommends that the Report clarifies how the additional assessment of the impact of degradation on or penetration into leaf surfaces, for example using CONSENSUS-PEARL, connects to the EVA 2.0 input/output. The PPR Panel recommends including in Figure 5.4-3 and 5.4-4 a box for this refinement option	Degradation and leaf penetration can potentially be included at the modelling step (Tier 2), provided that experimental data are available.	None
55	The PPR Panel recommends that Section 5.5 is not presented as dealing with 'special cases'. Instead, the PPR Panel recommends that the assessment schemes clarify what types of pesticide application are to be covered under the Directive 91/414/EEC, which are addressed in the schemes, and which are not. Amongst others amenity use, wind erosion, and gassing of warehouses and commodities should be addressed In the Report.	refer to comment 21	None

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56	<p>The PPR Panel is of the opinion that the way LRT models are discussed is insufficient in view of the state of art of science and of the remit of FOCUS Air. The PPR Panel recommends a more thorough analysis of the uncertainty in the calculated exposure concentrations by the models, which could result in another conclusion.</p>	<p>The workgroup acknowledge that an analysis of uncertainty is important with respect to modelling. Given the validation status of LRT models as they relate to pesticides and in particular the difficulty of characterising emissions the workgroup deliberately decided to only evaluate the potential suitability of models to address the problem of LRT, without making specific recommendations on how this should be done or what uncertainties were involved in any potential estimates. In addition there is no regulatory statement of the regulatory protection aim with respect to LRT.</p>	None
57	<p>On page 116 the Report proposed that multi-media models should be used to rank substances and compare them to substances like lindane and PCBs. However, this proposal is not further mentioned nor considered for (long range) assessment. The PPR Panel recommends clarifying this recommendation in Chapter 6.</p>	<p>This is specifically mentioned in Section 6.1.2 and implicitly in the Conclusions to Chapter 6</p>	None
58	<p>The PPR Panel considers that the analysis that the DT50 trigger of 2 days is suitable to assess the need for exposure assessment of long range transport, is appropriate for practical reasons since it is also consistent with other assessment schemes (e.g. in UNECE (1998)). The PPR Panel notes that applying this</p>		No change required

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	trigger value does not guarantee that a substance with a shorter DT50 will not end up in media far (>1000 km) from the application.		
59	The PPR Panel is concerned whether the Guidance provided is useful for risk assessment. Indeed the chapter addresses a lot of items of which it is not always clear what is meant and what could be done in a risk assessment concerning long range transport.	The Workgroup stated clearly and repeatedly throughout Chapter 6 and in the Conclusions to the Report that since there is no definition of protection goals for LRT it was beyond the remit of the group to give definitive guidance on how to perform risk assessment for substances exceeding the LRT trigger. Instead the workgroup aimed to give general guidance what approaches could be used and how they might be evaluated. Specific, detailed recommendations were not possible.	None
60	the idea of assessing substances that fit certain criteria for entering an exposure assessment based on 1) their evaporation potential, 2) the transport and deposition behaviour and 3) the potential impact is good. However, it is not elaborated further. This conclusion should be clarified.	See response to comment 59	None
61	<ul style="list-style-type: none"> the issue of persistence in media (e.g. soil, water) is not addressed. 	Persistence is specifically mentioned in Sections 6.2.4 and in the Conclusions to the Chapter	None
62	<ul style="list-style-type: none"> For an appropriate interpretation of measurements of long range transport spatially and temporally distributed 	At present these data are lacking at an EU level.	None

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	emission inventories for each pesticide are needed.		
63	<ul style="list-style-type: none"> to state that the in-field and edge-field scale scenarios of the guidance documents for supporting the assessments under Directive 91/414/EEC could be used, is not sufficient. The crux is essentially in the safety factors that would have to be included. This is not elaborated at all in the Report 	The potential need for safety factors was discussed in Section 6.2.4. The group have been extremely clear that the establishment of exposure scenarios, safety factors and risk assessment procedures were specifically beyond its remit	None
64	the conclusion on models is meagre compared to the conclusions of the Health Council Report. In the last years a lot of effort has been put into modelling. A further consideration of the possibilities and uncertainties in the models could lead to a more positive conclusion.	The option to use modelling to address LRT concerns is still possible. The absence of an appropriate regulatory protection aim is a significant limitation to understanding the uses to which models can be used.	None
65	The conclusion on page 163 of the Report should be backed up with an analysis of pesticide properties.	These should be Henry's law constant, vapour pressure and K_{ow} where available	Add an extra bullet point to the list on p163: The most relevant physical properties of pesticides to consider are: Henry's law constant, vapour pressure and K_{ow} .
66	<ul style="list-style-type: none"> The Chapter should give clear guidance on how and when potential hazardous properties of a pesticide to the atmospheric environment should be assessed. 	The group concluded that pesticides are likely to have a negligible effect upon the atmosphere, and therefore decided not to establish guidelines in this respect.	None

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67	<ul style="list-style-type: none"> • Pesticides sold as liquid formulations and fumigants often contain volatile and reactive co-formulants and active ingredients which may contribute to groundlevel ozone formation in the presence of NOx. The issues of co-formulant emissions and reactivity should be addressed especially in regions with reduced air quality. 	not relevant under 91/414	None
68	<ul style="list-style-type: none"> • The PPR Panel suggests clarifying whether the Global Warming Potential is determined relative to CFC-11 or relative to CO₂ 	Global warming potential should be measured relative to CO ₂	Add sentence to first bullet on p163 starting Global warming potential. Global warming potential should be measured relative to CO ₂