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Pesticides in air and in precipitation and effects on plant communities

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Preface

The admission of pesticides on plants, water and soil surfaces may come from either direct application or unintentionally through spillage, run off and dry or wet deposition. Increasing efforts has been made to protect against the unintended pollution of the aquatic and terrestrial environments. The present project was started in 1996 as a co-ordinated research initiative to elucidate pesticide distribution via the atmosphere and consequences to plant life.

To cover this broad range of information, the project consisted of four parts to cover both emissions to the atmosphere, modelling of spreading in the atmosphere, deposition in precipitation and effects on plants. The participating institutes were The Danish Technological Institute (Laboratory system to determine pesticide volatility), National Environmental Research Institute (Modelling of atmospheric transport and deposition) and Danish Institute of Agricultural Sciences (Analysis of pesticides in precipitation and Effects of herbicides in precipitation on plants). The project was supported by The National Environmental Protection Agency (Miljøstyrelsen).

Besides the expected finding of pesticides in use in Denmark in the precipitation, an unexpected experience from the project was the finding of high concentrations of the herbicide DNOC in precipitation. This compound has not been used in Denmark since the end of the eighties. DNOC appeared in rainwater all over the sampling period, and it was concluded, that DNOC hardly came from pesticide use, but was due to photochemical reactions with toluene and nitrogen oxides in the atmosphere. The concentrations of DNOC were much higher than for the other pesticides and probably also a number of other chemicals are deposited on plants from the atmosphere.

Information gathered in such broad co-operative projects are of great importance for the elucidation of the spreading of pesticides and to calculate the load of pesticides on agricultural and non-agricultural areas. Further these values are important for the evaluation of pesticides in relation to their registration.

The current interest of the project was shown by an inquiry from members of parliament about spreading of pesticides to Denmark from other European countries and by the need for a technical report on causes of DNOC-pollution in the atmosphere.

A management group for the project was established with participants from University of Odense (Christian Lohse) and The National Environmental Protection Agency (Inge Vibeke Hansen). Chairman of the Management group was Erik Kirknel (DIAS), who also took the initiative to the project. The management of the project was taken over by Arne Helweg in 1998.

A laboratory model system for determining the volatility of pesticides

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Executive summary

In the present study the volatilisation potential of pesticides is discussed and illustrated based on both physical/chemical properties of the pesticides and on experimental volatilisation experiments. A laboratory model system for the direct determination of the volatilisation of pesticides from different surfaces has been developed. In this system it is possible to evaluate volatilisation of pesticides relative to each other. Experiments have been carried out with mecoprop-P (MCPP-P), mecoprop methylester (MCPP methyl), and lindane as test substances. The volatilisation of these pesticides has been tested in different volatilisation chambers, at different temperatures, airflows and from different surfaces. Furthermore, recommendations of important aspects that should be included in the development of a new guideline on assessing pesticide volatilisation are described. The main conclusions regarding the experimental set-up are drawn taking practical aspects of testing and the demand for simple cost-effective tests into account.

At the beginning of the experiments, MCPP-P and lindane were applied on a filter-paper corresponding to an application rate of 1.5; 15; 75, and 150 kg ai ha-1 for MCPP-P and 1; 10; 50; and 100 kg ai ha-1 for lindane; corresponding to the recommended application rate; 10×; 50×; and 100× the recommended application rate. During the experimental duration of 24 hours only insignificant volatilisation of MCPP-P was measured (less than 1%) while the volatilisation of lindane varied from 3.6 to 75.6 % of the applied dose depending of the concentrations. However, the actual amount of volatilised lindane was relatively constant at concentrations above 10× the recommended doses. The results indicate that MCPP-P does not appreciably volatilise from an artificial surface whereas lindane volatilises. In contrast to MCPP-P, a great deal of the applied MCPP methyl volatilised under the present test conditions. Thus, when MCPP methyl was applied at a rate equivalent to the recommended application rate, about 90% of the applied dose were volatilised during a 24 hours period. Furthermore, the results revealed comparable volatilisation of the test substances when the experiments were carried out in different volatilisation chambers with varying design.

Interpreting the volatilisation as a function of time from various volatilisation experiments with pesticides, it seems that the air sampling 1, 3, 6, and 24 hours after application asked for in the German guideline are reasonable. Normally, high volatilisation rates are seen within the first few hours after application, and the 24 hours values after application are measured at a time when the volatilisation process has decreased considerably.

To test the influence of the temperature on the volatilisation of the two pesticides lindane and MCPP methyl were applied to filter paper at the recommended dose and the volatilisation was tested at 15oC and 23oC under otherwise identical conditions. The volatilisation of lindane increased significantly with temperature (from about 46% to 80% of the applied dose) whereas only a slight increase was noted for MCPP methyl (from 90% at 15oC to 96% of the applied dose at 23oC).

At the recommended application rate, about 80% of the applied lindane volatilised, while at 10× the recommended dose only about 20% of the applied amount volatilised corresponding to the actual amount of lindane volatilising increased with a factor of 2.4. When the amount of MCPP methyl was increased with a factor of 10, the amount of MCPP methyl volatilising increased with a factor of 8.9 illustrating the higher volatilisation potential of this compound.

Volatilisation of lindane and MCPP methyl was also tested at two different airflows. The two airflows were 0.17 and 0.67 m per sec and the application rate corresponded to the recommended application rate and 10 × this dose. The results revealed that an increase of the airflow by a factor of 4 does not significantly increase the amount of volatilisation of the two pesticides.

MCPP methyl and lindane were applied as active ingredients to the surface of two artificial surfaces, filter paper representing an absorbent surface and a bowl of stainless steel illustrating a non-absorbent surface. Volatilisation of the two pesticides after 24 hours were comparable when applied to the two selected surfaces. However, it seems that the volatilisation of MCPP methyl was faster at the non-absorbent surface, while the rate of volatilisation of lindane was comparable when applied at the two different surfaces. In contrast to the artificial surfaces only a small fraction (about 15% of the applied dose) of the pesticides volatilised when applied to a typical Danish soil.

Dansk sammendrag

I denne undersøgelse diskuteres fordampningspotentialet af pesticider ud fra pesticidernes iboende fysisk/kemiske egenskaber samt ud fra eksperimentelle fordampningsforsøg. Der er udviklet en eksperimentel forsøgsopstilling, hvor det er muligt at måle fordampningen af pesticider fra forskellige overflader. I denne forsøgsopstilling er det muligt at sammenligne fordampningspotentialet af forskellige pesticider. De eksperimentelle undersøgelser er blevet udført med mecoprop-P (MCPP-P), mecoprop methylester (MCPP methyl) og lindan, og fordampningen af disse pesticider er blevet undersøgt i forskellige fordampningskamre, ved forskellige temperatur, luftflow og fra forskellige overflader. Baseret på erfaringerne fra disse og andres undersøgelser er der udarbejdet forslag til, hvilke elementer der skal inddraget i forbindelse med udarbejdelsen af en ny guideline til vurdering af pesticiders fordampning.

Ved starten af forsøgsrækken blev MCPP-P tilført filtrerpapir i følgende koncentrationer 1,5; 15; 75 og 150 kg ai per ha. og lindan i 1, 10, 50, og 100 kg ai per ha, svarende til den anbefalede dosering samt 10×, 50×, og 100× den anbefalede dosering. Gennem forsøgsperioden på 24 timer blev der kun registreret en ubetydeligt fordampning af MCPP-P (mindre end 1% af den tilførte mængde), mens fordampningen af lindan varierede fra 3,6 til 75,6% af den tilførte mængde (den totale mængde af lindan, der fordampede, var dog relativt konstant ved koncentrationerne over 10× den anbefalede dosis). Disse resultater viser, at MCPP-P ikke forventes at fordampe fra sprøjtede overflader, mens lindan forventes at fordampe i store mængder. I modsætning til MCPP-P blev der iagttaget en meget stor fordampning af MCPP metyl. Således fordamper 90% af den tilførte mængde indenfor 24 timer, når MCPP metyl tilføres i en koncentration svarende til den anbefalede mængde. Der blev iagttaget samstemmende resultater i forsøg udført i forsøgskamre med varierende design.

Ved at gennemgå kinetikken hvormed forskellige pesticider fordamper gennem forsøgsperioden, virker prøveudtagningsintervallerne på 1, 3, 6 og 24 timer, som angives i den tyske guideline, rimelige. Normalt ses der en høj fordampning de første timer efter stoftilførslen, og efter 24 timer er fordampningen aftaget markant.

For at undersøge temperaturens indflydelse på fordampningen blev der udført forsøg med MCPP methyl og lindan ved både 15^{o}C og 23^{o}C. Ved disse forsøg blev der iagttaget en markant forøget fordampning af lindan (fra ca. 46% ved 15oC til ca. 80% af den tilførte mængde ved 23^{o}C), mens der kun blev iagttaget en mindre stigning i fordampningen for MCPP methyl (fra 90% ved 15^{o}C til ca. 96% ved 23^{o}C).

Ved den anbefalede dosering fordampede ca. 80% af den tilførte mængde efter 24 timer, mens der ved en stoftilførsel på 10× den anbefalede dosering kun blev iagttaget en fordampning på ca. 20% af den tilførte mængde svarende til, at den absolutte mængde af lindan, der fordampede, blev forøget med en faktor på 2,4. Når den tilførte mængde af MCPP methyl blev forøget med en faktor 10, blev den absolutte mængde MCPP methyl, der fordampede, forøget med en faktor 8,9 hvilket illustrerer, at dette stof fordamper lettere.

Fordampningen af lindan og MCPP methyl blev undersøgt ved to forskellige luftgennemstrømninger (ved en lufthastighed på henholdsvis 0,17 og 0,67 meter pr. sekund). Resultaterne viste, at en forøgelse af hastigheden på luftgennemstrømningen med en faktor 4 ikke forøgede den mængde af pesticid, der fordampede.

MCPP methyl og lindan blev tilført til to forskellige kunstige overflader, filtrerpapir, der illustrerer en absorberende overflade, og en metalbakke, som illustrerer en ikke absorberende overflade. Fordampningen af de to pesticider fra de to forskellige overflader var sammenlignelige efter 24 timer, men der blev iagttaget en hurtigere fordampning af MCPP methyl fra den ikke absorberende overflade. Ved tilførsel af lindan og MCPP methyl til en typisk dansk jordtype fordamper der til forskel fra de kunstige overflader kun en lille andel (ca. 15%) af den tilførte pesticidmængde.

1 Introduction

Since the late 1960s, losses of pesticides by volatilisation and subsequent atmospheric transport have been increasingly recognised as a process, sometimes of major importance, in the loss of pesticides from the areas where they are applied (a process limiting their effectiveness), and as a pathway for general environmental contamination (extensive lists of literature are provided in Nolting. *et al.* 1988; Gottschild, *et al.* 1995; Jansma and Linders 1995; Spencer *et al.* 1973; Hartley, 1969; Plimmer 1976; Willis et al. 1983). Therefore, volatilisation is assumed to be the reason why some pesticides are widely distributed, contributing to pollution of air, rain, soil, surface, and seawater. Recently, rather high concentrations of pesticides in rainwater have been determined (Buser, 1990; Gath *et al.* 1992; Gath *et al.* 1993; Siebers *et al.* 1994; Glotfelty *et al.* 1990; Schomburg *et al.* 1991; Nations and Hallberg 1992; Scharf and Bächmann 1993, Felding *et al.* 1999).

Volatilisation rates from plant or moist soil surfaces can be very large for more volatile compounds, with losses approaching 90% within a few days (Taylor, 1978; Jansma and Linders, 1995). Although pesticides range in volatility from fumigants, such as gaseous methyl bromide, to herbicides, with vapour pressures below 10^{-6} Pa, the same physical/chemical principles are assumed to govern their rates of volatilisation. However, even though factors, influencing volatilisation in principle, have been clarified and understood for a long time (Spencer *et al.* 1973; Hartley, 1969; Plimmer, 1976), many problems concerning volatilisation still remain unsolved.

Since volatilisation is an important factor in the fate of pesticides in the environment, it is necessary to have an experimental design to measure this process. In 1990 a German Guideline on assessing pesticide volatilisation was developed. This BBA guideline (Nolting *et al.* 1990) was prompted not only by the legal demands for protecting the air, but also by increasing public concern for pesticide residues found in precipitation and ground water. It was decided to start with a "liberal" guideline with only a few specific demands, which then later on could be refined, based on the results obtained. Since then a number of methods have been developed, ranging from very simple to high-tech designs.

The volatilisation rate is not only determined by the properties of the compound, the application rate, and the crop, but also by other factors like meteorological and soil conditions. As these other factors are highly variable field experiments for the same compound, application rate and crop can show highly variable results. This makes it difficult to determine whether the volatilisation rate of a particular compound is comparable with other compounds. Moreover, field experiments are rather expensive. For that reason it would be preferable if laboratory experiments could be undertaken that could complement field experiments and could indicate the volatilisation potential of different compounds relative to each other.

For this reason a simple laboratory model system has been designed for the present study, in which a wide range of outdoor conditions can be simulated. The finalised method has then been used to measure the volatility of selected pesticides from different surfaces and under different "climatic" conditions such as temperature, wind speed etc.

2 Materials and methods

2.1 Test system

A simple laboratory model system for the direct determination of the volatilisation of pesticides has been developed for this study. The system permits a direct determination of the volatilisation of a compound from a surface. Moreover, it gives the possibility to check the mass balance at the end of the study. Furthermore, the system permits determination of the volatilisation potential of different compound added on varying surfaces, at different airflows, temperatures etc.

2.1.1 **Volatilisation chamber**

Two chambers of different sizes have been used in the present study. Both chambers were made of stainless steel, and each chamber was made up of 3 parts:

The wind tunnel (1) in which a rectangular bowl of stainless steel (2) containing the test sample can be placed. By the open side (3), opposite to the air outlet, the bowl can be introduced and removed for changing of the test substrate. The open side also permits the cleaning of the chamber inner walls.

The test sample is placed in the rectangular metal bowl that is introduced into the volatilisation chamber immediately after application of the pesticides to the surface. After the bowl has been placed in the “wind tunnel”, the open side of the chamber is closed with a plate of stainless steel in which the air inlet is placed. The air inlet is connected to an ORBO-42 (large) adsorption tube to remove potential contamination of pesticides from the inlet air.

The volatilised pesticides are collected on three ORBO-42 (large) adsorption tubes connected in series to the outlet of the chamber. A given air flow in the “wind tunnel” is ensured by a constant flow pump, SKC model 224-17SD connected at the end of each series of adsorption tubes. Each series of adsorption tubes can be replaced at different sampling intervals during an experiment.

2.1.2 **System set-up**

Test compounds

The volatilisation of mecoprop –P (MCPP-P), mecoprop methylester (MCPP methyl) and lindane have been tested in this study. A range finding test has been carried out with concentrations corresponding to the recommended dose, 10×, 50×, and 100× the dose to determine which dose would be useful to apply in the final test. In the final test the pesticides were applied at an application rate equivalent to 1 and 10 kg ai ha^{-1} for lindane and 1.5 and 15 kg ai ha^{-1} for MCPP methyl corresponding to the recommended and 10× the recommended dose.

Size of the chambers

Initially the experiments were performed in two volatilisation chambers of different sizes in order to test the influence of the size of the test chamber on the volatilisation of the pesticides.
One set of experiments was carried out in a ”short” volatilisation chamber in which the ”wind tunnel” was 12 cm long, 3.5 cm wide and 1.7 cm high. Another set of experiments was carried out in a ”longer and lower” chamber in which the ”wind

tunnel” was 23 cm long, 3.6 cm wide and 1.0 cm high. The metal bowl in the ”short” chamber had the following inner dimensions: 11.1 cm long, 2.25 cm wide and a depth of 0.3 cm. The dimension of the bowl in the ”longer chamber” was 22.9 cm long, 2.4 cm wide and 0.3 cm deep.

Temperatures and air humidity

The volatilisation of the pesticides were tested at two different temperatures. Normally the experiments were carried out in a climatic room at a temperature of 23C° +/- 0.5° C and an air humidity of 50%. The volatilisation was also tested at 15°C +/- 0.5° C and in these cases the volatilisation chamber was placed in an incubator and the air was passed through an air glass bubbler containing a calcium chloride solution. The air arrived in the volatilisation chamber at about 50% relative humidity.

Air temperature and moisture were monitored during the study period using a Testo 600, Testoterm.

Airflow

Different airflows in the “wind tunnel” can be created by opening different numbers of air outlet from the volatilisation chamber which each was connected to a set of adsorption tubes and an air pump. This was done to ensure the recommended flow rate through the ORBO tubes. In the present study, an airflow rate of 0.08 m/sec and 0.31 m/sec was tested in the “short chamber”. In the “longer and lower chamber”, an airflow rate of 0.17 m/sec and 0.67 m/sec was tested.

The airflow was measured using a Termo-Anemometer, Alnor GGA-65P.

Application on different surfaces

The pesticides were applied to three different surfaces:

- Filter paper (Whatman 1) illustrating an artificial absorbent surface.
- Directly to the bowl of stainless steel illustrating a non-absorbent surface.
- A coarse sandy soil from the Danish National Agricultural Research station at Jyndevad, typical Danish soil. The relevant soil characteristics are described in table 2.1. The test was carried out using 8.5 g sieved soil less than or equal to 2 mm which has been stored air-dried and re-equilibrated with deionised water just before the experiment to give an overall moisture content of about 35 per cent of the dry weight.

Table 2.1
Soil characteristics for the Jyndevad soil.

Jordkarakteristika for Jyndevadjorden.

Clay	3.9 %
Silt	4.1%
Sand	89.0%
Humus	3.0%
Soil water capacity (a)	34.0%
PH	6.5

2.2 Performance of the test

2.2.1 **Chemicals and standards**

All solvents used were of analytical grade. MCPP-P, MCPP methyl and lindane were obtained from Dr. Ehrenstorfer GmbH, Germany. Hexachlorbenzene-$^{13}C_6$ and dichlorprop-$^{13}C_6$ were obtained from Cambridge Isotope laboratories, Woburn, MA, USA. Standards were prepared using standard volumetric techniques.

2.2.2 **Preparation and spiking of the samples**

The test surface was placed in the rectangular metal bowl and spiked with the analytes dissolved in acetone. After evaporation of acetone at room temperature the metal bowl was placed in the volatilisation chamber. The application time was less than 3 minutes. For tests with filter paper the analytes were dissolved in 250 and 500 µl acetone for the “short” and “longer” chamber, respectively, and added by several applications by a Hammilton syringe. For tests in which the pesticides were applied directly to the metal bowl or to soil the analytes were dissolved in 3 ml acetone and applied to the metal bowl or to the soil by several applications.

Pre-test experiments

To investigate whether some part of the pesticides applied to the test surface would evaporate together with the acetone during application before the test sample was placed in the volatilisation chamber, spiked samples were placed at room temperature for 30 minutes after which they were analysed. To test the recovery from the adsorption tubes, the analytes were dissolved in 200 µl acetone and added to the ORBO-42 (large) adsorption tubes after which the tubes were connected to an air pump. Airflow of 2 l/h was maintained during 24 hours. After this period, the absorption tubes were analysed.

2.2.3 **Sample preparation**

Sampling and samples treatment

When several samplings were taking during an experiment the adsorption tubes were immediately replaced with a new trap set-up. At the end of the experiments each set of adsorption tubes was removed from the chamber and each of the three tubes in a set was analysed, separately.

At the end of an experiment the volatilisation chamber and the bowl including the test surface applied with the pesticides were extracted with 200.0 ml methylene chloride in a Pyrex bottle by shaking for 30 minutes. 2.0 ml of the extract was diluted and spiked with internal standard(s).

The adsorption tubes were extracted with 5.0 ml methylene chloride by shaking for 5 minutes. 2.0 ml of the extract was diluted and spiked with internal standard(s).

The sample extracts to be analysed for MCPP-P and lindane were spiked with 20 µl HCB-$^{13}C_6$ (500 ng/µl) and 20 µl dichlorprop-$^{13}C_6$ (500 ng/µl) as internal standards. MCPP-P and dichlorprop-$^{13}C_6$ were methylated with diazomethan before analysing.

The sample extracts to be analysed for MCPP methyl and lindane were spiked with 20 µl HCB-$^{13}C_6$ (500 ng/µl) as internal standard.

The extracts were analysed by GC-MS-SIM.

2.2.4 GC-MS-SIM analysis

The extracts were analysed by GC-MS-SIM in the electron impact mode (EI, 70 eV).

Ions for qualification and quantification were selected on the basis of the mass spectra of the components. The ions 219 and 221 amu were selected for lindane, 169, 228 and 230 amu for MCCP methyl, 168 and 254 amu for dichlorprop-$^{13}C_6$ and 290 and 292 for HCB-$^{13}C_6$. The quantification was done on the basis of the area ratio analyte/internal standard for the selected ions.

The mass scale was calibrated using PFTBA as a calibration gas.

The calibration curves were established on solutions in methylene chloride of the analytes. This was done on the basis of experiments showing that the extraction efficiency of the analytes from the filter paper was 92-96 % and from the adsorption tubes 87-93 %.

Injection technique: on-column injection (35°C). Precolumn: 1 meter 0.25 mm id, 0.25 µm RTX-5. Column: WCOT fused silica 50m × 0.25 mm id, 0.4 µm CP Sil 13CB. Temperature programming: 35°C (0.5 min)-280°C, 30°C/min. Carrier gas: Helium (25 psi). GC-MS: HP5971.

3 Results

The test design includes two independent tests (on different days). Thus, all data represent the mean of two experiments. All experiments were carried out at 23°C unless something else has been stated. The detection limit for all analytes was 0.05 μg.

3.1 Pre-test of the experimental set-up

To investigate whether some of the pesticides applied to the test surface would evaporate together with the acetone during application before the test sample was placed in the volatilisation chamber, spiked samples were placed at room temperature for 30 minutes after which they were analysed. The analyses showed that the pesticides did not evaporate together with the acetone and a recovery of more than 90% was found in these experiments.

The extraction efficiency from the adsorption tubes was tested and the results revealed that the recovery was more than 95%.

3.2 Results of the experiments in a short volatilisationchamber after 24 hours

3.2.1 Volatilisation of MCPP-P applied to filter paper at different concentrations

The volatilisation of MCPP-P applied to filter paper was tested at different concentrations: 0.015, 0.15, 0.75, and 1.5 mg MCPP-P/cm^2, corresponding to the recommended doses, 10×, 50×, and 100× the recommended dose. The results revealed that less than 0.06% of the applied pesticide volatised after 24 hours in the volatilisation chamber with airflow of 0.08 m/sec. At the end of the experiment between 89 and 110% of the applied pesticide could be extracted from the filter paper and the volatilisation chamber.

3.2.2 Volatilisation of lindane applied to filter paper at different concentrations

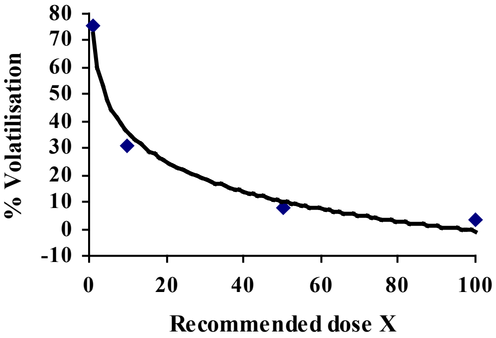
When lindane was applied to a filter paper at concentrations of 0.01, 0.1, 0.5, and 1.0 mg/cm^2 corresponding to the recommended application rate, 10×, 50×, and 100× the recommended dose a significant amount of the added pesticides volatised. The airflow was 0.08 m/sec. The results are depicted in table 3.1.

Table 3.1
Volatilisation of lindane after a 24 hours period. S.D. less than 10%.

Fordampningen af lindan efter en periode på 24 timer. S.D. mindre end 10%

Applied concentration of lindane	**Volatilisation of lindane (% of applied dose)**	**Extraction from paper and chamber (in %)**	**Total recovery (% of applied dose)**
Recommended dose	75.6	24.0	99.6
10× recomm. dose	31.2	60.0	91.2
50× recomm. dose	8.1	80.8	88.9
100× recomm. dose	3.6	86.8	90.4

Figure 3.1



The volatilisation of lindane relative to the applied amount (R^2 = 0.98).

Fordampning af lindan relativt i forhold til tilført mængde (R^2 = 0,98).

The volatilisation of lindane under the present experimental conditions corresponds to 7.6, 31.2, 40.5 and 36 µg lindane/cm² for the recommended doses, 10×, 50× and 100× the recommended doses, respectively. Thus, the results revealed that a comparable amount of lindane is volatised in concentrations corresponding to 10× 50× and 100× the recommended doses. It was therefore decided to investigate the volatilisation of the pesticides at the recommended dose and 10× the concentration in the further experiments.

3.2.3 Volatilisation of MCPP methyl and lindane applied to different artificial surfaces and at different airflows

Volatilisation of MCPP methyl from a non-absorbent surface

Since no volatilisation could be demonstrated in the MCPP-P experiments it was decided to start experiments with MCPP methyl. The results from these experiments revealed that a great deal of the applied MCPP methyl volatilised under the present test conditions. Application of MCPP methyl at a concentration corresponding to 10× the recommended dose to a non-absorbent metal surface resulted in a volatilisation of the pesticide corresponding to 85.5% of the applied amount after 24 hours (air flow 0.08 m/sec). Extraction of pesticides from the metal surface and the chamber revealed 4.8 % of the applied dose resulting in a recovery of 90.3%.

Volatilisation of lindane from a non-absorbent surface

The volatilisation of lindane from a non-absorbent metal surface was tested with airflow of 0.08 m/sec and at a pesticide concentration corresponding to 10× the recommended application. The results revealed that after 24 hours 30% of the applied dose was volatilised while 61% could be extracted from the metal surface and the chamber. This gave a recovery of 91%.

Volatilisation of lindane and MCPP methyl with an increased airflow

The volatilisation of lindane and MCPP methyl applied to filter paper at a concentration corresponding to 10× the recommended dose was tested in the volatilisation chamber with an increased airflow (0.31 m/sec). The results revealed that after 24 hours 34.1% of the applied lindane were volatilised and 64% could be extracted from the paper and chamber giving a recovery of 98%. For MCPP methyl 95,8% of the applied dose was volatilised and 0.3% was found on the filter paper and in the chamber a recovery was 96%.

3.3 Results of volatilisation of lindane and MCPP methyl in a “longer and lower” volatilisation chamber

3.3.1 Volatilisation of lindane and MCPP methyl applied at recommended dose during an experimental test of 30 hours

Figure 3.2 illustrates the accumulated volatilisation of lindane and MCPP methyl from filter paper during a 30 hours period at a temperature of 23°C and an air humidity of 50%. The application rate was 0.01 mg/cm^2 for lindane and 0.015 mg/cm^2 for MCPP methyl, corresponding to the recommended application rate. The airflow in the chamber was 0.17 m/s. About 10% and 30% of the applied dose had volatilised during the first hour after application of lindane and MCPP methyl, respectively. After 8 hours about 50% of the applied dose of lindane was volatilised corresponding to 2/3 of the total amount which volatised during a 30 hours period. For MCPP methyl about 80% of the applied pesticide was volatised after 8 hours, corresponding to about 9/10 of the total amount during a 30 hours test. At the end of the experiment 14.5% and 4.1% of the applied pesticides could be extracted from the filter paper and the chamber for lindane and for MCPP methyl, respectively. Thus, the recovery in these experiments was 90% for both pesticides.

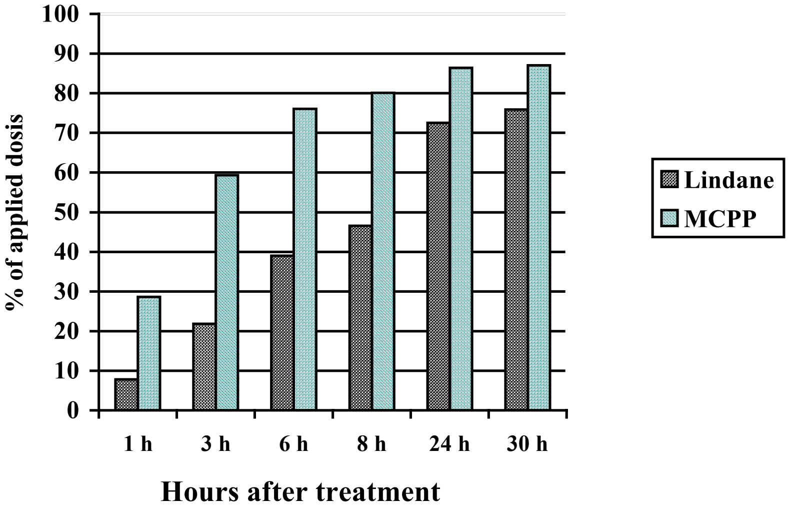


Figure 3.2
The figure illustrates the accumulated volatilisation of lindane and MCPP methyl from filter paper during a 30 hours period. The application rate was 0.01 mg/cm^2 for lindane and 0.015 mg/cm^2 for MCPP methyl. The airflow in the chamber was 0.17 m/s. All data represent the mean of at least two experiments (S.D. less than 5%).

Figuren illustrerer den akkumulerede mængde af fordampet lindan og MCPP methyl fra filterpapir over en periode på 30 timer. Stofferne blev tilført i en koncentration svarende til 0,01 mg/cm^2 for lindan og 0,015 mg/cm^2 for MCPP methyl. Luftgennemstrømningen i kammeret var 0,17 m/s. Alle data er middeltallet af mindst to forsøg (S.D. er mindre end 5%).

In table 3.2 the volatilisation is expressed as the amount of pesticide volatili-sed per hour during the experiment. The results revealed that the rate of volatilisation was significantly higher for MCPP methyl compared with the rate found for lindane during the first 6 hours after application. For MCPP methyl a very high but rapid decreasing volatilisation was seen during the first 8 hours. For lindane the rate of volatilisation was much lower, even though the same pattern was seen, in which a higher rate of volatilisation occurred during the first 8 hours after application. However in this case, the rate of decrease in the volatilisation was slower than the rate found for MCPP methyl and after 8 hours the rate of volatilisation of lindane was higher than the one found for MCPP methyl.

Table 3.2
Volatilisation of lindane and MCPP methyl per hour during a 30 hours period (S.D. less than 10%).

Fordampning af lindan og MCPP methyl udtrykt pr. time i en periode på 30 timer (S.D. er mindre end 10%).

Hours after treatment	Volatilisation of lindane per hour (% of applied dose)	Volatilisation of MCPP methyl per hour (% of applied dose)
0-1	7.8	28.6
1-3	7.0	15.4
3-6	5.7	5.6
6-8	3.8	2.0
8-24	1.6	0.4
24-30	0.6	0.1

3.3.2 **Volatilisation of lindane and MCPP methyl at different temperatures**

In order to test the influence of the temperature on the volatilisation of the two pesticides lindane and MCPP methyl were applied to filter paper at the recommended dose and the volatilisation was tested at 15°C and 23°C under otherwise identical test conditions.

As shown in figure 3.3, the volatilisation of lindane decreased significantly when the temperature was decreased from 23°C to 15°C. Each column illustrates the total amount of pesticide analysed after the test period. The lowest dark part of each column illustrates the amount of pesticide extracted from the filter paper and the volatilisation chamber, and the upper light part illustrates the amount of pesticides volatilised. The application rate was 0.01 mg/cm^2 for lindane and 0.015 mg/cm^2 for MCPP methyl. The airflow in the chamber was 0.17 m per sec. Thus, at 23°C about 80% of the applied lindane was volatised after 24 hours whereas only 46% was volatised at 15°C. In contrast the amount of MCCP, that volatised during a 24 hours period, only decreased from 96% at 23°C to 90% of the applied dose at 15°C.

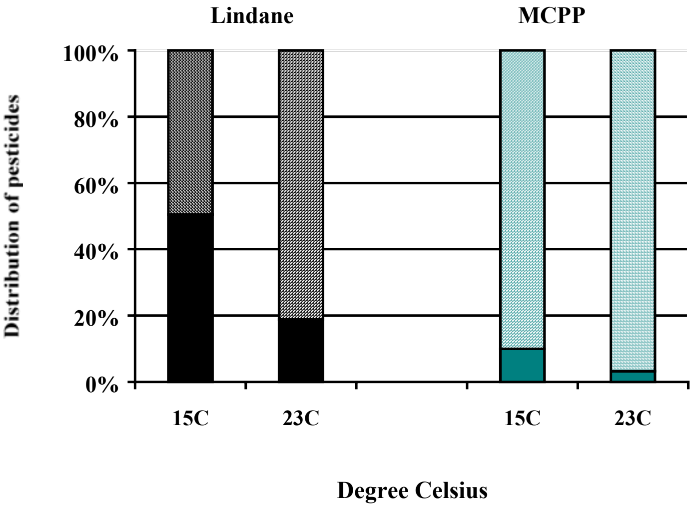


Figure 3.3
The figure illustrates the volatilisation and total recovery (whole column) of lindane and MCPP methyl at 15°C and 23 °C from filter paper after a 24 hours period. Each column illustrates the total amount of pesticide analysed after the test period (total recovery). The upper light part illustrates the amount of pesticides volatilised. All data represent the mean of at least two experiments (S.D. less than 10%).

Figuren illustrerer fordampningen og den totale "recovery" af lindan og MCPP methyl ved 15°C og 23°C fra filterpapir efter en periode på 24 timer. Hver søjle illustrerer den totale mængde pesticid, der blev analyseret efter testperiodens ophør (total "recovery"). Den lyse del illustrerer den mængde pesticid, der er fordampet. Data repræsenterer et gennemsnit af mindst to forsøg (S.D. er mindre end 10%).

3.3.3 **Volatilisation of lindane and MCPP methyl applied at two different doses**

Figure 3.4 illustrates the volatilisation and the total recovery of lindane and MCPP methyl from filter paper after a 24 hours period. Each column illustrates the total amount of pesticide analysed after the test period (total recovery). The lowest dark part of each column illustrates the amount of pesticide extracted from the filter paper and the volatilisation chamber, and the upper light part illustrates the amount of pesticides volatilised. The airflow in the chamber was 0.17 m per sec. The application rate was 0.01 mg/cm^2 and 0.1 mg/cm^2 for lindane and 0.015 and 0.15 mg/cm^2 for MCPP methyl, corresponding to the recommended application rate and 10× the recommended application rate. At the recommended application rate 80.5% of the applied lindane volatilised corresponding to 0.439 mg, while at 10× the recommended doses only about 19.6% of the applied amount volatised corresponding to 1.068 mg lindane. At the recommended application rate 95.9% of the applied MCPP methyl volatilised while the corresponding values were 85.5% at 10× the recommended dose.

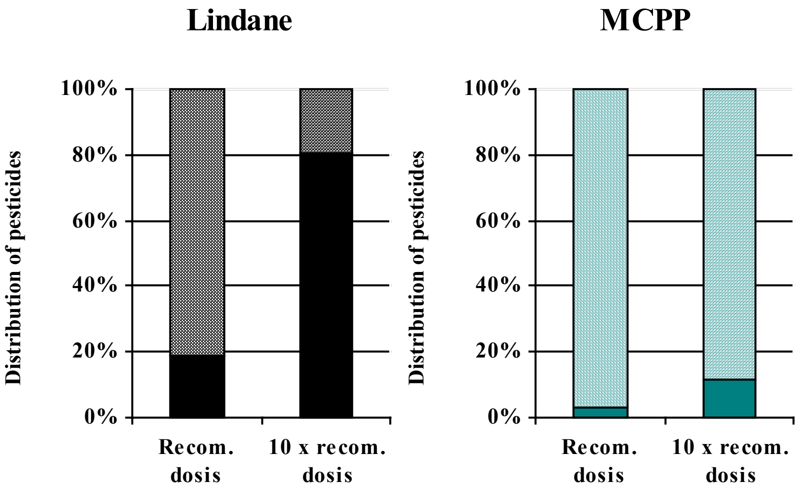


Figure 3.4
The figure illustrates the volatilisation and the total recovery of lindane and MCPP methyl at two different doses from filter paper after a 24 hours period. Each column illustrates the total amount of pesticide analysed after the test period (total recovery). The upper light part illustrates the amount of pesticides volatilised. The application rate was 0.01 mg/cm^2 and 0.1 mg/cm^2 for lindane and 0.015 and 0.15 mg/cm^2 for MCPP methyl. All data represent the mean of at least two experiments (S.D. less than 8%).

Figuren illustrerer fordampningen og den totale recovery af lindan og MCPP methyl ved to forskellige doseringer 24 timer efter tilførsel til filterpapir. Hver søjle illustrerer den totale mængde pesticid, der blev analyseret efter testperiodens ophør (total "recovery"). Den lyse del illustrerer den mængde pesticid, der er fordampet. Doseringen var 0,01 mg/cm^2 og 0,1 mg/cm^2 for lindan og 0,015 mg/cm^2 og 0,15 mg/cm^2 for MCPP methyl. Data repræsenterer et gennemsnit af mindst to forsøg (S.D. var mindre end 8%).

3.3.4 **Volatilisation of lindane and MCPP methyl at different air flow**

Figure 3.5 illustrates the volatilisation and the total recovery of lindane and MCPP methyl from filter paper after a 24 hours period at two different airflows and at two different application rates. Each column illustrates the total amount of pesticide analysed after the test period (total recovery). The lowest dark part of each column illustrates the amount of pesticide extracted from the filter paper and the volatilisation chamber, and the upper light part illustrates the amount of pesticides volatilised. The two airflows were 0.17 and 0.67m per sec and the application rate was 0.01 mg/cm^2 and 0.1 mg/cm^2 for lindane and 0.015 and 0.15 mg/cm^2 for MCPP methyl, corresponding to the recommended application rate and 10× the recommended application rate. The results revealed that an increase of the airflow by a factor of 4 does not significantly increase the amount of volatilisation of the two pesticides at the two selected concentrations.

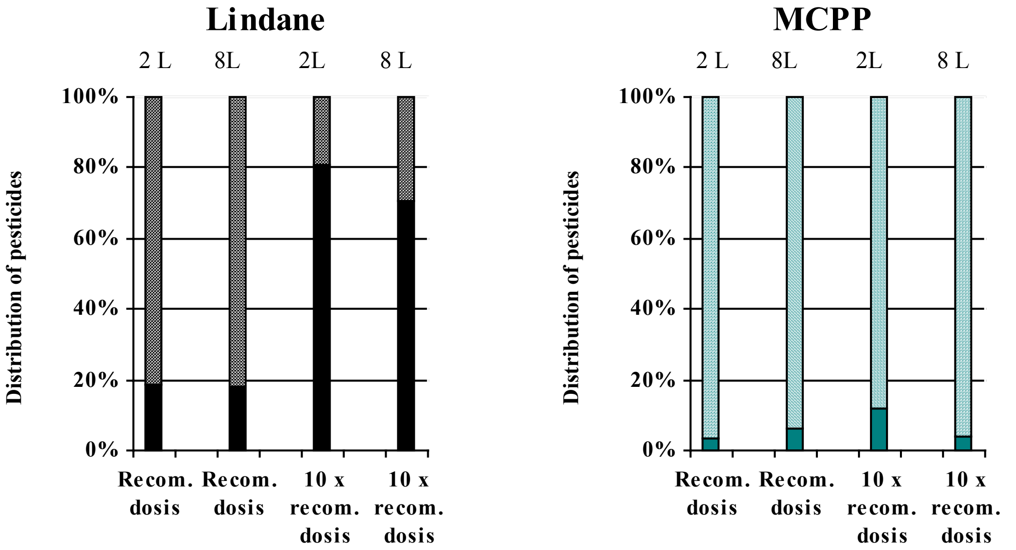


Figure 3.5
The figure illustrates the volatilisation and the total recovery of different concentrations of lindane and MCPP methyl at two different airflows. Each column illustrates the total amount of pesticide analysed after the test period (total recovery). The upper light part illustrates the amount of pesticides volatilised. The application rate was 0.01 mg/cm^2 and 0.1 mg/cm^2 for lindane and 0.015 and 0.15 mg/cm^2 for MCPP methyl. The airflow in the chamber was 0.17 and 0.67 m/s., respectively (corresponding to an air exchange rate of 2 and 8 l/min). All data represent the mean of at least two experiments (S.D. less than 10%).

Figuren illustrerer fordampningen og den totale recovery af forskellige koncentrationer af lindan og MCPP methyl ved to forskellige lufthastigheder. Hver søjle illustrerer den totale mængde pesticid, der blev analyseret efter testperiodens ophør (total "recovery"). Den lyse del illustrerer den mængde pesticid, der er fordampet. Stofferne blev tilført i koncentrationer på 0,01 og 0,1 mg/cm^2 for lindan og 0,015 samt 0,15 mg/cm^2 for MCPP methyl. De to undersøgte lufthastigheder var henholdsvis 0,17 og 0,67 m/s.(svarende til en luftgennemstrømningshastighed på 2 og 8 l/min). Data er et gennemsnit af mindst to forsøg (S.D. er mindre end 10%).

3.3.5 **Volatilisation of lindane and MCPP methyl applied to different surfaces**

Artificial surfaces

Table 3.3 illustrates the volatilisation of lindane and MCPP methyl applied to two different artificial surfaces. The pesticides were applied to a filter paper illustrating an absorbent surface and to a metal plate illustrating a non-absorbent surface. Measurements were taken during a 24 hours period. The application rate was 0.01 mg/cm^2 for lindane and 0.015 mg/cm^2 for MCPP methyl. The airflow in the chamber was 0.17 m per sec. The recovery in the experiments with filter paper was 91.4% for lindane and 90.3 for MCPP methyl. For the non-absorbent surface a recovery of 90.3 and 91.7% was found for lindane and MCPP methyl, respectively. All data represent the mean of at least two experiments (S.D. less than 10%).

Table 3.3
Volatilisation of lindane and MCPP methyl applied to an absorbent surface and a non-absorbent metal surface during a 24 hours period (S.D. less than 10%).

Fordampning af lindan og MCPP methyl tilført en absorberende overflade og en ikke absorberende metaloverflade i en 24 timers periode (S.D. mindre end 10%).

Hours after treatment	**Volatilisation of lindane (% of applied dose)**		**Volatilisation of MCPP methyl (% of applied dose)**	
	Applied to absorbent paper surface	**Applied to non absorbent metal surface**	**Applied to absorbent paper surface**	**Applied to non-absorbent metal surface**
0-1	7.8	10.1	28.6	38.2
1-3	14.0	17.2	30.7	38.2
3-6	17.2	13.0	16.8	9.2
6-24	33.5	33.3	10.3	5.1
Total	**72.5**	**73.5**	**86.4**	**90.6**

The results revealed that the volatilisation of each pesticide was comparable when applied to the two selected surfaces. However, even though the total amount of volatilised pesticides was the same after 24 hours it seems that the volatilisation of at least MCPP methyl was faster at the non-absorbent surface during the initial volatilisation phase. Thus, 3 hours after application 76.4% of the applied MCPP methyl was volatilised when applied to the metal surface compared with 59% when applied to the filter paper.

Soil surfaces

Table 3.4 illustrates the volatilisation of lindane and MCPP methyl applied to a typical Danish soil. Measurements were made during a 24 hours period. The application rate was 0.01 mg/cm^2 for lindane and 0.015 mg/cm^2 for MCPP methyl. The airflow in the chamber was 0.17 m per sec.

Table 3.4
Volatilisation of lindane and MCPP methyl applied to a typical Danish soil during a 24 hours period. All data represent the mean of at least two experiments (S.D. less than 10%).

Fordampning af lindan og MCPP methyl tilført en typisk dansk jord i en 24 timers periode. Alle data repræsenterer et gennemsnit af mindst to forsøg (S.D. mindre end 10%).

Hours after treatment	**Volatilisation of pesticides (% of applied dose)**	
	Lindane	**MCPP methyl**
0-1	1.7	3.3
1-3	2.6	3.2
3-6	2.0	2.4
6-24	6.7	7.0
Total	**13.0**	**15.9**

In contrast to the artificial surfaces only a small fraction of the pesticides volatised when applied to a soil. Furthermore, it was interesting to notice that no marked difference was seen between the volatilisation of lindane and MCPP methyl when applied to the soil. At the end of the experiment 76.6 % and 64.9 % of the applied pesticides could be extracted from the soil and the chamber for lindane and MCPP methyl, respectively. Thus, the recovery in these experiments was 89.6% for lindane and 80.8% for MCPP methyl.

4 Discussion

Volatilisation plays an important role in the dispersion of pesticides in the environment. Volatilisation also leads to a rapid transport and distribution of pesticides in the atmosphere, resulting in considerable wet and dry deposition. Since volatilisation is an important factor in the fate of pesticides in the environment, it is necessary to have a method to evaluate the process.

According to Thomas *et al.* (1990), volatilisation can be defined as the process by which a compound evaporates in the vapour phase to the atmosphere from another environmental compartment. For pesticides and other chemicals potential volatility is related to physical/chemical parameters such as vapour pressure and Henry´s law constant of the compound. However, actual volatilisation rate will also depend on environmental conditions such as wind speed and temperature among others, and all factors that modify or attenuate the effective vapour pressure of the pesticide (Spencer, W.F. *et al.* 1973).

In spite of all the work that has been done in this field, up till now, measuring or assessing volatilisation is not a simple task. Many models simulating or predicting volatilisation have been published (e.g. Chen C *et al.* 1995; Lindhardt *et al.* 1994; Lindhardt and Christensen, 1994; Jansma and Linders, 1995, Smit *et al.*, 1997, 1998). For a survey of part of the literature cf. Nolting *et al.*, 1988. However, all the models can only be applied under certain, usually very restrictive, conditions. Therefore, the search for a better understanding of the volatilisation process and for methods accurately assessing pesticide volatility still goes on.

In the present study the volatilisation potential of pesticides is discussed and illustrated based on both physical/chemical properties of the pesticides and on experimental volatilisation experiments with the three pesticides: MCPP-P, MCPP methyl, and lindane. A laboratory model system for the direct determination of the volatilisation of pesticides from different surfaces has been developed. The purpose of this laboratory set-up is to evaluate volatilisation of pesticides relative to each other.

4.1 Estimation of volatility of pesticides based on physical/chemical parameters of the test substance

One of the most important physical/chemical properties influencing a substance's volatility is its vapour pressure. Every chemical has a characteristic saturation vapour pressure which varies with temperature. Volatile substances, such as water, ethanol, and methanol, have comparatively high vapour pressures at room temperature (10^3 – 10^4 Pa). In contrast, pesticides have generally a comparatively low vapour pressure (approx. 10^{-7} – 10^{-2} Pa), however, many still volatilise at considerable rates (Krasel and Pestemer, 1993; Boehnke *et al.*, 1990). The vapour pressure of lindane is measured to 5.6 x 10^{-3} Pa and 4.0 x 10^{-4} Pa for MCPP-P (at 20°C). No measured value was found for MCPP methyl (Meylan *et al.* 1994). Thus, judging from the measured vapour pressure lindane is expected to have a higher volatility than MCPP-P, which is in agreement with our experimental data. To make a relative comparison of all three pesticides the calculated vapour pressure was compared using a model of all 3 pesticides. The calculated values were 1.04 x 10^{-1} Pa for lindane, 1.1 x 10^{-2} Pa for MCPP-P, and 2.5 x 10^{-1} Pa for

MCPP methyl (all at 25^{o}C). Even though a direct comparison between the measured and calculated values can not be made due to the use of different temperatures the relative difference between the pesticides is not changed significantly. Thus, based on these calculated vapour pressures it is expected that MCPP methyl has a higher volatility than lindane which has a higher volatilisation than MCPP-P. This is in agreement with our experimental measurements.

Another property that is often used in evaluation of the volatility of pesticides is their air-water partition coefficient, the Henry´s law constant. The Henry´s law constant is usually calculated by dividing vapour pressure (dimension Pa) by water solubility (dimension mol m^{-3}). Consequently, uncertainties in vapour pressure values are reflected by Henry´s law constants as well. A high Henry´s law constant (> 1 Pa m^{3} mol^{-1}) indicates a high volatility from aqueous solution (e.g., from moist soil). However, based on how the Henry´s law constant is calculated a substance with very low water solubility may have a rather high Henry´s law constant even if its vapour pressure is comparatively low. For the three pesticides used in the present study the calculated Henry´s law constant for lindane, mecoprop methyl and mecoprop P is 4.1, 1.03, and 2.7×10^{-3} (Pa m^{3} /mol), respectively. These values are based on calculated vapour pressure and a temperature of 25^{o}C. Based on these values a much higher volatility for lindane and MCPP methyl would be expected compared with MCPP-P, which is in agreement with the present experimental measurements. However, based on Henry´s law constant a higher volatility of lindane would also be expected compared with MCPP methyl that is not in agreement with our experimental results. It may be due to the fact that the water solubility of lindane is decidedly lower than the solubility of MCPP methyl, contributing to the high Henry´s law constant. A comparable phenomenon has also been described by Walter *et al.* (1996) where the volatilisation of 3 different pesticides were compared (the active ingredients were not named because the study was a part of an interlab comparison). In spite of a higher Henry´s law constant of active ingredient this compound volatilised considerably less than the other two compounds which both have a higher vapour pressure, suggesting a higher volatilisation. Therefore, while these physico/chemical properties may be used to estimate relative volatility, deducing actual volatilisation behaviour from them may be erroneous. However, volatilisation of pesticides seems to be more related to the vapour pressure than to the Henry´s law constant.

4.2 Experimental measurement of volatilisation of pesticides with special reference to lindane, MCPP-P and MCPP methyl

It is evident that there are other factors besides vapour pressure and Henry´s Law constant that influence volatilisation, such as climatic parameters e.g. wind speed, temperature and humidity. Volatilisation of pesticides from natural surfaces is also influenced by their formulations, the application techniques and interactions of the substance to which it is applied (e.g. adsorption, desorption).

Looking at the practical field situation, many different factors and their interactions determine volatilisation from plant and soil surfaces. The results obtained from field experiments can fully be transferred to practical outdoor conditions. The disadvantages are, however, the high variability of results for the same compound due to many highly variable factors in field experiments. To overcome these disadvantages laboratory experiments can be helpful tools. A number of methods have been developed, ranging from very simple to high-tech designs. However, most of the experimental volatilisation measurements of pesticides in Europe are based on the German BBA test guideline.

In the present study a simple laboratory model system has been designed, in which a wide range of outdoor conditions can be simulated. The finalised method was then used to measure the volatility of selected pesticides from different surfaces and under different "climatic" conditions such as temperature, wind speed etc. The aim of the experimental set-up was to develop a simple, cost-effective and sensitive laboratory test system to assess and evaluate the volatilisation of pesticides relative to each other under different conditions.

4.2.1 The German BBA test guideline

In 1990 a BBA Guideline concerning volatilisation of pesticides was published (Nolting H-G *et al.*). This guideline was design as a "liberal" guideline with only a few specific demands to be met by the method applied. The intention was that after some years of experience, the methods, in use at that period, should be compared and evaluated, and it should then be decided whether a more specific guideline would have to be issued (Walter *et al.*, 1996).

The German guideline requests details on the percentage of active ingredient volatilised 1, 3, 6, and 24 hours after application, the 24 hours value being the crucial value for the authorisation process. A few other details are requested by the BBA guideline such as: the relative humidity of the air shall be about 35% and the wind velocity shall be > 1 m/s directly above the surface**.** In soil experiments a standard 2.1 soil or a similar soil with maximum 1.5% organic bound carbon shall be used, and the sand quota shall be at least 70%. The water level in the soil shall be 60% of the maximum water holding capacity and must be kept at this level during the experiments.

4.2.2 Experimental measurement and evaluation of selected factors influencing on the volatilisation, and of pesticides with special focus on MCPP-P, MCPP methyl, and lindane

Model system for determination of volatilisation of chemical substances

A simple laboratory model system for the determination of the volatilisation has been used for the present study. It permits a direct determination of the volatilisation of a compound from a given surface and a mass balance can be made at the end of the study. Furthermore, different airflows, temperatures, etc. can be obtained in this experimental set-up.

The recovery and stability experiments showed that the pesticides were absorbed quantitatively by the adsorption tubes used in this test design and the total recovery was sufficient. Furthermore, the test results revealed that the substances were stable during the test period of up till 30 hours.

Design and dimension of the chamber

The BBA guideline neither requests nor suggests a specific method for assessing volatilisation. Various laboratory model systems for direct and indirect determination of volatilisation of pesticides from treated surfaces are described in the literature. Designs and dimensions of volatilisation chambers differ widely, which may be one reason for a considerable variation among the results obtained in different studies. With respect to the volatilisation chamber properties, the differences in size, experimental area, and air exchange rate are the most apparent. For practical reasons, the volatilisation is often studied in small laboratory volatilisation chambers like that used in the present study (chamber size of about 0.00008 m^3) (Stork A. *et al.* 1994, Walter U. *et al.* 1996). However, some studies are also carried out using a large scale wind tunnel system with a chamber size of several m^3 (Rüdel H. 1997) or under field-like conditions in a wind-tunnel /lysimeter system with a chamber size of 0.3-0.9 m^3 (Stork A. *et al.,* 1994). The volatilisation rate may also be influenced by the size of the treated area in the volatilisation chamber. Thus, when testing the volatilisation of lindane from soil in a wind tunnel under defined conditions, it was observed that from a larger soil surface (0.84m^2) a lower amount of lindane (23%) volatilised than from a smaller surface (31% at 0.28m^2) under otherwise identical conditions (Waymann B. and Rüdel H., 1995).

The volatilisation rate

Volatilisation of lindane and MCPP methyl applied at the recommended dose to filter paper during a 30 hour period indicates that about 28% and 8% of the applied dose was volatised during the first hour after application for MCPP methyl and lindane, respectively. After 8 hours about 80% and 50% of the applied MCPP methyl and lindane, were volatised. Only about 7% of the applied MCCP methyl volatised in the period between 8 and 30 hours after application while it was about 30% in the case of lindane. The most important objective of a volatilisation experiment according to the BBA Guideline is the determination of the volatilised quantity of the substance within 24 hours after application. This time interval seems to be reasonable when examing the experiments reported here. They document the high volatilisation rates within the first few hours after application, and the 24 hours value is measured at a time when the volatilisation process has considerably slowed down. The same pattern has also been seen in other laboratory volatilisation experiments with other pesticides (e.g. Walter *et al.*, 1996). The results from the present experiments also show that when MCCP-P was applied to filter paper no volatilisation took place during a 24 hours period. These results are in agreement with previous investigations of the volatilisation of MCPP-P from plant surfaces and soil under laboratory conditions (Mossin J. personal communication, Danish EPA, Division of Pesticides, 1999).

Application rate

The rate of loss by volatilisation depends on the concentration on and in a given medium e.g. a soil and the concentration-vapour density relationships at the soil surface. According to Letey and Farmer (1974) there are two general mechanisms whereby pesticides move to the evaporating surface, i.e. diffusion and mass flow. Diffusion is the process by which material is transported as a result of random molecular motion caused by the molecule’s thermal energy. The random molecular motions gradually cause the molecules to become uniformly distributed in the system (Letey and Farmer, 1974). Diffusion occurs whenever a concentration gradient is present. In general the diffusion rate of a pesticide is increased with increasing concentration applied. In the present study the two pesticides were applied at a rate corresponding to the recommended application rate and 10× the recommended application rate. When the doses were increased with a factor of 10 the amount of lindane volatising also increased, however, only with a factor of 2.4 under the present experimental conditions. In contrast, when the amount of MCPP methyl applied was increased with a factor of 10, the amount of MCPP methyl volatising increased with a factor of 8.9 illustrating the higher volatilisation potential for this compound. A comparable phenomenon has also been described in soil experiments with different application doses of lindane in a wind tunnel experiment (Waymann and Rüdel, 1995). Thus, when the application dose is increased the volatilisation is normally also increased, however, the actual increase in volatilisation is highly depended on the physical/chemical properties of the pesticides and of other environmental conditions.

Volatilisation at different airflow and humidity

Wind speed, turbulence, and relative humidity play an important role in the overall loss of pesticides by volatilisation in the field. The direct effect of increased air movement involves a more rapid removal of pesticide vapours from the soil surface, and results in an increased movement of pesticide to the soil surface (Guenzi and Beard, 1974). According to Hartley (1969) the rate of movement away from the evaporating surface is a diffusion-controlled process.

Close to the evaporating surface the air is relatively still. The vaporising substance is transported from the surface through this stagnant air layer only by molecular diffusion. Diffusion away from the surface is related to the vapour density and the molecular weight of the pesticide. The thickness of this stagnant air layer above the evaporating surface depends on the airflow rate. The studies of Farmer *et al.* (1972) and Igue *et al.* (1972) found more volatilisation of chlorinated insecticides with increasing flow rates. Waymann and Rüdel (1995) also found an increase in the volatilisation rate of lindane from both soil and plants with increasing air velocities in a wind tunnel with laminar airflow.

In the present study the volatilisation of lindane and MCPP methyl was tested at two airflows (0.17 and 0.67 m per sec.) but no significant increase in the amount of volatilisation of the two pesticides was found with increasing airflow. The airflow was measured at a distance less than 0.7 cm. from the surface which would correspond to a calculated wind speed of more than 1 m per sec at a height of 1 m above the surface (Asman, 1999). Furthermore, the airflow reached the volatilisation chamber as a turbulent flow. This increased the volatilisation of pesticides compared with a laminar airflow situation since the primary effect of wind on pesticide disappearance from foliage is assumed to be through turbulent transfer of volatilised pesticide from plant surfaces to the atmosphere (Spencer *et al.*, 1973). Since no significant increase in the amount of volatilisation of the two pesticides was observed after an increase of the airflow by a factor of 4, it is expected that an airflow of 0.17 m per sec. is sufficient to ensure that the rate of the airflow is not the limiting factor for a high evaporation under the present experimental conditions.

Influence of the relative humidity of the air

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

Normally pesticides volatilise much more rapidly from wet than from dry soils because the polar water molecules are strong competitors for adsorption sites on the soil, especially to non-polar organic compounds (Dörfler *et al.* 1991, Petersen *et al.*, 1994). Passing moist air over moist soil will result in little water loss. Therefore, pesticide volatilisation will continue for a long time. However, with dry air (low relative humidity), the soil dries rapidly and pesticide vapour pressure is decreased within a relatively short time. The drying effect, decreasing the volatilisation, is reversible, since remoisting the air-dry soil will increase the vapour density again to its original maximum value (Jansma and Linders, 1995).

Grass *et al.* (1994) measured the influence of air humidity on the volatilisation of triflualin. At a relative air humidity of 31, 49, and 78% the measured percentage of volatilised trifluralin over the first day was 66, 64, and 96%, respectively (temperature 20°C, air velocity 1.0-1.2 m/s.). In the present study a relative humidity of the air was maintained at 50% in all experiments and the test-substrate (filter paper or soil) was in equilibrium with this humidity before the pesticides were added just to ensure relative constant water content of the substrate.

Effects of different temperatures

The temperature influences the characteristic saturation vapour pressure of a given pesticide. The overall effect of an increasing temperature is an increasing volatilisation of the pesticide. This is also illustrated in the present study where an increase in the temperature from 15°C to 23°C increases the volatilisation of especially lindane.

In the field the effects of different temperatures on volatilisation of pesticides are more complex. Temperature affects the volatilisation of a given pesticide from soil by a direct influence on the vapour density of the pesticide and by temperature influences on the physical and chemical properties of the soil. Thus, temperature may influence the volatilisation of soil-incorporated pesticides through its effect on movement of the pesticide to the surface by diffusion or by mass flow in the evaporating water, or through its effect on the soil water adsorption-desorption equilibrium. Ehlers *et al.* (1969) reported an exponential increase in the apparent diffusion coefficient in the soil for lindane after increasing the temperature from 20°C to 40°C. However, an increase of temperature may also increase the drying rate of the soil surface. Depending on the results of the temperature effect on soil drying and the effect on vapour pressure, volatilisation will increase or decrease (Deming, 1963).

Volatilisation when applied on different surfaces

Adsorption reduces the chemical activity and, thus, also the volatilisation rate of the compound. The rate of loss by volatilisation depends on the concentration-vapour density relationships at the surface and is highly depended on the type of surface that the pesticide is applied to. It should be noted that the variation in the plants and soils used in different investigations is significant. This may be one reason for a considerable variation among the results published for many substances. To overcome these disadvantages, laboratory experiments using a standardised artificial surface can help to assess and evaluate the volatilisation of pesticides relative to each other under different conditions.

In the present volatilisation study lindane and MCPP methyl were applied to two different artificial surfaces, a filter paper illustrating an absorbent surface and a metal plate illustrating a non-absorbent surface. The results revealed that the volatilisation of each pesticide after 24 hours was comparable (about 73% for lindane and 90% for MCCP methyl of the applied doses). However, it seems that the volatilisation of at least MCPP methyl was faster at the non-absorbent surface. In contrast to the artificial surfaces only a small fraction of the applied doses volatised when the pesticides were applied to a typical Danish soil (13% for lindane and 15.9% for MCPP methyl). The results are comparable with the results found for lindane tested in a huge wind tunnel where the soil volatilisation was found to vary between 12 and 31% and volatilisation from plant varied from 52 to 62% of the initial dose after 24 hours, depending on the test conditions (Waymann and Rüdel, 1995). Furthermore, our results are also comparable to evaporative losses of lindane from plant leaf and soil surfaces after field application. Boehncke *et al.* (1990) observed an evaporative loss of lindane from leafs of 77 to 95% (different plant leafs) and 28% from a soil after 24 hours. Jansma and Linders, (1995) presented a review of the literature about volatilisation of selected pesticides from soil and plants after spraying. In this paper the volatilisation of lindane from plants varied from 64 to 89% in 5 different laboratory studies after a 24 hours period. From the soil surface the volatilisation of lindane varied after 24 hours from 3.1 to 22.6% of the applied dose in 8 different laboratory experiments. However, in one field experiment in USA up till 50% of the applied dose was volatilised within 24 hours.

In general the volatilisation of pesticides from soil is much smaller than from plant surfaces (e.g. Boehncke *et al.* 1990; Rüdel, 1997). However, significant variation is found depending on the soil used for the experiments. This is in agreement with the results found in the present study where the filter paper is more comparable with a plant surface. The volatilisation of pesticides from soil is very complex e.g. the diffusion rate of a pesticide from soil is controlled by soil bulk density, pesticide concentration, organic matter, pH, the soil water and clay contents in addition to climatic parameters like temperature, wind velocity etc. Furthermore, vertical transport is an important parameter in the evaluation of the volatilisation of pesticides from soil and occurs as a result of external forces. The pesticide is considered to be either dissolved or suspended in water, present in the vapour phase, or adsorbed on solid mineral or organic components of the soil. Mass flow of the pesticide is therefore the result of the mass flow of water and/or soil particles with which the pesticide molecule is associated. Although many factors contribute to mass transport of pesticides through soil by water, the most important factor appears to be adsorption between the pesticide and soil (Letey and Farmer 1974). Mass flow due to air movement in soil is considered negligible (Letey and Farmer, 1974).

4.3 Conclusions and suggestions for further validation work

Looking at the practical field situation, many different factors and their interactions determine volatilisation from plant and soil surfaces. The results obtained from field experiments can fully be transferred to practical outdoor conditions. The disadvantages are, however, the lack of reproducibility. To overcome these disadvantages laboratory experiments can be helpful tools.

In 1990 a German BBA guideline on assessing pesticide volatilisation was developed. This guideline was design as a “liberal” guideline with only a few specific demands. Since then a number of methods have been developed, ranging from very simple to high-tech designs.

In 1994 the volatilisation of three pesticides from plant and soil surfaces was assessed using eighteen different laboratory methods and one field method, all following the BBA guideline. With respect to the volatilisation chamber properties, the differences in size, experimental area, and air exchange rate are the most apparent. Furthermore, the height at which wind is measured varies from 0-3 cm to more than 10 cm. The aim of the present study was to see whether the different methods yielded results that were consistent among the methods and a number of terms were agreed (dose, temperature and humidity etc.). The results revealed that for all three substances tested, a considerable amount of variation among the results obtained with the different methods was observed (Walter *et al.* 1996).

From the scientific point of view, the inter-laboratory comparison once again proved that the problems of assessing pesticide volatilisation have not been solved yet, and that it is necessary to be very cautious when comparing volatilisation rates assessed with different methods.

In the present study a laboratory system for the direct determination of the volatilisation of pesticides from different surfaces has been developed. With the system it is possible to evaluate volatilisation of pesticides relative to each other. Taking practical aspects of testing and the demand for simple cost-effective tests into account, the main conclusions of the present study regarding the experimental set-up are as follows:

The BBA guideline on assessing pesticide volatilisation was designed as a “liberal” guideline with only a few specific demands. This guideline is a good basis, however, it should be improved and be more specific.

Design and dimension of the chamber

Design and dimension of the volatilisation chamber must be specified. The conditions of most experiments are so different that comparative considerations are difficult or impossible. An exact determination of volatilisation of pesticides can be achieved only by direct measurement of volatilisation rates using some means of trapping the vapourised pesticide. A small chamber is recommended. Such a chamber can be extracted at the end of an experiment and a mass balance can be made.

Sampling intervals

Interpreting the kinetics graphs from various volatilisation experiments with pesticides it can generally be said that the air sampling 1, 3, 6, and 24 hours after the application asked for in the German guideline seems to be reasonable. Normally, high volatilisation rates are seen within the first few hours after application, and the 24 hours values after application are measured at a time when the volatilisation process has slowed down considerably.

Airflow

According to the BBA guideline the wind velocity shall be > 1 m/s directly above the surface. However, the guideline does not exactly stress in which height the measurement should be made. When evaluating the volatilisation of a test substance from a surface the height above the surface, where the air velocity measured is very important. Thus, if the assumed wind speed at 30 cm height above a bare soil surface is 1 m/s the calculated wind speed is about 0.7 and 0.3 m/s at a height of 5 and 0.5 cm above the surface, respectively (Asman, personal communication, 1998, National Environmental Research Institute, Roskilde, Denmark). Furthermore, it is important to decide whether turbulent or laminar airflow should be used. If a small chamber with a turbulent airflow is used an airflow with a velocity of less than 1 m/s 1-5 mm above the surface might be sufficient.

Humidity of the air

The relative humidity of the air shall be about 35% according to the BBA guideline. Since the air humidity value is relatively low and not realistic for field situations, this condition should be changed. Mostly, a more realistic value of approximately 50% relative humidity should be used. However, the most important aspect is that the surface to which the pesticide is applied has the same humidity during the whole experiment.

Selected surfaces

According to the BBA guideline pesticides should be applied to two different surfaces one illustrating a leaf surface and one soil. It is important to specify the selected surface and an artificial surface e.g. a filter paper may be used to illustrate a leaf surface, however, some work has to be done to find a well-defined surface that can simulate a leaf surface. In soil experiments a German standard 2.1 soil or a similar soil is recommended in the BBA guideline. The water level in the soil must be 60% of the maximum water holding capacity and must be kept at this level during the experiments. This soil can be used as a reference soil. However, another soil, which is typical for the area of concern, should be included in the test. Furthermore, the pH value of the soil should be specified since dependency of volatilisation seems to be strong for some pesticides (Walter *et al.*, 1996). However, data from the present study and many other studies suggest that plant (or an artificial surfaces illustrating plant surfaces) volatility is always higher than soil volatility. Therefore, it should be considered to omit the volatilisation tests with bare soil and only perform plant volatilisation tests. In most cases these results will be sufficient to assess the volatilisation behaviour of pesticides.

Application rate and technique

Several concentrations of a given pesticide should be tested and the application technique must be more explicit. Application devices used in different experiment differ greatly. Everything from nozzles used in agricultural practice to modified TLC applicators to simple Hamilton syringes has been used. Furthermore, experiments must be carried out with the formulated product as well as with the active ingredient.

Temperatures

The temperature must be kept constant e.g. at 20°C or even better measured at two different temperatures e.g. 10 °C and 30°C representing different temperatures in Europe.

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Modelling atmospheric transport and deposition of pesticides up to 2 km from a source

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Table of contents

Executive summary

In the present study an overview is given of the atmospheric processes relevant to pesticides. This knowledge is then incorporated in an atmospheric transport and deposition model that is used to give and upper estimate of the accumulated fraction of the emission that can be deposited within 2 km from a field where pesticides are applied.

Pesticides occur in the atmosphere in gaseous and particulate form. Close to areas where they evaporate they will be mainly in gaseous form.

The exchange of a gaseous pesticide between the atmosphere and the surface (soil, vegetation, water) depends on the wind speed (turbulence) and the difference in concentration between the atmosphere and the surface. If the concentration in the surface is higher than in the air, net emission will occur. In the opposite case net dry deposition will occur.

Both emission and dry deposition depend on processes in the surface that influence the concentration in the surfaces. These processes can e.g. be vertical transport in the surface or degradation.

Both the emission and dry deposition rate will increase with wind speed. Processes in the surface will determine to what extent they will increase. If processes in the surface are much slower than the transport in the air from/to the surface, the emission and dry deposition rate will mainly depend on the processes in the surface and almost not increase with wind speed.

Dry deposition

The dry deposition velocity will be highest for highly soluble gaseous pesticides. For moderately and slightly soluble gaseous pesticides the dry deposition velocity will be lower and will to a large extent depend on processes in the surface.

The dry deposition velocity for particulate pesticides depends not only on the wind speed but also on the particle size. Particles are in general not removed by dry deposition at such high rates as highly soluble gases. Particles in the size range 0.1 - 1 μm are removed at the lowest rate. Smaller or larger particles are removed at a higher rate.

Dry deposition of gases and particles is difficult to measure. High precision is often needed because the measurements are usually based on smal concentration differences. Only for highly soluble gases it is possible to get reasonable results. Even in that case dry deposition is usually not monitored continuously, because that is very expensive. In stead, dry deposition models and measured meteorology are used to infer dry deposition. Dry deposition of pesticides has almost never been measured in the field.

Atmospheric diffusion increases also with wind speed. This is also the case for the mixing height, i.e. the height of the lowest layer in the atmosphere where mixing occurs.

The maximum rate at which vertically well-mixed airborne gaseous pesticides will be removed from the atmosphere under Danish conditions will be about 13% hr^{-1} over cropland and about 25% hr^{-1} over forests.

Wet deposition

The removal rate of both gaseous and particulate pesticides by precipitation increases with the precipitation rate.

The removal rate of gaseous pesticides from the atmosphere due to in-cloud processes is a function of the solubility of the pesticide in water; it increases with solubility. For that reason highly soluble gaseous pesticides are removed from the atmosphere by in-cloud processes at a high rate (64% hr^{-1} at a rainfall rate of 1 mm hr^{-1} and about 99.9% hr^{-1} at a rainfall rate of 10 mm hr^{-1}). Less soluble gaseous pesticides are removed at a lower rate. Particulate pesticides will in general be removed from the atmosphere by in-cloud processes at the same high rate as highly soluble gases.

Gaseous pesticides under the cloud are removed at a lower rate by raindrops than in the cloud. For highly soluble gases the rate is 13% hr^{-1} at a rainfall rate of 1 mm hr^{-1} and about 33% hr^{-1} at a rainfall rate of 10 mm hr^{-1}.

The removal rate of the same particulate pesticides by raindrops under the cloud is in general much lower than the removal rate from the cloud. Moreover, it will also depend on the size of the particles.

Reactions, conversion from gaseous to particulate form

Both dry and wet deposition of gaseous pesticides will increase with their solubility in water. So there is a general tendency that their atmospheric lifetime is related to their solubility. Other factors, however, can also play a role. Pesticides can react with other compounds that are formed in the atmosphere under influence of solar radiation. In this way they can “disappear” from the atmosphere, but then instead reaction products will appear. Gaseous pesticides can also be converted to particles and pesticide present in particles can evaporate again. The reaction product or conversion product will usually have different properties than the precursor and will for that reason be removed at another rate from the atmosphere.

The rate at which highly soluble and particulate pesticides are removed from the atmosphere by in-cloud processes is rather high compared to other removal mechanisms, including dry deposition. It is, however, only raining 5-10% of the time, whereas dry deposition goes on all the time. As a result the yearly average removal rate by dry deposition can nevertheless be of the same order as the average removal rate by wet deposition. The ratio wet to dry removal will depend on the properties of the compound and on the meteorological and surface conditions of the area where the deposition occurs.

It is relatively easy to monitor wet deposition of pesticides.

Relatively close (e.g. 2 km) to a gaseous pesticide source the removal rates are different from the removal rates mentioned before, because it has not yet been mixed over the whole mixing layer. Most pesticides are emitted from fields onto which pesticides are applied. i.e. from low-level sources. Close to the source is the ground-level concentration relatively high, which will lead to higher dry deposition rates, which leads to a relatively high removal rate by dry deposition. Moreover, the pesticide “plume” from the field has not yet reached the clouds at short distance from the source and the pesticide is not exposed to the more efficient removal processes in clouds. In general it can be concluded that for gaseous pesticides close to the source, dry deposition can be relatively more important and wet deposition is relatively less important, than further away from the source.

Model development

Within the framework of this project a model was developed to describe the situation up to 2 km from a source. In this model pesticide emissions were generated by assuming a concentration at the surface. It depends then on the wind speed and other meteorological factors how large the emission rate will be. The model includes also transport by wind, vertical diffusion, dry deposition and removal by precipitation under the cloud.

Deposition up to 2 km from the source

The main conclusion from the model calculations is under average Danish conditions that less than 25% of the emission is deposited up to 2 km from a field where pesticide is applied. This holds for highly soluble gaseous pesticides. For less soluble pesticides this number will be considerably less, more of the order of 1%. This means that the largest part of the emitted pesticide will be transported over long distances (>100-1000 km).

Dry/wet deposition vs. deposition caused by spray drift due to sedimentation

Dry/wet deposition at distances less than 20 m from the field onto which the pesticides are applied can be of the same order as deposition caused by spray drift due to sedimentation. At larger distances dry/wet deposition dominates in this case.

Recommendations for further research

Recommendations for further research are made. One of the most important conclusions is that it is only possible to model the emission and dry deposition of pesticides if the concentration of the pesticides in the surface (soil, vegetation, water) is modelled at the same time.

Dansk sammendrag

Dette afsnit af rapporten beskriver de atmosfæriske processer med relevans for transport, spredning og deposition af pesticider. Endvidere angives modelresultater for transport og deposition af pesticider til estimering af den maksimale afsætning af fordampede pesticider i nærmiljøet (< 2 km) fra sprøjtet mark.

Pesticider eksisterer i atmosfæren i både gas- og partikelform. Tæt ved de områder, de fordamper fra, vil de hovedsagelig være i gasform. Udvekslingen mellem atmosfæren og overfladen (jord, vegetation, vand) afhænger af vindhastigheden (turbulens) og koncentrationsforskellen mellem atmosfæren og overfladen. Netto-emission finder sted, hvis koncentrationen er større i overfladen end i atmosfæren. Netto-deposition finder sted hvis det omvendte er tilfældet.

Både emissions- og tørdepositionshastigheden afhænger af processer i overfladen, som styrer koncentrationen i overfladen. Det kan være processer såsom vertikal transport i overfladen eller nedbrydning. Hvis processerne i overfladen foregår meget langsommere end transporten mellem atmosfæren og overfladen, så bliver det overflade-processerne der bestemmer emissions- og tørdepositionshastigheden. I dette tilfælde vil emissionen næsten ikke tiltage med vindhastigheden.

Tørdeposition

Tørdepositionshastigheden er størst for letopløselige gasser. For moderat og tungtopløselige gasser vil tørdepositionshastigheden være mindre og den vil i høj grad afhænge af processer som foregår i overfladen.

Både emission og tørdeposition tiltager med vindhastigheden. Hvor meget de tiltager afhænger af processerne i overfladen.

Tørdepositionshastigheden for partikelformige pesticider afhænger ikke kun af vindhastigheden, men også af partiklernes størrelse. Generelt set er tørdepositionshastigheden lavere for partikler end for letopløselige gasser. Der er minimum for tørdepositionshastigheden i størrelsesintervallet 0.1-1 µm, mens både større og mindre partikler afsættes hurtigere omend stadig langsomt sammenlignet med letopløselige gasser.

Det er svært at måle tørdeposition af gasser og partikler. Metoderne kræver en meget stor præcision til bestemmelse af små koncentrationsforskelle. For det meste er det kun muligt at opnå rimelige resultater for letopløselige gasser. Endvidere er det ofte meget dyrt at monitere tørdeposition. I stedet anvendes tørdepositionsmodeller og meteorologiske målinger til at estimere tørdepositionen. Der findes næsten ingen feltmålinger af tørdeposition for pesticider.

Atmosfærisk diffusion tiltager med vindhastigheden. Det samme gælder for blandingshøjden, som er højden af det nederste lag i atmosfæren, hvor luften er blandet godt op.

Under danske forhold kan gasformige luftbårne pesticider, der er fordelt over hele blandingslaget, maksimalt tørdeponeres med en fjernelseshastighed på ca. 13% i timen over afgrøder og ca. 25% i timen over skov.

Våddeposition

Hastigheden hvormed både gasformige og partikelformige pesticider fjernes fra atmosfæren med nedbør tiltager med nedbørsintensiteten.

Hastigheden, hvormed gasformige pesticider fjernes fra atmosfæren forårsaget af processer i skyer, stiger med vandopløseligheden af pesticidet. Af denne grund fjernes letopløselige gasformige pesticider med stor hastighed fra atmosfæren (64% i timen ved en nedbørsintensitet af 1 mm i timen og 99.9% i timen ved en nedbørsintensitet på 10 mm i timen). Gasser med en ringere opløselighed fjernes med en lavere hastighed. Partikelformige pesticider vil for det meste fjernes fra atmosfæren ved processer i skyerne med samme hastighed som letopløselige gasser.

Gasformige pesticider som befinder sig i atmosfæren under skyerne fjernes med lavere hastighed af regndråber end i skyerne. Fjernelseshastigheden er 13% i timen ved en nedbørsintensitet på 1 mm i timen og 33% i timen ved en nedbørsintensitet på 10 mm i timen.

Fjernelseshastigheden for den samme partikelformige pesticider er for det meste lavere under skyen end i skyen. Desuden vil den også afhænge af partiklernes størrelse.

Reaktioner, omdannelse til partikler

Både tør- og våddeposition af gasformige pesticider tiltager med vandopløseligheden af pesticidet. Der er dermed en generel tendens, til at pesticiders atmosfæriske levetid afhænger af deres vandopløselighed. Andre faktorer kan dog også spille en rolle. Pesticider kan reagere med andre stoffer som dannes i atmosfæren under indflydelse af sollys. På denne måde kan de "fjernes" fra atmosfæren, men i steder for kommer deres reaktionsprodukter. Gasformige pesticider kan også optages i partikler, eller et pesticid kan fordampe fra partikler. Reaktionsprodukterne har andre egenskaber end udgangsstofferne og fjernes defor med en anden hastighed fra atmosfæren.

Hastigheden hvormed letopløselige gasser og partikler fjernes fra atmosfæren forårsaget af processer i skyer er forholdsvis høj sammenlignet med andre fjernelsesmekanismer, inklusive tørdeposition. Det regner dog kun 5-10% af tiden, mens tørdeposition foregår hele tiden. Af denne grund kan den årlige tørdeposition alligevel være af samme størrelsesorden som våddepositionen. Forholdet mellem våd- og tørdeposition afhænger af stoffernes egenskaber samt meteorologiske og overfladeforhold hvor depositionen finder sted.

Det er relativt enkelt at monitere våddeposition af pesticider.

Forholdsvist tæt (f. eks. 2 km) ved en kilde for gasformige pesticider er fjernelseshastighederne forskellige fra de ovennævnte idet pesticidet endnu ikke er blandet op i hele blandinslaget. De fleste pesticider fordamper fra marker, dvs. at kilderne har en lav højde. Tæt ved kilder er koncentrationen i jordhøjde relativ høj, hvilket vil give anledning til en forholdsvis stor fjernelse ved tørdeposition. Desuden er "pesticidfanen", som stammer fra marken endnu ikke nået op i skyhøjde og pesticidet kan ikke udsættes for den mere effektive fjernelsesproces i skyen. Det kan konkluderes, at tæt ved kilder kan tørdeposition af letopløselige gasformige pesticider være af større betydning end våddeposition, mens det omvendte er tilfældet længere væk fra kilden.

Modeludvikling

Indenfor rammerne af dette projekt er der udviklet en model til at beskrive situationen op til 2 km fra en kilde. I modellen genereres emissionerne ved at antage en koncentration i overfladen. Selve emissionen vil så afhænge af vindhastigheden og andre meteorologiske forhold. Transport med vinden, vertikal diffusion, tørdeposition og fjernelse af stoffer under skyerne beskrives også i modellen.

Deposition indenfor 2 km fra en kilde

Den vigtigste konklusion som afledes fra modelberegnigerne er, at mindre end 25% af emissionen er tørdeponeret i et område op til 2 km fra en mark, der er sprøjtet med pesticid. Det gælder for letopløselige gasformige pesticider. For pesticider, som ikke er så vandopløselige vil tallet være mindre, mere i størrelsesorden 1%. Det betyder, at den største del af den fordampede mængde pesticid transporteres over store afstande (> 100-1000 km).

Tør/vådeposition sammenlignet med deposition forårsaget af afdrift pga. sedimentation

Tør/våddeposition på afstande mindre en 20 m nedstrøms fra en sprøjtet mark kan være af samme størrelsesorden som deposition forårsaget af afdrift pga. sedimentation. På større afstande dominerer tør/våd deposition.

Anbefalinger for videre forskning

Der gives anbefalinger for videre forskning. En af de vigtigste konklusioner er, at det kun er muligt at modellere emission og tørdeposition for pesticider, hvis koncentrationen i overfladen (jord, vegetation, vand) er modelleret samtidig.

1 Modelling atmospheric transport and deposition of pesticides up to 2 km from a source

1.1 Introduction

Pesticides can enter the atmosphere by volatilisation and by resuspension of soil particles where they can be attached to. After they have entered the atmosphere they can be transported over some distance before they are removed from the atmosphere.

Figure 1 shows an overview of the important pesticide processes, not only in the atmosphere, but also in other parts of the environment. The processes that are most relevant to the atmospheric behaviour of pesticides and their interactions will be discussed in the following sections.

This report focuses on the following processes in the atmosphere:
a) Emission (mainly the atmospheric aspect of emission is treated).
b) Atmospheric transport and diffusion; these processes have a great influence on where a pesticide is deposited
c) Dry deposition, which is an important removal process.
d) Wet deposition, which is also an important removal process.

This is a logical order going from the emission via transport to deposition.

Limited attention will be paid to important processes as conversion of pesticides from the gaseous to the particulate phase and to photochemical processes. The reason for this is that the scope of the report is limited to the first 2 km from a source. At such a short distance from the source these processes are not likely to be very important and these processes are therefore not treated extensively.

A model will be presented that incorporates emission, atmospheric transport and diffusion and dry and wet deposition, so that interactions between these processes can be revealed. The implications of the model results will also be discussed.

Order in which the processes are presented

The order in which the processes are discussed in this report is not the same logical order as mentioned under a) to d) above. This is done for pedagogical reasons.

Knowledge of the properties of pesticides will be presented first because they determine the rate at which emission and dry and wet deposition occur.

Then turbulence, atmospheric transport and diffusion are discussed because this knowledge is necessary to describe surface exchange in the following section. This includes the meteorological aspects of emission and dry deposition. The emission is not only determined by meteorological processes but also by processes in the surface (soil, plants). Although this is not within the scope of the project, a brief section on these processes was added. In this way the reader can see how they interact with the meteorological processes and what the important factors are that govern the emission from these surfaces.

Then wet deposition is treated including removal of compounds from the atmosphere by processes in clouds (in-cloud scavenging) and below the clouds (below-cloud scavenging).

Then very briefly some information is given on conversion of compounds from the gaseous to the particulate phase and on photochemical reaction and spray drift.

Then a model is presented that integrates the presented knowledge on emission, atmospheric transport and diffusion and dry and wet deposition. The diffusion part of the model is tested against measurements and it is shown how the results of the vary with important parameters as the surface roughness, the dry deposition velocity and the precipitation rate. Then the main result of this project is presented: An estimate of the maximum accumulated fraction of the emission that can be deposited within 2 km from a field where pesticides are applied.

Finally the results are discussed and conclusions are drawn, including recommendations for further research.

Summarising conclusions

The first and largest part of this report discusses more general principles relevant to emission, atmospheric transport and dry and wet deposition, but almost no results specific to pesticides are given. As this report is rather large, the reader would easily miss the overview and, moreover, the reader is interested in pesticides would be discouraged. For that reason, “intermezzo sections” were included, that summarise the knowledge on important processes and discuss their interactions with reference to pesticides.

Such “intermezzo sections” are presented after the following subjects have been treated:

- Turbulence, atmospheric transport, diffusion and surface exchange (including dry deposition and meteorological aspects of the emission) (section 1.5).
- Removal of material by precipitation (compares also dry and wet deposition) (section 1.8).
- Model results (section 1-13).

In the last section on discussion and conclusions, the information from the “intermezzo sections” is not repeated. In stead, more general conclusions are presented and discussed and recommendations for further research are given.

Relation to other pesticide processes

Figure 1 shows how the atmospheric processes involving pesticides are related to other pesticide processes, so that the reader gets an impression how they interact.

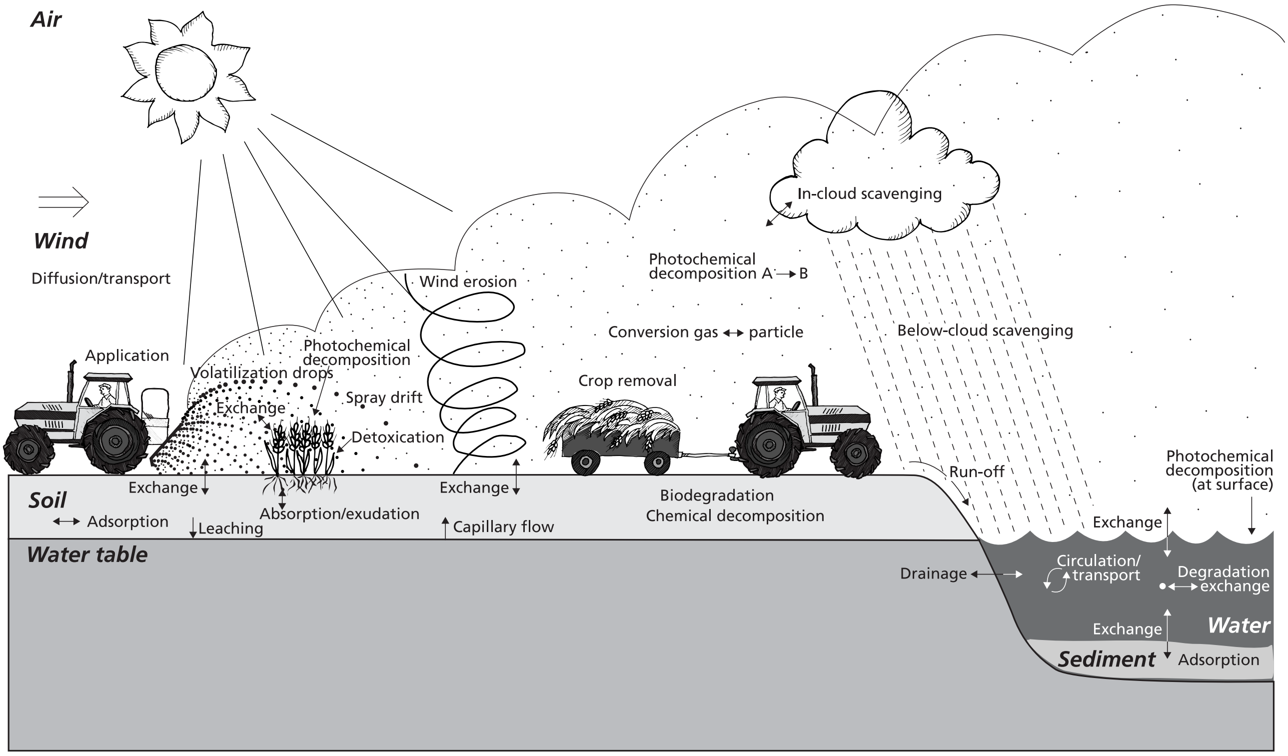


Figure 1
Processes for pesticides in the environment, starting at the left side with application.

Processer for pesticider i miljøet, begyndende til venstre med sprøjtning.

1.2 Some important properties

The atmospheric behaviour of pesticides is influenced by their properties and by meteorological conditions. In the following some important properties will be discussed that can influence the atmospheric behaviour of pesticides.

1.2.1 **Solubility in water**

The solubility of a substance in water is defined at the maximum amount of that substance that will dissolve in pure water at a specified temperature. Above this concentration, two phases will exist if the pesticide is a solid or a liquid at that temperature: a saturated aqueous solution and a solid or liquid phase of the substance. The solubility is a function of the substance and of the temperature and can vary over many orders of magnitude.

1.2.2 **Vapour pressure**

The vapour pressure of a pesticide is defined as the pressure exerted when a solid or liquid is in equilibrium with its own vapour. It is a function of the substance and of the temperature. The vapour pressure increases with temperature. The vapour pressure of pesticides can vary over many orders of magnitude and is expressed in mPa. Compounds with a vapour pressure larger than 0.1 mPa show a noticeable volatilisation (Smit et al., 1998).

1.2.3 **Henry's law coefficient**

The solubility of a gas is an important parameter that influences behaviour of the pesticide in the soil, in vegetation, water bodies and removal of pesticides from the atmosphere by precipitation. A measure of the solubility of a slightly soluble gas in water is the Henry's law coefficient, which simply states that there is a linear relation between the concentration of a dissolved gas and the concentration in air just above it. The Henry's law coefficient can only be applied to that part of a gas that is present as dissolved gas in the solution. If the dissolved gas e.g. dissociates in the solution, the Henry law coefficient describes only the relation between the concentration of the gas in the gas phase and the undissociated part of the dissolved gas. There are different definitions of the Henry's law coefficient, using different units and different ratio's (gas phase concentration/liquid phase concentration or liquid phase concentration/gas phase concentration). In this report we use the following definition:

$$K_H = \frac{c_g}{c_l} \qquad (1)$$

Where K_H is the Henry's law coefficient, c_g is the concentration in the gas phase (kg m^{-3}) and c_l is the concentration in the water phase. K_H is a function of the compound and the temperature. The solubility of gases generally decreases with temperature, i.e. K_H decreases with temperature. K_H of different pesticides can vary over at least 10 orders of magnitude.

Relation between Henry's law coefficient, solubility and vapour pressure

The partial pressure of the pesticide over a saturated pesticide solution is equal to the vapour pressure above the pure pesticide. This has some important consequences (Stork, 1995):

- Compounds with a low solubility like DDT have always Henry's law coefficients with high values. For that reason they are already very volatile at low concentrations in water.
- The Henry's law coefficient be found from the solubility and the vapour pressure above the pure compound. This method can be useful in the case the Henry's law coefficient has not been determined directly.

1.2.4 **The adsorption coefficient Koc**

Adsorption: Freundlich equation

Pesticides dissolved in the soil solution can adsorb onto soil particles. After some time equilibrium will be reached where part of the pesticide is adsorbed and another part is still in the solution. The relation between those parts is given by the empirically derived power function known as the Freundlich equation:

$$S = K_f C^N \qquad (2)$$

where S is the sorbed concentration (kg pesticide kg^{-1} dry soil), C is the solution concentration (kg m^{-3} soil solution). K_f and N are empirical constants. The value of N in the Freundlich equation is usually less than 1 (commonly between 0.75 and 0.95; Green and Karickhoff, 1990). It should be noted, that K_f in this equation has a dimension that depends on the value of N. Although this is not strictly correct N is sometimes set to 1, because then the equation is linear, which allows simpler mathematical solutions in models:

$$S = K_f C \qquad (3)$$

For many pesticide-soil combinations K_f is not known and should either be determined or be estimated. For hydrophobic pesticides, that is non-ionic pesticides with a water solubility less than 10^{-3} mole l^{-1}, the adsorption to the soil is mainly determined by the adsorption to organic material in the soil.
This means that the ratio K_f to the fraction of organic material in the soil is approximately constant for these pesticides. It is then useful to define an adsorption coefficient K_{oc}:

$$K_{oc} = \frac{K_f}{f_{oc}} \qquad (4)$$

where f_{oc} is the mass of organic carbon per mass of dry soil. If K_f (for the linear equation) is known for a soil with a certain content of organic carbon, K_f for the same pesticide for another soil type with know organic carbon content can be calculated with (4) using relation from $K_f = f_{oc}.K_{oc}$. But in many cases no K_{oc} value is known, and then K_{oc} can be estimated from empirical relations of the following type (Lyman et al., 1990):

$$\log K_{oc} = a \log Y + b \qquad (5)$$

where a and b are constants and Y is a relevant property of the pesticide, e.g. the K_{ow} (octanol-water partition coefficient) or the water solubility.
This approach to estimate K_f can strictly only be applied to hydrophobic pesticides that show a linear sorption isotherm and for which sorption mainly occurs to the soil organic carbon. It appears, however, that this approach is also practically suitable for many pesticides that are slightly polar and too water soluble to be considered hydrophobic (Green and Karickhoff, 1990).

1.3 Turbulence, atmospheric transport and diffusion

This report will mainly discuss atmospheric processes in the planetary boundary layer. The planetary boundary layer is defined as that part of the atmosphere that is directly influenced by the presence of the earth's surface with a time scale of about an hour or less. The planetary boundary layer is not constant, but varies from about 100 - 3000 m, depending on meteorological conditions.

Atmospheric movements are almost always turbulent. Wind speed, wind direction, temperature, pressure, humidity and concentration of atmospheric constituents show a spatial and temporal variability. This is caused by atmospheric whirls, called "eddies". Large atmospheric eddies can be observed on sequences of satellite pictures where clouds rotate around low pressure areas. There are eddies of all sizes in the atmosphere, also very small ones. Near the surface they manifest themselves through the flutter of leaves of trees, irregular movements of dust particles, ripples and waves on water surfaces. They cause e.g. diffusion of a plume perpendicular to the wind direction or exchange between the surface and the air.
There are two different mechanisms that generate turbulence: mechanical turbulence and thermal turbulence. It is important to differentiate between these two types of turbulence because they are associated with eddies of different sizes and lifetime, which influence diffusion and surface exchange in a different fashion.

Mechanical turbulence

Mechanical turbulence is generated due to friction exerted on the wind by the surface. This friction is caused by the roughness of the surface. As a result the wind speed increases with height. A rough surface like a forest generates more turbulence than a smooth surface like water. Essential for this form of turbulence is that it is generated by the wind. Mechanical turbulence is characterised by small eddies, with a relatively short lifetime especially near the surface.

Thermal turbulence

Thermal turbulence is caused by heating of the air near the surface due to solar radiation. This air is somewhat warmer than the surrounding air, has consequently a lower density, and is lifted up. Colder air is taking its place. Due to these air movements larger, so called “convective”, eddies are generated. They have relatively long lifetimes and cause diffusion due to upward and downward air movements that can last up to 10-20 minutes.

Influence of turbulence on diffusion of plumes

Close to a point source the plume is narrow. In this case only eddies of a size smaller than the plume width can cause diffusion, i.e. mixing by exchange of the polluted air parcels with the clean air parcels (Figure 2).

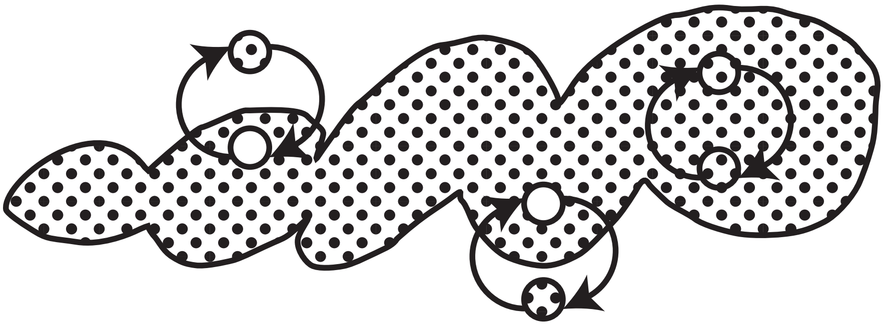


Figure 2
Schematic illustration of mixing of a plume by exchange of air parcels between the plume and the air outside the plume.

Skematisk illustration af blanding af en røgfane ved udveksling af luftpakker mellem fanen og luften udenfor røgfanen.

Larger eddies close to the source do not cause diffusion of the plume, but lead to a displacement (“meandering”) of the whole plume (Figure 3). At larger distance from the source, when the plume has become wider, larger and larger eddies will also play a role in the diffusion.

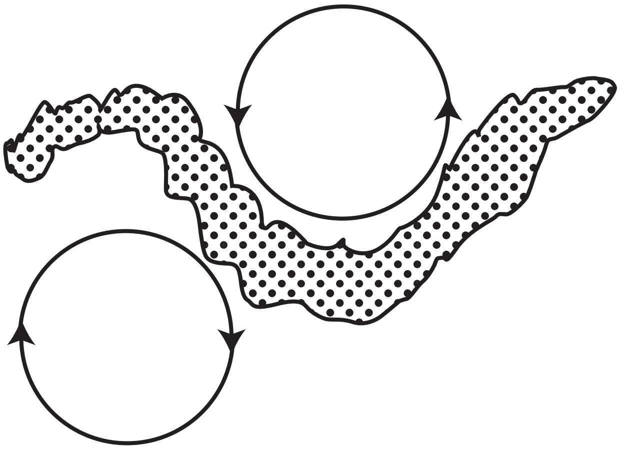


Figure 3
Effect of large eddies on the shape of a plume.

Effekt af store hvirvler på røgfanens form.

Vertical temperature gradient

In the atmosphere the pressure decreases with height. Due to this pressure decrease an air parcel that is lifted up rapidly by e.g. atmospheric turbulence will expand. Some energy is needed for this expansion and this will be taken from the air parcel itself, so that the air cools down and consequently gets a higher density. As a result the temperature of the air parcel will decrease with height at a rate of 0.01°C m^{-1} if there are no other processes that influence the temperature. If an air parcel is moved downward rapidly its temperature will due to the same mechanism increase with 0.01°C m^{-1}. In that case the air parcel will get a lower density. Parcels that are lifted upward or downward will show this temperature change if their movement is relatively fast, so that no other mechanisms can influence their temperature. Ideally one would expect a temperature gradient of -0.01°C m^{-1} in the atmosphere. But over longer time periods other processes than expansion/compression, like solar radiation, cooling due to long wave radiation from the air ("radiative cooling"), condensation of water vapour to clouds or evaporation of clouds may lead to vertical temperature gradients in the real atmosphere that deviate from the theoretical gradient of -0.01°C m^{-1}.

Stable atmosphere

Is the vertical temperature gradient in the real atmosphere less than -0.01°C m^{-1}, then a rising air parcel (of which the temperature still changes with -0.01°C m^{-1}) will become colder and hence more dense than the surrounding air and will show a tendency to move downward to the level where it came from. If an air parcel is forced to move downward in the same situation it will become warmer and hence less dense than the surrounding air and will show a tendency to move upward to the level where it came from. In such a situation the vertical movements, e.g. generated by mechanical turbulence are suppressed and the atmosphere is called "stable". This situation occurs often in a cloudless atmosphere during night time, when the air close to the surface is cooled down because it looses its energy by radiation. In such an atmosphere there is not much turbulence at all.

Temperature inversion

An extreme case is where the temperature in the real atmosphere increases with height ("temperature inversion"). Vertical movements are then suppressed so much that there is almost no exchange across the inversion and the wind speed at either side of the inversion can differ much.

Unstable atmosphere

Is the vertical temperature gradient in the real atmosphere more than -0.01°C m^{-1}, then a rising air parcel of which the temperature still changes with -0.01°C m^{-1} will become warmer and hence less dense than the surrounding air and will continue to rise and even accelerate, until it reaches a part of the atmosphere where the vertical temperature gradient is less than -0.01°C m^{-1}. If in the same situation an air parcel is forced to moved downward it will become colder and hence more dense than the surrounding air and will continue to move downward and even accelerate, until it reaches a part of the atmosphere where the vertical temperature gradient is less than -0.01°C m^{-1} or it reaches the surface. In such a situation the vertical movements generated by e.g. mechanical turbulence are stimulated, and mixing up to larger heights occurs. The atmosphere is called “unstable” in such situations. This situation occurs often in a cloudless atmosphere during daytime in the summer, when the earth’s surface is warmed up by radiation and warm “air bubbles” rise from the surface and can even rise so high up that they lead to formation of cumulus clouds. In this situation thermal turbulence is important.

Neutral atmosphere

In a neutral atmosphere the temperature gradient is -0.01°C m^{-1} and mechanical turbulence dominates. This situation occurs often when it is cloudy and windy. In Western Europe the atmosphere is much more frequently neutral or nearly neutral than stable or unstable. For that reason most examples that are presented in this report are for a neutral atmosphere.

Effect of stability on diffusion

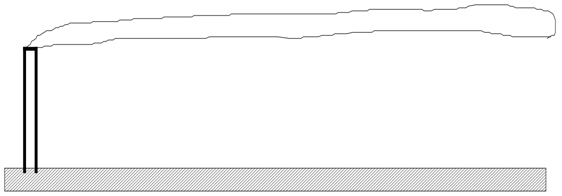
Atmospheric stability has an effect on diffusion. The effect of atmospheric stability on diffusion in the vertical for an elevated point source is illustrated by Figure 4.

Diffusion in a stable atmosphere

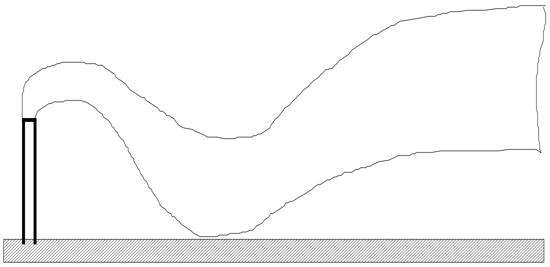
In a stable atmosphere the plume is narrow and can be observed at long distances from the chimney, because the diffusion is reduced and consequently the plume is not diluted much. Usually the wind speed is relatively low in a stable atmosphere and the variation in wind direction can be relatively large. The plume is said to be “fanning”. In the case of a ground-level source, like a field after application of pesticides, the plume is also very narrow and the concentration is relatively high close to the ground.

Diffusion in an unstable atmosphere

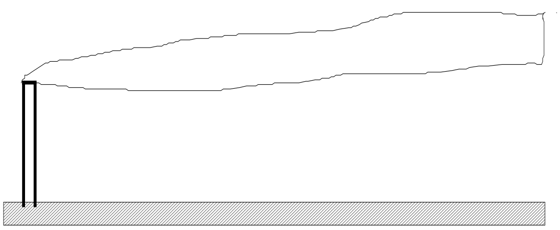
In an unstable atmosphere there are strong vertical movements. This does not only lead to faster diffusion and dilution, but causes also to plume to reach the surface at a relatively short distance from the chimney. The plume is said to be “looping” in this case. In the case of a ground-level sources the average concentration at ground-level is relatively low compared to the stable case, but at some distances during a short time relatively high concentrations can be observed.



a. Stable atmosphere.



b. Unstable atmosphere.



c. Neutral atmosphere.

Figure 4
The influence of atmospheric stability on the vertical mixing of a plume.

Indflydelse af atmosfærisk stabilitet på vertikal opblanding af en røgfane.

Diffusion in a neutral atmosphere

In the neutral atmosphere the plume is somewhat wider than in a stable at mosphere, is better mixed and cannot be observed over such long distances because it is diluted more rapidly by diffusion. In this case high concentrations are not observed close to the source as is the case in an unstable atmosphere. The plume is said to be "coning" in this case.

Figure 4 illustrates that it is important to take atmospheric stability into account when describing atmospheric diffusion. Atmospheric stability also influences the exchange between the surface and the atmosphere. The higher up in the atmosphere, the more important it is to take atmospheric stability into account when describing the exchange between the surface and that height.

Wind speed profile

As mentioned previously, the wind speed near the surface is retarded by friction at the surface. By how much, will depend on the surface roughness. The wind speed at above about 500 m is generally not influenced by the surface, but at lower heights it is influenced. At about 60 m height the wind speed is influenced more by the surface roughness of a larger area (about 5×5 km^2). At lower height the wind speed is more influenced by the local surface roughness.

Wind speed profile in a neutral atmosphere

Measurements of the wind speed as a function of height have revealed that the wind speed increases with the logarithm of the height:

$$u(z) = \frac{u_*}{\kappa} \ln\left(\frac{z}{z_{0m}}\right) \qquad (6)$$

where u(z) is the wind speed (m s^{-1}) at height z (m); z_{0m} is the surface roughness length (m) and is the extrapolated height at which the wind speed is 0, z_{0m} is of the order of 1/10th of the height of the obstacles (vegetation, trees etc.); u_* is the friction velocity (m s^{-1}) and is a measure of mechanical turbulence; κ is the von Karman's constant $\approx$ 0.4 (dimensionless). With this equation it is possible to calculate the wind speed at one height from the wind speed at another height if the surface roughness is known. The wind speed profile can be described with the same type of function for stable and unstable conditions. It has then to be corrected somewhat so that the non-neutral situation is described correctly (Arya, 1988).

Surface roughness

In Table 1 values for the surface roughness length are presented for different surfaces.

Table 1
Surface roughness length of different surfaces (Stull, 1988).

Ruhedshøjder for forskellige overflader (Stull, 1988).

Surface	Surface roughness length (m)
Ice, mud flats	0.00001
Open sea at wind speed of 3 m s^{-1} [a)]	0.00005
Snow covered flat or rolling ground	0.00006
Open sea at wind speed of 10 m s^{-1} [a)]	0.0003
Cut grass (~ 0.03 m high)	0.006
Long grass, crops	0.04
Farmland incl. some trees	0.25
Forest	1.00
Centres of cities	2.00

[a)] The surface roughness of the sea depends on the wind speed, see (7).

It should be noted that the surface roughness is not constant in agricultural areas, but depends on the heights of the crops, which vary during a year. The surface roughness length for the open sea is not constant either, but is a function of the wind speed (Lindfors et al., 1991):

$$z_{0m} = \frac{0.13\nu}{u_*} + \frac{0.0144 u_*^2}{g} \tag{7}$$

where ν is the kinematic viscosity of air (~ 1.5x10^{-5} m^2 s^{-1}) and g is the gravitation (9.81 m s^{-2}). In the wind speed range of 0-3 m s^{-1} the roughness length decreases with wind speed, for larger wind speeds the roughness length increases, mainly because the wave height increases.

Effect of surface roughness on wind speed profile

The surface roughness varies with the nature of the terrain. For that reason the wind speed near the surface will be a function of the surface roughness. This means that under the same meteorological conditions (i.e. same wind speed at greater height) the wind speed near the surface will be different for e.g. bare soil, crops, forest and water. The friction velocity u_*, which is a measure of the mechanical turbulence, is in that case larger for a more rough surface like a crop than for bare soil. As a result the wind speed near the surface will decrease with surface roughness. Figure 5 shows some vertical wind profiles for two different surfaces under neutral conditions: a crop and an almost bare soil. The surfaces are chosen so that they represent typical situations encountered in agricultural areas on or near fields where pesticides are applied.

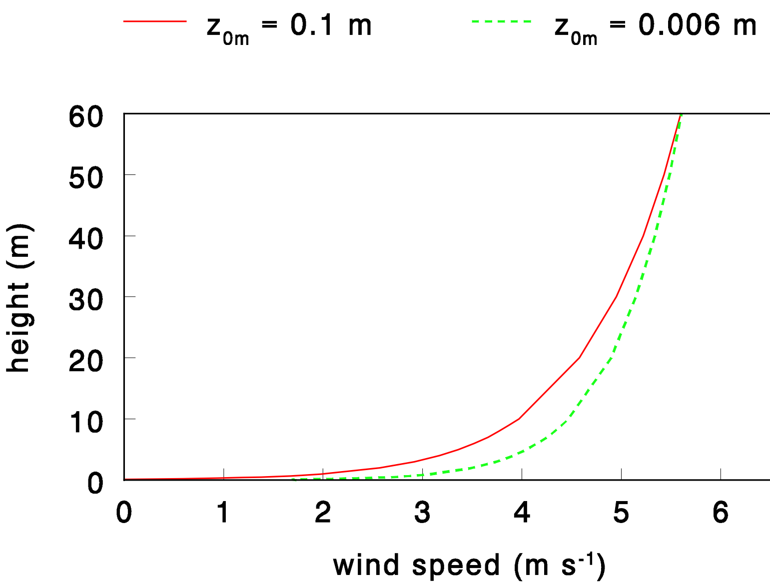


Figure 5
Vertical wind speed profile over a crop with a surface roughness length of 0.1 m and almost bare soil with a surface roughness length of 0.006 m. It is assumed that in both cases the wind speed at 60 m height is the same.

Vertikal vindhastighedsprofil over en afgrøde med en ruhedshøjde på 0,1 m og næsten bar jord med en ruhedshøjde på 0,006 m. Det er antaget, at vinhastigheden i 60 m højde er det samme i begge tilfælde.

Effect of wind speed profile on atmospheric transport

The existence of a wind speed profile influences the average speed at which a released compound is transported in the atmosphere. At some distance from the source part of the released compound has been transported upward by diffusion and encounters a higher wind speed than near the surface. This means that the average speed at which a compound is transported increases with the distance to the source until it is mixed over the whole mixing layer (see below).

Effect of surface roughness on atmospheric transport

Figure 5 shows that the wind speed is higher in the case of the bare soil. This means that a compound released from a field with almost bare soil is transported at a greater speed, than a compound released from a field with a crop. At some distance from the released point, however, this difference is not any longer so large, because the air has been transported over areas with other surface roughness lengths. Moreover, the compound is then transported higher up in the atmosphere where the wind speed is less influenced by the surface.

Wind direction profile

Not only the wind speed is influenced by the presence of the surface, but also the wind direction. Usually the wind direction is veering with height in the Northern Hemisphere. This means that the origin of the air at greater heights is different from that at ground-level.

Mixing height

In some parts of the atmosphere stable layers may exist, where vertical air movements are suppressed. This means that air originating from below cannot be transported across this layer and this layer is than functioning as a “lid” on the atmosphere below, where mixing can occur. Air from above this layer can also not be transported downward. In case of tall stacks that emit pollution above this lid, this is a favourable situation, because the pollution cannot reach the earth’s surface where humans live. In case of emission of pollution from low or ground level

sources, as is the case for pesticides, this is an unfavourable situation, where very high concentrations can occur near the ground. This can especially be the case during night time when temperature inversions close to the ground are observed frequently.
The “mixing layer” is the layer nearest to the earth’s surface where mixing takes place. It is bounded by the surface and the first layer where vertical movements are suppressed. The height of the mixing layer is called “mixing height”, It is important to know the mixing height, at least when transport of pollutants at some distance from the source has to be described, because the pollution plume may then have come so wide that it has reached the mixing layer height. Further dilution in the vertical is then not any longer possible and this will influence the concentrations at the surface.

The mixing height shows large diurnal variations. During a cloudless night, radiative cooling may cause the temperature near the surface may to drop so much that a temperature inversion is observed. As we have seen before this leads to high concentrations at ground-level near low sources. If the atmosphere is also cloudless after sunrise the next day, the earth’s surface will be heated and the inversion disappears. Also wind can have an effect on the mixing height. If there is much wind during a cloudless night, the air is well-mixed and air that is cooled down near the surface is transported upward so that the mixing height will not be close to the surface. It must be noted here that water bodies (lakes, seas) do not show the large diurnal temperature variations as the upper layer of the soil. For that reason the mixing height over sea will generally be different than over land.

During night time the mixing height is often below 200 m, whereas it is often higher than 500 m during day time. If the atmosphere is very unstable the mixing height can be indefinite (i.e. over 2000 m).

For neutral and stable conditions there is a relation between the friction velocity and the mixing height:

$$z_{mix} = \frac{c_1 u_*}{|f_{cor}|} \tag{8}$$

where z_{mix} = mixing height (m); c_1 = a constant; f_{cor} = Coriolis parameter (s^{-1}) and is given by 2Ωsin(lat), where Ω = angular velocity of the earth (radians s^{-1}) and lat = latitude (radians), for a latitude of 50° N the f is 1.11×10^{-4} s^{-1}. Van Jaarsveld (1995) uses a value of 0.08 for c_1. This value is chosen so that reasonable results are obtained for compounds that are transported over long distances. It should be noted, that other scientists use different values. In the short range dispersion model OML developed at the National Environmental Research Institute, Roskilde, Denmark a value of 0.25 is used for c_1 (Berkowicz, National Environmental Institute, Roskilde, Denmark, personal communication). The reason for using this much higher value is that otherwise observed concentrations near power plants with high stacks cannot be reproduced by the OML model. So there is considerable uncertainty in the function for the mixing height. Equation (8) shows that the mixing height increases with the friction velocity u_*, i.e. with the wind speed. As u_* also depends on the surface roughness, the mixing height is in principle a function of the surface roughness. This is, however, not a local surface roughness, but a surface roughness of the whole landscape as “seen” from the mixing height.

The mixing height under unstable conditions can only be found from measurements (vertical temperature profile) or from a more complicated model that describes the development of the mixing height during the day as a function of e.g. solar radiation.

Atmospheric diffusion near a point source

The diffusion near a point source produces a normally distributed time-averaged concentration perpendicular to the plume axis. Such a Gaussian distribution can be described with a standard deviation, just as the normal distribution used in statistics. In this case, however, the standard deviation is not constant, but is a function of the distance to the source. As there is diffusion in all directions, the concentration can be described with a normal distribution in all directions. If the point source is continuous, the diffusion in the wind direction can be neglected, because the effect of diffusion at subsequent time steps will compensate each other in this case. Figure 6 illustrates how the concentration distribution at ground-level as a function of distance from a point source looks like. It can be seen that the plume becomes wider and the maximum concentration lower as a function of the distance to the source. In this case the x direction is parallel to the wind direction (the wind blows from left to right), the y direction is in the horizontal perpendicular to the wind direction. On the vertical axis the concentration is shown.

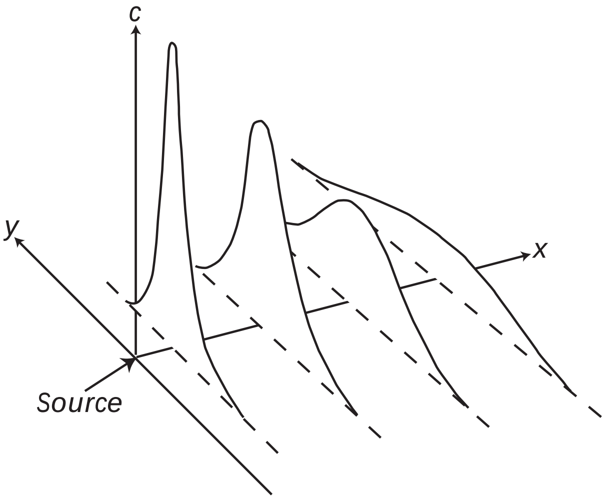


Figure 6
Ground-level concentration due to a point source for several downwind cross-wind sections.

Koncentration i jordniveau på tværs af vinden i forskellige afstande fra en punktkilde.

Mathematical description

The diffusion of airborne material from a point source can be described mathematically with the Gaussian distribution:

$$c(x,y,z) = \frac{Q}{2\pi\bar{u}\sigma_y(x)\sigma_z(x)} e^{-\frac{y^2}{2\sigma_y(x)^2}} \left[e^{-\frac{(z-h)^2}{2\sigma_z(x)^2}} + e^{-\frac{(z+h)^2}{2\sigma_z(x)^2}} \right] \qquad (9)$$

In this model it is assumed that the wind direction is parallel to the x axis, that the y axis is perpendicular to the plume axis in the horizontal direction, and that the z axis is perpendicular to the plume axis in the vertical direction. The coordinate system starts at ground level at the position of the point source (there x,y and z are 0); c(x,y,z) is the concentration (kg m^{-3}); Q is the source strength (kg s^{-1}); $\bar{u}$ is the average wind speed at stack height (m s^{-1}); h is the stack height (m), $\sigma_y(x)$ and $\sigma_z(x)$ are the standard deviations of the concentration distribution in the y and z direction (m). The second exponential function within the brackets results from reflection of the plume at the earth's surface. c(x,y,z), $\overline{u}$, $\sigma_y(x)$ and $\sigma_z(x)$ should reflect the same averaging time. The standard deviations of the concentration $\sigma_y(x)$ and $\sigma_y(x)$ are determined experimentally and depend on meteorological conditions (atmospheric stability), surface roughness, averaging time and to some extent on the source height.

Standard deviations for concentration

For neutral conditions $\sigma_y(x)$ (m) and $\sigma_z(x)$ can be described by estimates of Briggs for a rural situation (equations (10) and (11); Pasquill and Smith, 1983).

$$\sigma_y(x) = \frac{0.08x}{\sqrt{1 + 1.0 \times 10^{-4}x}} \tag{10}$$

$$\sigma_z(x) = \frac{0.06x}{\sqrt{1 + 1.5 \times 10^{-3}x}} \tag{11}$$

It should be noted here that these equations are, in fact, only valid for elevated releases. The values for surface releases can be up to a factor 2 larger. $\sigma_y(x)$ and $\sigma_z(x)$. For other than neutral conditions there are also equations for $\sigma_y(x)$ and $\sigma_z(x)$ available (Pasquill and Smith, 1983).

Figure 7 and equation (11) show how $\sigma_z(x)$ increases as a function of distance to the source. Close to the source it increases linearly with x and at greater distance proportionally with $\sqrt{x}$. This is important to notice, because that means that the diffusion close to a source is not the same as the diffusion at some distance from the source.

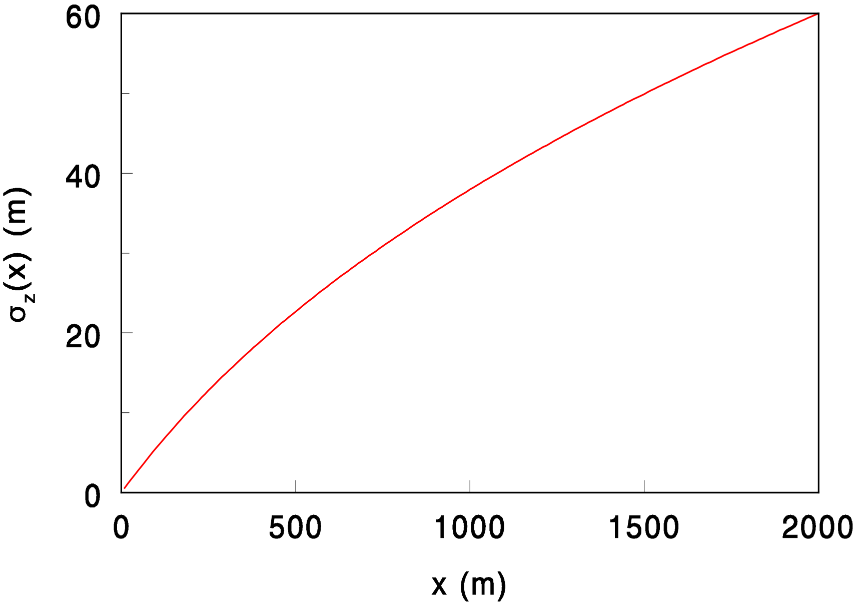


Figure 7
Standard deviation for concentration in the vertical ($\sigma_z(x)$) according to Briggs as a function of distance to a point source.

Standardafvigelse for koncentrationen i vertikal retning ($\sigma_z(x)$) i følge Briggs som en funktion af afstanden til en punktkilde.

Area source

A field onto which pesticides have been applied does not act as a point source, but as an area source because the whole area is covered with pesticides. The diffusion from an area source can be described in the same way as the diffusion from a point source. For that reason it can be simulated in a model by putting many small point sources on the field. Another method to simulate an area source in a model is by using one point source that is at such an upward distance from that $\sigma_y(x)$ has the same width at the position of the field in the model as the field itself ("virtual point source"). These approaches give good results at some distance from the field, but near the field and especially on the field itself they do not give an accurate description.

K-model

There exists another type of diffusion model, a so called "K-model". In such a model the atmosphere is divided into cubic air parcels and the diffusive transport between these air parcels in all directions is described with so called "eddy diffusivity coeffcients". We will here only focus on the diffusion in the vertical, which is described in the following way: The atmosphere is divided into vertical layers. Between these layers the diffusion is described by an eddy diffusivity coefficient ($m^2\ s^{-1}$), which for a neutral atmosphere is:

$$K_{Heat}(z) = \kappa u_* z \qquad (12)$$

From the equation it can be seen that the $K_{Heat}(z)$ increases with height. This assumption is, in fact, not entirely correct as $K_{Heat}(z)$ decreases short before the mixing height is reached, but the above equation leads nevertheless to good simulations of ground-level concentrations. It can be seen from (12) that $K_{Heat}(z)$ is a function of the friction velocity u_*. This type of model is called a K-model, because it uses eddy diffusivity coefficients K to describe the diffusion. For other than neutral conditions (12) can still be used, but then some corrections have to be made.

Difference between a K-model and a Gaussian plume model

It should be noted, that there is a difference in how a K-model and a Gaussian plume model describe the diffusion as a function of distance to the source. The results of a K-model for which $K_{Hear}(z)$ does not vary with height as in (12) behaves in the same fashion a Gaussian plume model for which the $\sigma_z(x)$ increases is everywhere with $\sqrt{x}$. This is different from the description of a real plume, where $\sigma_z(x)$ increases with x close to the source and with $\sqrt{x}$ at greater distance. If a K-model is applied where $K_{Heat}(z)$ increases with height the diffusion will increase with distance to a ground-level source. The reason is that an increasing fraction of the released compound is transported upward, where the diffusivity is greater than near the surface. This effect will be enhanced if also the wind speed is made a function of the height. So the approach in the two types of models is different and for that reason they will also give somewhat different results.

A K-model can adequately describe area sources and even concentrations within the area source (a field onto which pesticides are applied) can be modelled well. Gaussian plume models are not able to describe concentrations within area sources well. A K-model can also better handle dry deposition, i.e. deposition that takes place at the surface (see also the next section). As a result of dry deposition the concentration near the surface decreases, which is more difficult to reproduce with a Gaussian plume model.

Effect of surface roughness on diffusion

Equation (12) shows that the diffusion depends u_*. As was noted before u_* increases with surface roughness. Consequently the diffusion increases also with the surface roughness.

1.4 Surface exchange

Exchange of material between the atmosphere and the surface is caused by eddies in the atmosphere. The simplest way of describing the process is using a “big leaf model”. In this model the surface is treated as one big leaf on a tree and not as a very complicated surface with differences in surface properties as in reality.

Big leaf model

The transport is considered to consist of three distinct steps. These steps can be described with resistances in series by analogy with electrical circuits. The first part is the transport by turbulent diffusion from a certain height in the atmosphere (reference height) to a very thin (~ 1 mm) layer just above the surface. The resistance belonging to this part is called aerodynamic resistance (r_a). The second part of the transport is through the thin layer. In this layer the flow is laminar (= not turbulent) and the transport has to occur by non-turbulent diffusion. For gases this is the molecular diffusion, for small particles this is the Brownian diffusion. For larger particles inertial and gravitational effects become important, the latter characterised by the settling velocity. The thin layer is called laminar boundary layer and the resistance is called laminar boundary layer resistance (r_b). Then the material arrives at the surface. The properties of the surface: solubility, reactivity/degradation, transport velocity into the surface determine how much of the material that arrives at the surface is taken up. This resistance associated with this step is called surface resistance (r_c). It is in fact an over-all resistance category describing many processes. The best thing to do is, in fact, not to use just a value for the surface resistance in the big leaf model, but to model the surface resistance by modelling all relevant processes that take place in the surface. In that way it is also possible to understand the underlying mechanisms and to model e.g. temporal variations in the surface resistance. This is especially necessary for pesticides, because there are no measurements of the exchange of pesticides between the atmosphere and the surface and because some pesticides can be re-emitted once they have been deposited. If models that describe the fate of pesticides in soil, vegetation and water bodies are coupled to models for the atmospheric part of the exchange, it will be possible not only to model deposition, but also emission from e.g. bare soil, crops etc.

Big leaf model for gases

Figure 8 shows the big leaf model for gases, which describes the dry deposition to land surfaces. Highly soluble/reactive gases like nitric acid (HNO_3) are immediately taken up by the surface, the surface resistance will be negligible and the over-all transport is determined by the aerodynamic and laminar boundary layer resistance. An inert gas like helium (He) is not at all taken up in the surface. The surface resistance will in that case be indefinitely large and determines the over-all transport: although He is transported to the surface it is also transported from the surface so that no net transport occurs. We can conclude that the exchange velocity depends both on the properties of the gas and the properties of the surface and that depending on theses properties either the atmospheric processes (characterised by the aerodynamic and laminar boundary layer resistance) dominate the velocity or the surface processes or both.

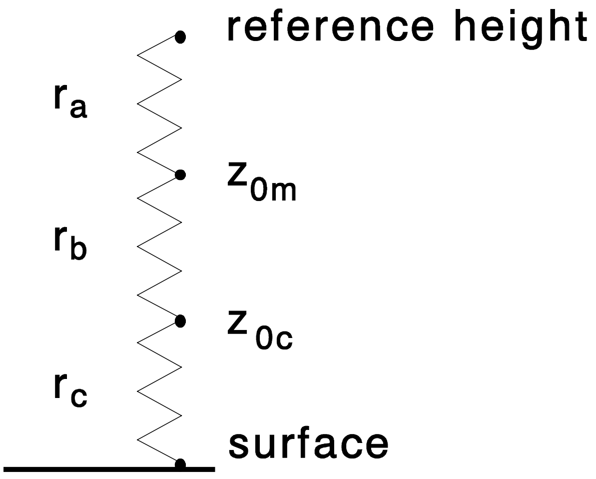


Figure 8
"Big leaf" model for dry deposition of gases.

"Big leaf" model for tørdeposition af gasser.

Aerodynamic resistance for gases and particles

The aerodynamic resistance is the same for gases and particles. For neutral conditions it is given by:

$$r_a = \frac{1}{\kappa u_*} \ln\left(\frac{z_r}{z_{0m}}\right) \tag{13}$$

where r_a = the aerodynamic resistance (s m^{-1}) and z_r is the reference height (m). Equation (13) shows that r_a decreases with u_*. This means that the exchange increases with u_* and therefore also with the wind speed. This way of expressing the exchange gives exactly the same results as the eddy diffusivity concept presented in the previous section. The same type of function but then with correction factors can be used to describe the aerodynamic resistance for other than neutral conditions.

Laminar boundary layer resistance for gases

For gases the laminar boundary resistance is given by Hicks et al. (1987):

$$r_b = \frac{2\left(\frac{Sc}{Pr}\right)^{\frac{2}{3}}}{\kappa u_*} \tag{14}$$

where r_b = laminar boundary layer resistance (s m^{-1}); Pr = Prandtl number (dimensionless = 0.72); Sc = Schmidt number (dimensionless) which can be found from $Sc = \nu/D_g$, where ν = kinematic viscosity of air ($m^2\ s^{-1}$) and D_g is the diffusivity of the gas in air ($m^2\ s^{-1}$). Sc is not a function of temperature, so for ν and D_g the values for 25° C can be taken; ν at 25° C is $1.55 \times 10^{-5}\ m^2\ s^{-1}$ and D_g depends on molecular mass of the gas. The larger the molecule the smaller the diffusivity, because large molecules do not move so fast. If D_g is not known, it can be estimated by:

$$D_g = \frac{1.05\text{x}10^{-4}}{\sqrt{M_g}} \tag{15}$$

where D_g is in $m^2\ s^{-1}$ and M_g is the molecular mass of the gas (g mol^{-1}). This description of r_b is still somewhat uncertain. It is important to note that pesticides have much higher molecular masses (typical 200-300 g mol^{-1}) than more frequently studied atmospheric gases. Equations (14) and (15) show us that r_b decreases with the molecular mass of the compound that is exchanged.

Gaseous flux

The exchange of gases between the atmosphere and the surface depends on both the concentration in the atmosphere and the concentration in the surface and is given by:

$$F_g = v_e(c_{g,air} - c_{g,surf}{}^*) = -\frac{1}{r_a + r_b}(c_{g,air} - c_{surf}{}^*) \tag{16}$$

where F_g = flux (kg $m^{-2}\ s^{-1}$), which is by definition negative if the material is removed from the atmosphere; v_e is the exchange velocity (m s^{-1}) and is equal to $1/(r_a + r_b)$; $c_{g,air}$ is the concentration of the compound in the air at reference height (kg m^{-3}); $c_{g,surf}{}^*$ is the (theoretical) gas phase concentration in the surface. If the gas phase concentration in the surface is not known it can be calculated from the concentration in the water phase and the Henry's law coefficient: $c_{g,surf}{}^* = Hc_w$, where c_w is the water phase concentration (kg m^{-3}). If $c_{g,air}$ is larger than $c_{g,surf}{}^*$ dry deposition will occur. If $c_{g,surf}{}^*$ is larger than $c_{g,air}$ emission will occur. Pesticides like lindane can be re-emitted after being dry or wet deposited. So it is important that both ways can be described, but then processes in the surface that influence the concentration in that surface should be described as well. Both r_a and r_b decrease with u_*. This means that the flux increases with wind speed.

For compounds for which reemission is not important and for which the surface resistance has been measured (or can be modelled), the flux is described by:

$$F_g = -v_d c_{g,air} = -\frac{1}{r_a + r_b + r_c} c_{g,air} \tag{17}$$

In this equation v_d is the dry deposition velocity (m s^{-1}), which is equal to $1/(r_a + r_b + r_c)$; r_c is the surface resistance (s m^{-1}). In this case not only atmospheric processes are described as with (16), but also surface processes. The flux increases also in this case with the wind speed. It should be noted here that both r_a and r_b are a function of the wind speed, but r_c is not. If the surface resistance r_c is small compared to r_a and r_b (almost all material is taken up by the surface) the flux increases relatively much with wind speed. If the surface resistance r_{vc} is relatively large, the flux does not increase much with wind speed.

Dry deposition to the sea

The exchange of gases between the atmosphere and water surfaces depends on turbulence in the air, solubility of the gas,and also on the turbulence in the water (Liss and Slinn, 1983; Asman et al., 1994). As this deposition is beyond the scope of this report it will not be discussed here.

Maximum dry deposition velocity for gases to land surfaces

As can be seen from (17) the dry deposition velocity v_d has a maximum value if the surface resistance r_c is 0, i.e. the dry deposition velocity is then totally determined by the atmospheric processes. This maximum dry deposition velocity will be a function of the friction velocity, which can vary appreciably. The friction velocity depends on the wind speed at greater height and the surface roughness. It is possible, however, to calculate an average maximum dry deposition velocity for a area and surface roughness. For Danish conditions this average maximum dry deposition velocity will be of the order of 2×10^{-2} m s^{-1} for cropland (surface roughness length of 0.1 m) and of the order of 4×10^{-2} m s^{-1} for forests (surface roughness length of 1 m). Assuming that the concentration of the compound is the same everywhere over a mixing height of 500 m, only 13% and 25% of the compound is removed after 1 hour with dry deposition over cropland respectively forests (22). This shows that dry deposition is not a fast process, even not for the fastest depositing gas. The only exception is close to a low source where the compound is not yet mixed over the whole mixing layer and the concentration is relatively high for that reason.

Determination of the uptake rate by dry deposition of gaseous compounds in the laboratory

The dry deposition velocity for many organic compounds, like pesticides, is not so high and is more determined by the processes that play a role in the surface. This gives the possibility to study uptake by dry deposition in the laboratory, where it is difficult to generate realistic atmospheric turbulence. The only condition is then that there is enough turbulence in the experiment, created e.g. by a ventilator, that the diffusion in the atmosphere does not limit the uptake rate. In that case the uptake rate is only determined by processes in the surface. These processes in the surface are diffusion into the surface, adsorption and degradation. For water also mixing in the water itself plays a role. The uptake rate will not be constant in such experiments, but will decrease with time because the surface gets saturated with the pesticide.

Duyzer and van Oss (1997) performed laboratory experiments where they measured the uptake rate of organic chemicals by soil, fresh water, sea water and by grass as a function of time. They developed also simple models for uptake as a function of time and were in most cases able to obtain reasonable agreement between modelled and measured uptake rates.

Effective dry deposition velocities for soils for field conditions can be obtained by using the model developed for the laboratory experiments and then taking into account the occurrence of precipitation. The uptake rate by dry deposition in the field also decreases also with time due to saturation, just as in the laboratory. Rainfall will wash down compounds that are for a large part present dissolved in soil water. The surface will then become less saturated and can then again take up gas at a higher rate. In some cases also re-emission will occur. A more complicated of this type was presented by van Jaarsveld (1996). Van Pul et al. (1998) give also some useful parameterizations taking the degradation rate in the surface into account.

Big leaf model for particles

Particles of many different sizes are found in the atmosphere. Most particles are so small that gravitational settling is negligible compared to the vertical transport caused by turbulent diffusion in the atmosphere. As a result, most particles are transported and diffused in the atmosphere in the same fashion as gases. Once particles are deposited, they are usually not re-emitted to the atmosphere again. As a result, the surface resistance can usually be omitted in exchange models for particles, because it is zero. The dry deposition velocity is in that case given by:

$$F_p = v_d c_{p,air} = -\frac{1}{r_a + r_b} c_{p,air} \qquad (18)$$

Particles have some properties that cause their laminar boundary layer resistance to be much higher than for gases, because their transport through the laminar layer is much slower. Only very small particles with radius less than 0.1 µm, which do not contribute much to the total atmospheric aerosol mass, have reasonable Brownian diffusivities and are transported with a reasonable speed through the laminar boundary layer. For particles with a radius larger than about 1 µm, transport through the laminar boundary layer is more efficient because then impaction and interception at the surface are also important. But a large fraction of the particles has a radius between 0.1 and 1 µm and are only transported very slowly through the laminar boundary layer. The velocity at which particles are transported through the laminar boundary layer varies highly with their size an as a result the dry deposition velocity for particles varies also highly with their size. For particles with a radius > 5 µm gravitational settling is important and should be taken into account. As this mechanism is active at the same time as the other atmospheric transport mechanisms the big leaf model can be modified by adding an additional gravitational settling resistance r_{vg} to transport parallel to the other resistances (Figure 9).

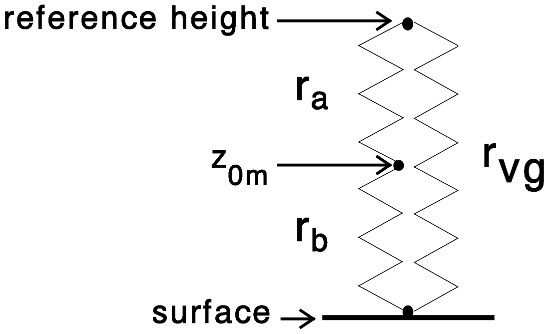


Figure 9
"Big leaf" model for dry deposition of particles over land.

"Big leaf" model for tørdeposition af partikler over land.

An important fraction of the atmospheric particles has a radius in between 0.1 and 1 µm. For these particles the laminar boundary layer resistance r_b is usually is larger than r_a and dominates the overall resistance to transport from the atmosphere to the surface. As a result the dry deposition velocity of particles is relatively low, because they do not cross the laminar boundary layer fast (Ruijgrok et al., 1995). For particles of a particular size the dry deposition velocity increases wind speed (u_*), mainly because the thickness of the laminar boundary layer is reduced. The dry deposition velocity for particles is also highly dependent on the properties of the surface. The knowledge on particle dry deposition is still insufficient.

Primitive model for dry deposition of particles to vegetation

For particles with a radius between 0.1 and 1 µm the estimated dry deposition velocity for neutral atmospheric conditions is (Erisman et. al, 1994):

$$v_d = 0.002u_* \text{ (for low vegetation)} \tag{20}$$

or

$$v_d = 0.01u_* \text{ (for forests)} \quad (21)$$

These equations show that the dry deposition velocity increases with the wind speed.

Dry deposition of particles to the sea

The dry deposition velocity of particles to the sea is generally thought to be less than the dry deposition velocity of particles to land surfaces, because the sea is relatively smooth. The deposition velocity is also influence by the fact that the particles are mostly hygroscopic, take up water and consequently grow if they come very near the water surface. Figure 10 shows how the dry deposition velocity of particles varies with particle size for various wind speeds (Slinn and Slinn, 1980).

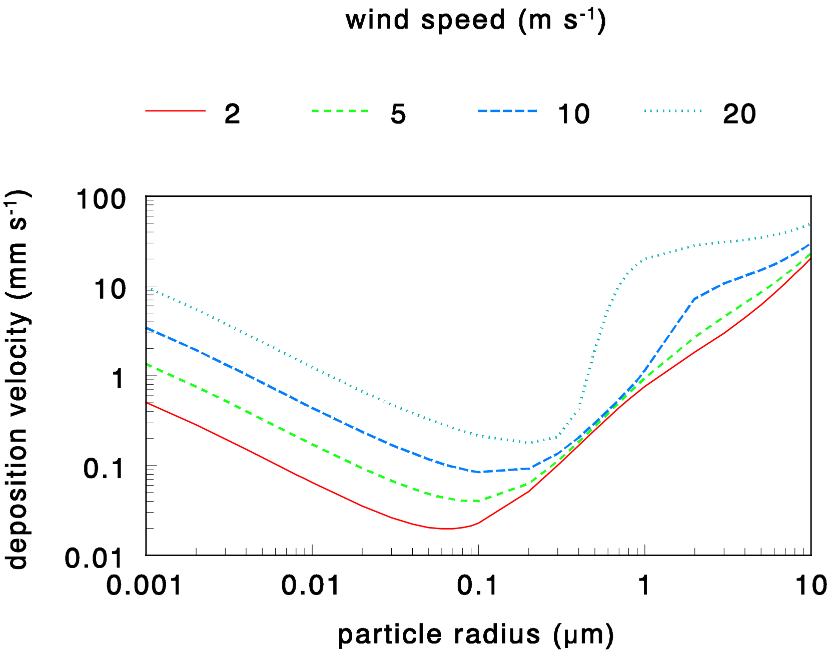


Figure 10
Dry deposition velocity of particles for sea areas as a function of size for different wind speeds.

Tørdepositionshastighed for partikler for havområder som funktion af størrelse og ved forskellige vindhastigheder.

Atmospheric lifetime of particles

As a result of the relatively low dry deposition velocity, particles have a relative long atmospheric residence time (~ 5 days). They are only removed well when they meet precipitation on their way. Particles can also coagulate and as a result larger particles are formed that are removed at another speed by dry and wet deposition than the particles they were formed of. Moreover, the pesticides bound in particles can volatilise if the particles are exposed to higher temperatures or to lower concentrations of pesticides in the gas phase.

Field measurements of the dry deposition velocity for pesticides

There almost no field measurements of the dry deposition velocity of gaseous of particulate pesticides. Some estimates have been made of the dry deposition velocity by using measured concentrations in the air and exchange models. For particles it is generally very difficult to measure the dry deposition velocity because it is so low. It has usually to be derived from very small concentration differences and the measurements are for that reason very uncertain. The same holds for the classical non-polar gaseous pesticides. But for the more soluble gases it would perhaps be possible to measure the dry deposition velocity. The dry deposition velocity of gaseous pesticides is not only determined by properties of the compound, the properties of the surface and the meteorological conditions, but also by the concentration in the surface. As a result the dry deposition velocity measured under the same meteorological and surface conditions at one site is not necessarily the same as the dry deposition velocity measured somewhere else, because the concentration in the surface can be different. For that reason it is also necessary to specify the surface concentration when a dry deposition velocity of a gaseous pesticide is reported. Only for highly soluble gases it can presumably be assumed that the concentration in the surface is so low that it has no influence on the flux and it is for that reason not necessary to report it. But most gaseous pesticides are not highly soluble.

Even in the case of highly soluble gases it is not likely that the dry deposition rate is measured continuously, because these measurements are extremely expensive. For such gases the dry deposition rate is usually estimated from a dry deposition velocity measured during a limited number of campaigns for different atmospheric conditions and continuous meteorological measurements.

Change in concentration in air due to dry deposition

If the compound is distributed homogeneously over the whole mixing layer the change in concentration c(t) due to dry deposition as a function of time t (s) is given by:

$$c(t) = c(0)e^{-\frac{v_d t}{z_{mix}}} \tag{22}$$

where v_d is the dry deposition velocity (m s^{-1}) and z_{mix} the mixing height (m). Close a source the compound will not yet be mixed over the whole mixing layer. This means that in the case of a low source the concentration near the surface can be very high and the removal rate close to the source can for that reason be much higher. In that case the change in concentration due to dry deposition will be much greater than that one derived from (22).

1.5 Intermezzo: Main conclusions on meteorology and surface exchange

In this section the information in the previous sections on meteorology and surface exchange is summarised.

Neutral atmosphere

Mechanical turbulence is generated due to friction exerted on the wind by the surface. This friction is caused by the roughness of the surface. A measure of the friction is the friction velocity. The friction velocity depends on the wind speed at greater height and the surface roughness. The friction velocity increases with the surface roughness. Under neutral atmospheric conditions the turbulence is entirely mechanical. In northwestern Europe the atmosphere is most frequently neutral. The friction velocity is a very important parameter. If influences the following:

- Wind speed. The wind speed increases with the friction velocity at one particular height (6). The wind speed itself increases with height.
- Atmospheric diffusion. The atmospheric diffusion increases with the friction velocity (12) and therefore also with the wind speed. The atmospheric diffusion increases with height in the lower part of the atmosphere.
- Surface exchange. The surface exchange increases also with the friction velocity (13,14,16,17) and therefore also with the wind speed. It does not only depend on the friction velocity, but also on processes in the surface, characterised by the surface resistance (see section 1.4). If the surface

resistance is low, the exchange is mainly governed by atmospheric turbulence, characterised by the friction velocity. In this case the surface exchange will show a relatively large increase with wind speed. If the surface resistance is high, the surface exchange will be mainly dominated by processes in the surface an will only slow a relatively small increase with wind speed. If the net flux is from the atmosphere to the surface the surface exchange is also called dry deposition. If the net flux is from the surface to the surface the surface exchange is also called emission.
- Mixing height. The mixing height increases with the friction velocity (8).

Non-neutral atmosphere If the atmosphere is stable or unstable thermal turbulence plays also an important role. The wind speed, atmospheric diffusion, surface exchange and to some extent the mixing height will in this situations also increase with the friction velocity and therefore also with the wind speed. The functions used to describe the increase are, however, somewhat modified. Under these conditions the heat and moisture flux at the surface play also a role. These heat and moisture fluxes also influence the emission of pesticides from the soil (see section 1.6). For this reason it is also important to describe these fluxes in the same fashion in the meteorological part of a pesticide surface exchange model as in the soil part of such a model.

Surface gas exchange: both directions possible The rate of exchange between the atmosphere and the surface depends on the friction velocity and on processes that occur in the surface. The direction of the flux depends on the difference of the concentration in the air and the gas phase concentration that would be in equilibrium with the concentration in the surface. If the concentration in the air is higher than the equilibrium gas concentration in the surface, the net flux will be from the atmosphere to the surface. Is the equilibrium concentration in the surface higher than the concentration in the air, net emission from the surface will occur. This is the case on a field after application of pesticides.

Highly soluble volatile pesticides can also be emitted from a field, but when they are transported to areas where no emission has taken place the surface concentration will so low that the surface can be considered as a perfect sink for these gaseous pesticides i.e. the concentration in the surface is rather low and the flux is always from the atmosphere to the surface.

For slightly soluble pesticides the surface is not a perfect sink. The concentration in the surface can be relatively high. Their net deposition flux will be lower for that reason. As a result they have a lower dry deposition velocity than highly soluble gases. Their concentration in the soil can even become so high that no net deposition occurs, but net emission. This means that they can be re-emitted again after deposition. Several cycles of dry deposition and re-emission result in a transport over considerable distances. For these pesticides is it extremely important to describe the processes in the surface in the same way as for emission (section 1.6). For slightly soluble pesticides it is possible to conduct laboratory measurements that give information on uptake by dry deposition.

Dry deposition of particles Particles are usually not re-emitted again after they have been dry deposited. The dry deposition velocity of particles depends on the friction velocity, size and properties of the particles and properties of the surface (presence of “hairs” on plants etc. It is usually much lower than the dry deposition velocity for highly soluble gases. The dry deposition velocity of particles is very different for particles of different size.

Measurements of the dry It is in principle very difficult to measure the dry deposition rate (= flux) at *deposition velocity*

all, both for gaseous as well as particulate pesticides. The only exception is presumably for highly soluble gases. In that case it is also not likely that it is monitored continuously, but that it is estimated from a limited number of measurements and continuous meteorological measurements.

Potential for long-range transport

The average dry deposition velocity cannot become higher for a certain combination of climate and surface roughness than a certain maximum value. This means for Danish conditions that after 1 hour with dry deposition 13% of the compound is removed from the air in the case of cropland and 25% in the case of forests. This indicates that there exists a general potential for long-range transport for all released compounds in the atmosphere as long as there is no precipitation. In the case of a low source the concentration near the surface can be very high and the removal rate close to the source can for that reason be much higher until the compound is fully mixed over the whole mixing layer. But even in this case there is a certain limit to the removal rate by dry deposition and a substantial part of the released compound will also be transported over long distances (see section 1.12).

1.6 Emission

The purpose of this report is only to describe the atmospheric processes related to pesticides. As we have seen in section 1.4, surface exchange (emission, dry deposition) of pesticides is also influenced by processes in or on the surface (soil, crops), which fall beyond the scope of this report. It was, nevertheless, decided to give some general information here on emission of pesticides after application to the soil and crops that include some processes in the soil and on the crops.

1.6.1 **Emission of pesticides from fallow soil**

After application of pesticides volatilisation from the soil starts. In the initial phase it is rather important to know the initial penetration depth of the pesticide as this determines the gaseous pesticides concentration in the upper layer of the soil, which drives the volatilisation (16). About this initial penetration depth not much is known. Moreover, if the soil is rather dry, drops with dissolved pesticide can just lay on the surface in stead of being adsorbed in the upper soil layer. Due to the uncertainty in these initial processes, it is difficult to model the emission of pesticides in this initial phase of the emission.

To model the emission of pesticides from fallow soil requires a description of all soil and atmospheric processes involved. In section 1.4 the exchange between the soil and the atmosphere was already discussed. So we will focus here on the description of the processes in the soil that are of importance.

Transport of pesticides in the soil

Pesticides are transported in the soil together with the solvent they are dissolved in. Moreover, transport occurs by diffusion in the soil water and in the gas phase in the soil. It should be noted that although the concentration of the pesticide in the gas phase in the soil is small, the transport by diffusion in the gas phase can nevertheless be as important as the diffusive transport in the water phase because the diffusivity of the pesticide in the gas phase is several thousand times larger than that in the water phase. The transport of pesticides in the soil is reduced by the fact that pesticides can be adsorbed onto soil particles. Pesticides compete with water for the adsorption onto soil particles. If more water is present a substantial fraction of non-polar pesticides can desorb from the soil. For that reason it is important to know the soil water content and the water transport that determines this content. The vapour pressure over an aqueous solution of pesticides is highly temperature dependent (see section 1.2.3). Due to the fact that the transport and adsorption of pesticides is influenced by water and by the temperature, volatilisation of pesticides can only be modelled if the water transport (including precipitation and evaporation) and the heat transport in the soil is modelled. When the heat transport is modelled, the temperature of the soil is known, which is not only essential to modelling of the volatilisation of the pesticide, but also to modelling of the evaporation of water from the soil. As a result a model for volatilisation of a pesticide contain a description of the following processes:

a) Transport of the pesticide dissolved in soil water including diffusion in the water phase.
b) Transport of the pesticide in gas phase in the soil by diffusion.
c) Adsorption of the pesticide to the soil particles.
d) Transformation of the pesticide in the soil.
e) Equilibrium between the pesticide in the gas phase and the water phase (Henry's law coefficient).
f) Transport of water in the soil.
g) Transport of heat in the soil.
h) Transport of pesticide from the soil across the laminar boundary layer into the atmosphere.
i) Transport of water (water vapour, rain) across the laminar boundary layer to/from the atmosphere.

Jury et al. (1983, 1984) were among the first to model the volatilisation of pesticides from the soil. Jury et al. (1984) and Spencer et al. (1988) distinguish between three categories of pesticides with regard to volatilisation from fallow soil: highly volatile pesticides, slightly volatile pesticides and moderately volatile pesticides. To which category a pesticide belongs depends on the Henry's law coefficient K_H.

Highly volatile pesticides

The volatilisation for this category of pesticides ($K_H > 2.65\times10^{-5}$) is controlled by diffusion in the gas phase in the soil. The volatilisation decreases with time, independent of the evaporation of water vapour. The pesticide is not concentrated at the soil surface.

Slightly volatile pesticides

The volatilisation of this category of pesticides ($K_H < 2.65\times10^{-5}$) is controlled by the rate at which the pesticide can diffuse through the laminar boundary layer in the atmosphere just above the soil surface. Evaporation of water causes concentration of the pesticide at the soil surface, because the pesticides are less volatile than water. The volatilisation can increase with time if evaporation of water continues. It can be expected that the emission of this category of pesticides depends rather much on the meteorological conditions, because they determine the thickness of the laminar boundary layer.

Moderately volatile pesticides

The volatilisation of this category of pesticides ($K_H \approx 2.65\times10^{-5}$) is controlled by diffusion in the gas phase in the soil if the soil humidity is low and by diffusion through the laminar boundary layer in the atmosphere just above the soil surface.

Emission of freshly applied pesticides from soil surfaces

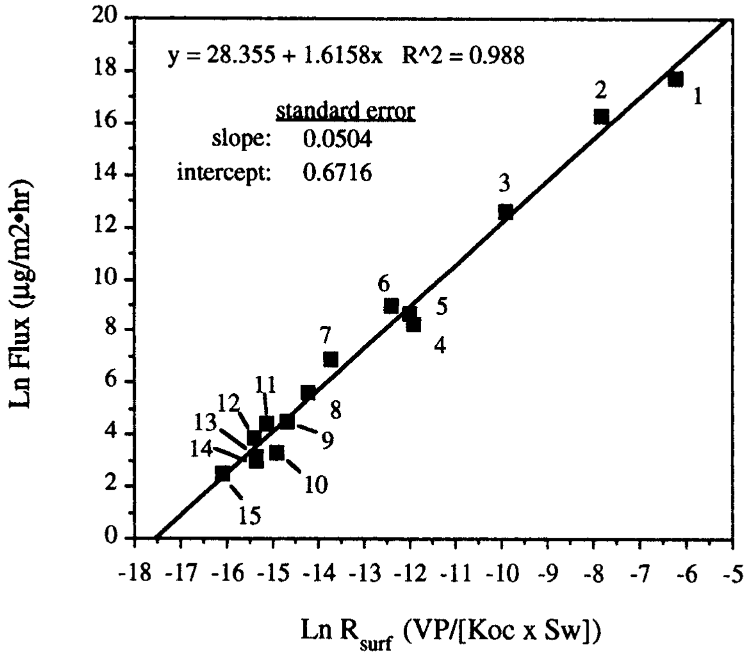
Woodrow et al. (1997) were interested in the worst case fluxes of pesticides, that often occur within a few hours after application. They were especially interested in these high values because they can be used to estimate the maximum concentrations and effects. They used published studies to derive a relation between the flux and physical and chemical properties of the compounds. They used compounds with vapour pressures that differed up to 10^7. They found the following relation (Figure 11):

$$\ln(\text{flux}) = 28.355 + 1.6158 \ln\left(\frac{VP}{K_{oc} S_w}\right) \tag{23}$$

where:

flux = flux ($\mu g\ m^{-2}\ hr^{-1}$)
VP = vapour pressure (Pa)
K_{oc} = soil adsorption coefficient (ml g^{-1})
S_w = water solubility (mg l^{-1})

It should be noted here, that VP, S_w and Henry's law coefficient K_H are related (see section 1.2.3)



1. Beacon oil
2. Chevron oil
3. Eptam
4. PCNB
5. Trifluralin
6. Fonofos
7. Lindane
8. Dieldrin
9. Chlorpyrifos
10. Diazinon
11. Atrazine
12. p,p′-DDT
13. Dacthal
14. Dacthal
15. Prometon

Figure 11
Correlation of pesticide flux from soil with chemical properties. Reprinted with permission from Woodrow et al., (1997). Copyright 1997 American Chemical Society.

Korrelation af pesticidfluxen fra jord med kemiske egenskaber.

For most experiments data were available on the application rate of the compound. So they tried to correlate the measured flux for those experiments with the properties of the compounds, but now also taking the application rate into account because it is logical to expect that the flux increases with the application rate. They found the following relation:

$$\ln(\text{flux}) = 19.35 + 1.0533 \ln\left(\frac{VP \times AR}{K_{oc} S_w}\right) \tag{24}$$

where AR is the application rate (kg ha^{-1})

It should be noted here that the uncertainty in the flux is still considerable (presumably a factor 2-3). They did not take any possible relationship with meteorological conditions (temperature, wind speed) into account as they would expect that these conditions were similar for the different studies used. This does not mean that meteorological conditions do not play an important role, it illustrates just that the flux is highly correlated e.g. the vapour pressure, because the compounds have such an extreme wide range of vapour pressures. Nevertheless, this approach can be useful to get a first estimate of a possible maximum flux.

Cumulative emission of pesticides from the soil

Smit et al. (1997) were interested in the cumulative emission from the soil after most of the pesticide had been volatilised and not in the worst case situation as Woodrow et al. (1997). They used also published experimental results to correlate the emission with physical and chemical properties. They found the following relations:

$$\mathrm{CV} = 71.9 + 11.6\ {}^{10}\log\left(100\mathrm{FP}_{gas}\right)$$

For moist soil. (25)

$$\mathrm{CV} = 42.3 + 9.0\ {}^{10}\log\left(100\mathrm{FP}_{gas}\right)$$

For dry soil.

where:
CV = cumulative volatilisation (% of dosage active ingredient).
FP_{gas} = faction of the pesticide in the gas phase in the soil.

FP_{gas} can be found from the concentration of pesticide in the soil, the volume fraction of gas in the soil, the volume fraction of moisture in the soil and the dry bulk density of the soil (see Smit et al., 1997 for further details).

1.6.2 **Emission of pesticides from plants**

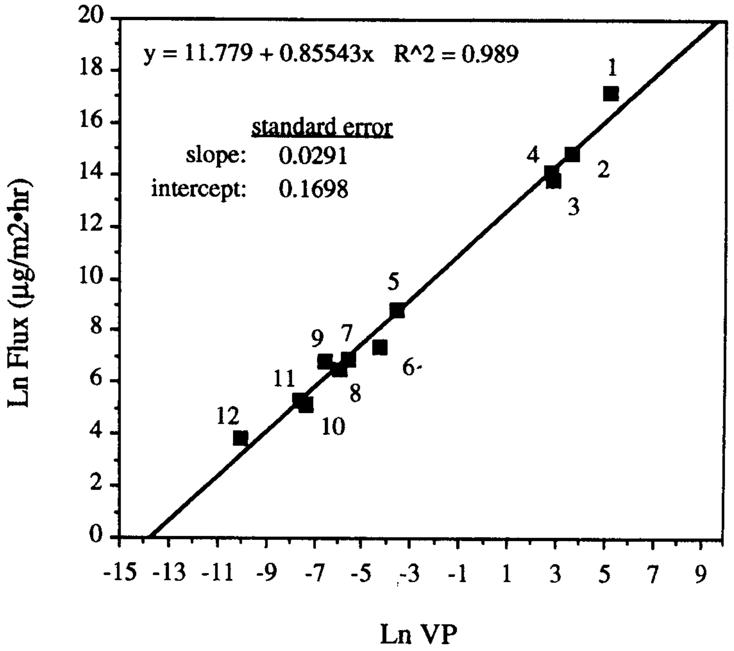
This is a more complicated case. One reason is that the pesticide is not only deposited onto the plants, but also onto the underlying soil. Other reasons are that different plants have different surfaces (wax layer, hairs, structure), that there are leaves on various heights of the plants and that they actively can take up the pesticide. Moreover, pesticides can be washed off by rain. As a result there are no real mechanistic models to calculate the emission of pesticides from plants as do exist for emission from soils.

Emission of freshly applied pesticides from plants

Woodrow et al. (1997) studied also the maximum volatilisation of pesticides from inert surfaces (glass, plastic) and from plant surfaces. It appeared that the flux from plant surfaces during this initial phase of volatilisation correlated in the same fashion with the vapour pressure as the fluxes from the inert surfaces. It was therefore concluded that plants were non-interactive, at least during the initial phase of volatilisation. This meant that they also could use the experimental data of volatilisation from inert surfaces to estimate volatilisation from plants, so that a greater data set could be used in the correlation studies. Figure 12 shows the correlation found:

$$\ln(\mathrm{flux}) = 11.779 + 0.85543\ln(\mathrm{VP}) \tag{27}$$

It should be noted here, just as in the case of volatilisation from the soil, that they find such a good correlation because they use compounds with a very wide range of vapour pressure. It does not mean that meteorological conditions do not play a role, but that the variation in the flux due to variations in meteorological conditions is much less than the variation in the flux due to variations in the vapour pressures.



1. Beacon oil
2. Chevron oil
3. Dodecane
4. n-Octanol
5. Tridiphane
6. Trifluralin
7. Pendimethalin
8. 2,4-D (iso-octyl)
9. Diazinon
10. Dieldrin
11. Toxaphene
12. p,p'-DDT

Figure 12
Correlation of pesticide flux from inert surfaces (plants, glass, plastic) with vapour pressure. Reprinted with permission from Woodrow et al., (1997). Copyright 1997 American Chemical Society.

Korrelation af pesticidfluxen fra inerte overflader (planter, glas, plastic) med damptrykket.

Cumulative emission of pesticides from plants

Smit et al. (1998) studied the cumulative volatilisation of pesticides at 7 days after application. They found the following relation:

$$^{10}\log(\mathrm{CV}) = 1.528 + 0.466\ ^{10}\log(\mathrm{VP}) \quad \text{For dry soil.} \tag{28}$$

In this equation is VP the vapour pressure in mPa.

They also found that the volatilisation was only to a minor extent influence by sorption processes in and on the leaves that are commonly represented by the K_{ow}. The volatilisation was also not very well correlated with the K_H, which indicates that the water in the pesticides drops evaporates relatively quickly and that the pure compound is left on the plant surfaces.

1.6.3 Improvement in the modelling of the emission of pesticides

Although it could be satisfactory for many purposes to estimate the initial volatilisation rate or the cumulative volatilisation by the statistical relations found by Woodrow et al. (1997), Smit et al. (1997) and Smit et al. (1998), mechanistic models are needed to better understand the underlying processes related to volatilisation. Only in this way it would be possible to get models to study the effects of a strategies to reduce the evaporation of pesticides, to study the influence of meteorological conditions on the volatilisation and to generalise the results. Measurements are needed for compounds with a wide range of properties to test these mechanistic models, because the number of experiments currently available is limited.

1.7 Removal of material by precipitation

Airborne material can be removed from the atmosphere by precipitation processes. This is called "precipitation scavenging”. It is an overall term, which covers the result of many different processes. Some of these processes will be discussed here.

1.7.1 Cloud physical processes

Cloud formation

The atmosphere contains aerosol particles, each of which consists of a variety of compounds, that can vary with particle size. Most aerosol particles contain hygroscopic substances. When the relative humidity is more than 40%, aerosols contain at least 30% water by weight. When the relative humidity increases, more water vapour condenses onto the aerosols and cloud droplets are formed. In this way aerosols act as “condensation nuclei” and as a result the compounds originating from the aerosols can be found in the cloud droplets. Cloud droplets are so small that they have small fall velocities compared to the vertical wind speed in the cloud. As a result many of them remain airborne. If they come outside a cloud, where the relative humidity is less than 100% they will evaporate in a few seconds. Cloud droplets can also take up gases. Table 2 gives some characteristic properties associated with different cloud types (Cotton and Anthes, 1989). It should be noted that the values can vary much within a cloud type and that there are not only droplet of one size in a cloud, but droplets of a whole range of sizes.

Table 2
Some characteristic properties of different cloud types.

Nogle karakteristiske egenskaber for forskellige skytyper.

Cloud type	Vertical wind speed in the cloud ($m\ s^{-1}$)	Liquid water content of the cloud ($10^{-6}\ m^3$ water/m^3 cloud)
Fog	0.01	0.2
Stratus/stratocumulus	0.1	0.05-0.25
Cumulus (humilis/mediocris)	3	0.3
Cumulus congestus	10	0.5-2.5
Cumulonimbus	30	1.5-4.5

Clouds as reactors

Most clouds will never give any precipitation. Their droplets will evaporate and the compounds present in the drops will remain as aerosols and gases. It is estimated that this cycle is repeated on the average about ten times before the content of the drops reaches the earth’s surface in the form of precipitation. Compounds present in the cloud droplets can react with each other. In that sense are clouds chemical reactors.

Precipitation formation Cloud droplets are very small, they have radii of 1-100 μm. Raindrops have a radii of 100-2500 μm. This means that about a million cloud droplets need to find each other to form one raindrop. Precipitation can already be formed relatively shortly (0.3-1 hours) after the first cloud has been formed. So there must be a very effective process leading to precipitation formation.

Warm clouds Cloud droplets of different sizes, have different inertia and may collide due to turbulence in the cloud to form a larger droplet. In the tropics this process can lead to precipitation, because the number of droplets is larger in these areas is larger than in the midlatitudes. This process is, however, not so effective that it can explain formation of precipitation in the midlatitudes. It can maybe lead to some drizzle, but not to significant amounts of precipitation.

Cold clouds Most clouds that give precipitation in the midlatitudes extend to heights where the temperature is below 0°C. At these heights water is "undercooled", i.e. it is still liquid and not frozen. This occurs at temperatures > - 15 °C. It is apparently difficult to start formation of ice crystals in the very clean water in the clouds. Some types of aerosols consisting of unsoluble material (soil particles or particles that originate from plants) can act as "ice nucleii", i.e. that the formation of ice crystals starts on this material. This because they contain molecules or crystals with a similar structure as ice crystals. At the same temperature the water vapour pressure over ice is lower than the water vapour pressure over liquid water. As a result the water from the undercooled cloud droplets will evaporate and be deposited on the ice crystals. In this way ice crystals will become so large that they fall fast enough to pick up other crystals and/or undercooled cloud droplets which will then freeze. In this way snowflakes are formed which are transformed into raindrops if they during their fall pass through a part of the atmosphere with a temperature above 0°C. This chain of processes is much more effective than collision of cloud droplets and can explain the formation of precipitation within a relative short time. As a result almost all rain in the midlatitudes has once been snow.

In-cloud scavenging The precipitation formation process leads to the removal of the compounds dissolved in the cloud water. This is the way compounds associated with condensation nucleii and gases dissolved in cloud and raindrops are removed from the part of the atmosphere where clouds are. Removal from this part of the atmosphere is called in-cloud scavenging.

Uptake by snowflakes and sleet Not much is known about removal by snowflakes and sleet under the cloud. Snowflakes and sleet can maybe take up aerosols more efficiently than raindrops because they have a large surface area combined with a relatively low fall velocity. Sleet consists of melting snowflakes which are covered by a layer of water and can take up gasses more efficiently than raindrops for the same reasons why it is a more efficient scavenger of aerosols. About 10% of the precipitation in Denmark arrives in the form of snow and sleet at the earth's surface, but a somewhat larger fraction of the precipitation has been scavenging the below-cloud part of the atmosphere partly in the form of snowflakes and sleet. Due to its relative unimportance and the fact that not much is known, uptake of airborne material by snowflakes and sleet is not treated in this report.

Precipitation in Denmark

The average annual amount of precipitation in Denmark is about 700 mm and varies from about 550 to 900 mm. The variation from year to year can be high.

Fall velocity of cloud and raindrops

When a drop starts to fall it will take a few seconds to accelerate to their terminal velocity. At this velocity the friction forces exerted by the surrounding are equals the gravitation forces (Pruppacher and Klett, 1997). Figure 13 shows the terminal velocity of water drops as a function of their size. (Rain)drops with a radius greater than about 3500 µm (3.5 mm) are unstable and break up into smaller droplets. Figure 13 shows that the terminal velocity is about 0.01 m s^{-1} for cloud droplets, about 1 m s^{-1} for the smallest raindrops and about 9 m s^{-1} for the largest ones. The terminal velocity influences the residence time of raindrops under the cloud. It influences the rate at which water evaporates from drops or the rate at which gases can be taken up. The smallest raindrops will evaporate before they reach the ground and will not give a contribution to precipitation. The larger ones fall so fast that they will only be able take up a very small amount of gas before they reach the ground. Droplets of different sizes can unite during their fall, because they have different terminal velocities. In the discussions in this report we will not take this process into account because we will illustrate the principles of the uptake of gases and particles by drops, rather than to give a complete description.

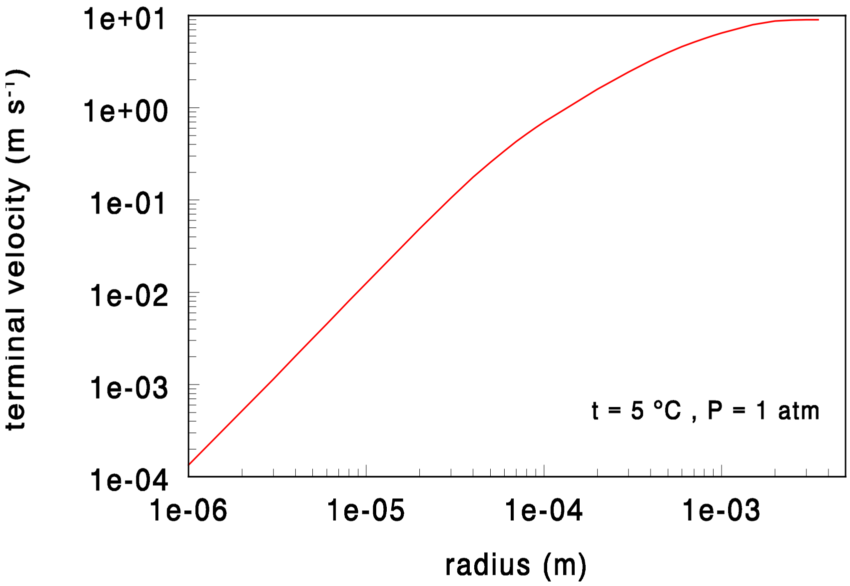


Figure 13
Terminal velocity of raindrops as a function of their radius.

Regndråbens faldhastighed som funktion af radius.

Size distribution of raindrops

There is a relation between the rainfall rate and the size distribution of raindrops. At higher rainfall rates the average radius of the drops is larger, as everybody knows by experience. Figure 14 shows number of raindrops as a function of their size for two common rainfall rates using an equation given by Marshall and Palmer (1948). Figure 15 shows the distribution of the liquid water content of air belonging to these size distributions. Both Figure 14 and Figure 15 are given for an arbitrary raindrop radius interval. This radius interval is not important here. What is important to note is the relative difference between Figure 14 and 15. This difference reflects the fact that the smallest drops are most abundant, but that their contribution to the liquid water content of the cloud is not large. The liquid water content of the cloud a maximum about a drop radius of 0.5-1 mm. Such raindrop distributions as show in Figure 14 are more representative for an average situation. The size distributions during events may deviate from the equation given by Marshall and Palmer. Moreover, different authors use different types of equations, which give somewhat different results. Most distributions of the raindrop size have been measured to relate the radar reflection of precipitation drops to measured size distributions at ground level. They give a good description of the larger raindrops, which are reflect the radar waves most and contribute most to the amount of precipitation, but the description of the smaller drops in the distribution, that are more important for the uptake of gases, is somewhat more uncertain. The resulting uncertainty in the removal rate of gases by raindrops will be discussed later. It should be noted that the liquid water volume of raindrops/snowflakes in cloud is much less than the liquid water volume of cloud water.

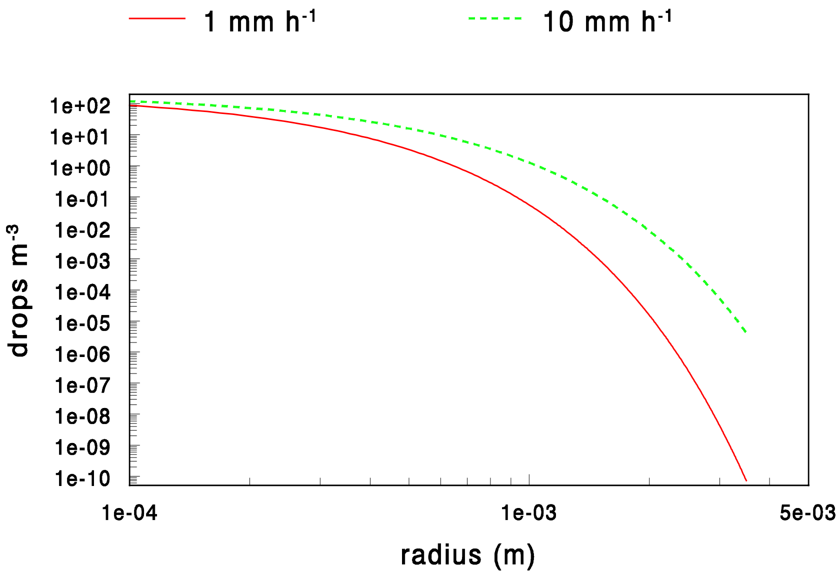


Figure 14

Number of raindrops per volume of air as a function of their radius for a drop radius interval of 1.25×10^{-5} m.

Antallet af regndråber per luftvolumen som funktion af deres radius med et dråberadiusinterval på 1,25×10^{-5} m.

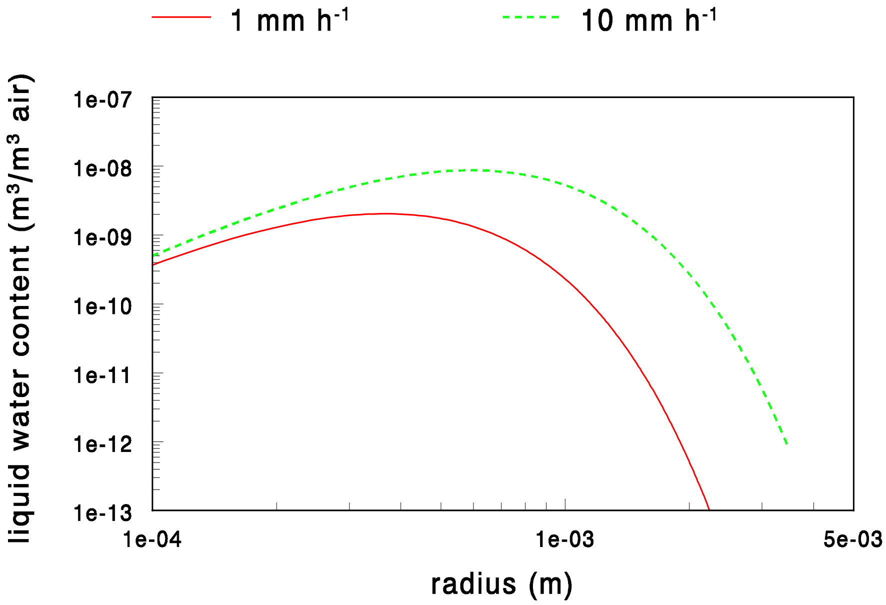


Figure 15
Liquid water volume of raindrops per volume of air as a function of their radius for a drop radius interval of 1.25×10^{-5} *m.*

Flydendevandindhold af regndråber per luftvolumen som funktion af deres radius med et dråberadiusinterval på $1{,}25\times10^{-5}$ *m.*

Cloud base height

During unstable conditions (convection) an air parcel which is unsaturated with water vapour can from near the earth's surface will be transported upward and will be cooled down with -0.01°C m^{-1}. As the saturation pressure (Pa) over liquid water decreases with temperature, the air parcel will become more and more saturated with height due to cooling and if the saturation pressure is reached, a substantial condensation of water vapour on aerosols will occur and a cloud is formed. The cloud base is in this case at the height, where the first cloud droplets form. During these unstable conditions, there is a relation between the relative humidity and the temperature at the ground and the cloud base height. During neutral and stable conditions there is no such relation. The layer with the clouds may have a totally different origin than the air at ground level. This is especially the case near warm and cold fronts, where warm and cold air meet. It is important to know the cloud base height, because airborne material is removed by precipitation by different processes in and below the cloud and what is even more important material is removed at different rates.

Estimated cloud base height

The cloud base height is either measured (usual at large airports) or estimated by meteorological observers. Figure 16 shows the frequency distribution of the cloud base height during precipitation in Denmark for 5 stations (Asman and Jensen, 1993). The cloud base height is given as a code, which refers to height intervals (Table 3). It should be noted here that the height intervals are not the same for all codes. On the basis of the frequency distribution an average cloud base height was calculated for each of the five stations (Table 4). The uncertainty in these values is rather large due to the procedure and because the estimated cloud base height depends also to some extent on the observer.

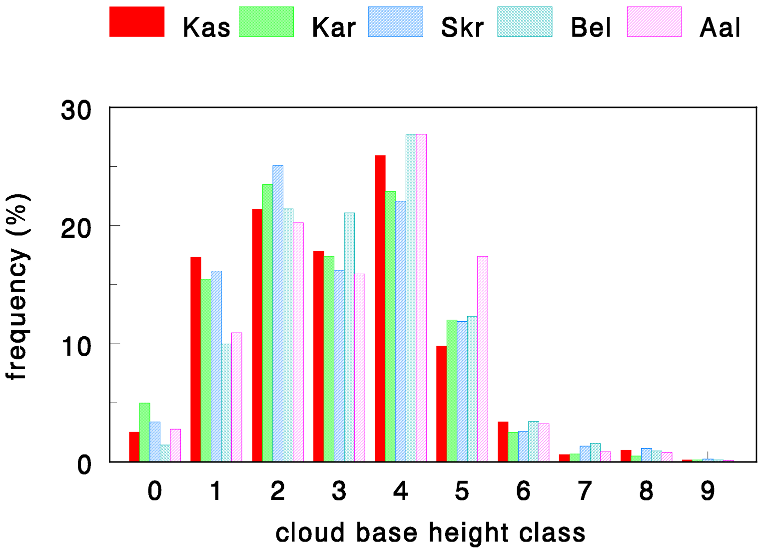


Figure 16
Frequency distribution of the cloud base height during precipitation for 1979-1988. Data from the Danish Meteorological Institute (DMI).

Station code: Kas = Kastrup, Kar = Karup, Skr = Skrydstrup, Bel = Beldringe, Aal = Aalborg. The cloud base height classes are explained in Table 3.

Frekvensfordeling af skybasehøjden under nedbørhændelser for 1979-1988. Data fra Danmarks Meteorologiske Institut (DMI).
Stationskode: Kas = Kastrup, Kar = Karup, Skr = Skrydstrup, Bel = Beldringe, Aal = Aalborg. Skybasehøjdeklasserne er forklaret i Tabel 3.

Table 3
Explanation of the cloud base height code and the height interval used in Figure 16.

Forklaring af koden for skybasehøjde og højdeinterval anvendt i Figur 16.

Code	Height interval (m)
0	0-49
1	50-99
2	100-199
3	200-299
4	300-599
5	600-999
6	1000-1499
7	1500-1999
8	2000-2499
9	2500 or more

Table 4
Average cloud base height during precipitation for five Danish meteorological stations.

Gennemsnitlige skybasehøjde under nedbørsperioder for fem danske meteorologiske stationer.

Station	Cloud base height (m)
Kastrup	365
Karup	349
Skrydstrup	373
Beldringe	412
Aalborg	420

1.7.2 **Exchange of gases between drops and the air**

The uptake of gases by cloud and rain drops can be described by a sequence of steps that must be taken (Seinfeld, 1986):

1. Diffusion of the gas from some distance of the drop to the drop surface.
2. Transfer of gas across the gas-water interface.
3. Extremely fast reactions in the water phase near the surface of the drop. This reaction should be so fast, that it is completed before the diffusing gas has been mixed throughout the whole drop. This is usually only the case for ionisation reactions. If this occurs, not the dissolved gas will diffuse into the water phase, but the reaction products
4. Diffusion of the dissolved gas or extremely rapidly formed reaction products in the water phase throughout the drop.
5. Other, not extremely fast reactions in the water phase.

In this report we will only focus on uptake of gases where no reaction occurs, as this seems to be more relevant for pesticides.

After less than 0.1 seconds a steady state situation is achieved for cloud and raindrops that are exposed to a gas. The steady state situation is defined as the situation where the flux in the gas phase from some distance to the drop equals the flux through the gas-water interface, which equals the flux into the water phase. The overall rate at which a gas can be taken up depends on the resistance to transport in the gas phase, across the interface and in the water phase. Although it cannot be excluded that in some cases the resistance in the water phase is considerable, this seems not to be the case in general. One of the reasons is that drops with a radius > 100 µm develop during their fall an internal circulation leading to mixing within the drops and as a result the resistance in the water phase is small compared to the resistance in the water phase.

Flux in the gas phase

The transport of the gas in the gas phase and transfer across the gas-water interface is given by (Pruppacher and Klett, 1997):

$$F_g = \frac{f_g D_g^{*}}{r}(c_g - c_w H) \qquad (29)$$

where:

Fg = flux in the gas phase to/from the droplet surface (kg m-2 s-1).

D_g^* = apparent diffusivity of the gas in the gas phase ($m^2 s^{-1}$). D_g^* depends on the diffusivity of the gas in the gas phase, but includes also a factor that depends on the probability that a gas molecule that hits the water surface is absorbed by the drop (see Appendix 1). If the probability is large enough D_g^* will become approximately equal to D_g, the real diffusivity of the gas in the gas phase ($m^2 s^{-1}$). This factor is unknown for pesticides and for that reason D_g^* is set D_g in the calculations. In this way a maximum value is obtained of D_g

f_g = ventilation coefficient for gases (dimensionless). This is a correction factor. It is the ratio between the flux for a stagnant drop and the flux for a drop that moves relative to the air at its terminal velocity. The exchange is greater for moving drops, because they all the time will meet "fresh", i.e. air that has not yet been depleted with gas.

The ventilation coefficient is approximately given by:

$$f_g = 1 + 0.3\,\mathrm{Re}^{\frac{1}{2}}\,\mathrm{Sc}^{\frac{1}{3}} \tag{30}$$

where Re is the Reynolds number: Re $=2rv_t/\nu$ (dimensionless), where r = radius of the drop (m), v_t = terminal velocity of the drop ($m s^{-1}$) , ν = kinematic viscosity of the air ($m^2 s^{-1}$) and Sc is the Schmidt number (dimensionless). The Schmidt number is ν/D_g, where D_g is the diffusivity of the gas in the gas phase ($m^2 s^{-1}$).
The ventilation coefficient f_g is 1 for small, almost not moving cloud droplets to up to about 20-30 for the largest falling raindrop and gases with molecular weights varying from 200-400. It depends mainly the radius of the drop (which also determines the terminal velocity) and the diffusivity of the gas.

c_g = gas phase concentration in the bulk phase, i.e. at some distance from the drop interface (kg m^{-3}).
cw = dissolved gas concentration in the bulk water phase (kg m-3).
H = Henry's law coefficient (kg m-3 gas/kg m-3 water)

F_g is the flux, i.e. kg of the gas that passes through 1 m^2 of drop surface per second. It is more useful to have a change in concentration per second in the drop in stead. This can be done by multiplying the flux with the surface of the drop ($4\pi r^2$) and dividing by the volume of the drop ($(4/3)\pi r^3$):

$$\frac{dc_w}{dt} = \frac{3 f_g D_g}{r^2}\left(c_g - c_w H\right) \tag{31}$$

It is interesting to note that c_wH is just equal to the gas phase concentration that would be in equilibrium with the concentration in the bulk water phase in the drop. This equation is, in fact, much alike the equation for the dry deposition flux (16), which also depends on a concentration difference.

If we integrate (31) and assume that $c_w = 0$ at $t = 0$, the following equation is obtained:

$$c_w = \frac{c_g}{H}\left(1 - e^{-k_1 t}\right) \tag{32}$$

where:

$$k_1 = \frac{3f_g D_g H}{r^2} \tag{33}$$

$$\tau_{abs} = \frac{r^2}{3f_g D_g H} \tag{34}$$

The characteristic time constant of absorption is $\tau_{abs} = 1/k_1$. If $t = \tau_{abs}$ about 63% of the gas that can potentially be absorbed has been absorbed. The value of τ_{abs} for drops of different size can be calculated from Table A2-1 in Appendix 2.

For raindrops, which have a noticeable terminal velocity it is more convenient to express the concentration in the drop as a function of the fall distance. Realising that the fall distance (m) is $z_f = v_t{*}t$ the following is found from (32):

$$\frac{dc_w}{dz_f} = \frac{3f_g D_g}{r^2 v_t}\left(c_g - c_w H\right) \tag{35}$$

If we integrate (35) and assume that $c_w = 0$ at $z_f = 0$, the following equation is obtained:

$$c_w = \frac{c_g}{H}\left(1 - e^{-k_2 z}\right) \tag{36}$$

where:

$$k_2 = \frac{3f_g D_g H}{r^2 v_t} \tag{37}$$

$$\Delta_{abs} = \frac{r^2 v_t}{3f_g D_g H} \tag{38}$$

The characteristic distance of absorption is $\Delta_{abs} = 1/k_2$. If the drop has fallen a distance $z_f = \Delta_{abs}$ about 63% of the gas that can potentially be absorbed has been absorbed. The value of Δ_{abs} for drops of different size can be calculated from Table A2-1 in Appendix 2.

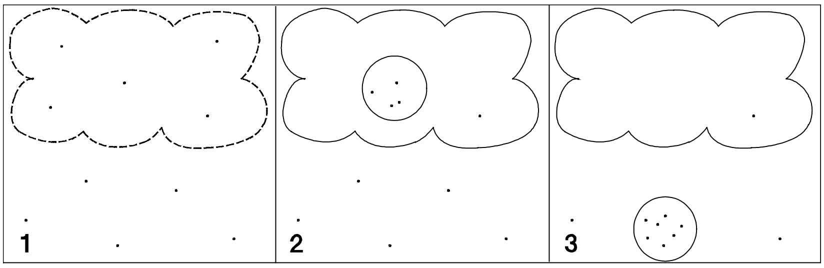
It can be seen from (36) that the concentration approaches the equilibrium concentration c_g/H (saturation) if t is relatively large. It can also be seen from k_1 and k_2 that if H is larger (the gas is more volatile, i.e. less soluble) it takes less time/fall distance to get saturation of the drop. The ventilation coefficient f_g in (33) increases with r, but much less than with r^2, so k_1 decreases with the drop radius. This means, that it takes more time for larger drops to get saturated. The value of k_2 decreases even faster with the drop radius, because here v_t is in the denominator and v_t increases with the drop radius (see Figure 13).

1.7.3 Scavenging of gases

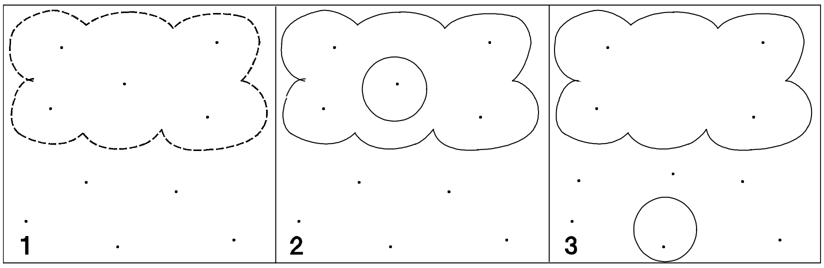
General situation

Figure 17 illustrates the differences between uptake of highly and slightly soluble gases in clouds (in-cloud scavenging) and below-clouds (below-cloud scavenging). In each “comic” three situations are shown:

1) The situation before formation of the cloud.
2) Effect of in-cloud scavenging.
3) Effect of below-cloud scavenging.



highly soluble gases



slightly soluble gases

Figure 17
Differences in in-cloud and below-cloud scavenging of highly (upper figures) and slightly soluble gases (lower figures).

Forskelle mellem in-cloud scavenging og below-cloud scavenging af letopløselige (øverste figurer) og tungtopløselige gasser (nederste figurer).

1. Before the formation of the cloud

Before the formation of the cloud the concentrations in the air are the same everywhere for both gases in this example (situation 1).

2. Uptake of gases in the cloud water after cloud formation

After formation of the cloud (situation 2) equilibrium is reached between concentrations in the gas and water phase in the cloud droplets. This holds for both the highly and the slightly soluble gas. Most of the highly soluble gas can be found in the droplets (one droplet is shown) and the concentration in the air within the cloud is very low, i.e. much lower than the concentration in the air outside the cloud. It will take somewhat more time to reach equilibrium for highly soluble gases than for slightly soluble gases, because a larger amount of gas has to be transported into the droplets. But even then it will take less than a minute before these small cloud droplets have reached equilibrium. Their lifetime is much more than a minute (see Table A2-1 in Appendix 2), so equilibrium is reached rather fast compared to their lifetime. The situation for the slightly soluble gas is somewhat different. The concentration in the cloud droplets is rather low and as a result the concentration in the air within the cloud has not changed much due to the uptake of the gas and is almost equal to the concentration of the gas in the air outside the cloud.

3. Uptake of gases below the cloud

After some time precipitation is formed and the raindrops that contain about the same concentration as the cloud droplets, they will start to fall and take up gas on their way (situation 3). In the case of a highly soluble gas the drops are not saturated at all compared to the surrounding air and they will take up a additional gas. Due to the relatively short time drops are under the cloud base (1-6 minutes for a cloud base of 400 m; see Table A2-1 in Appendix 2) the drops do not get saturated as there is a physical limit as to how much gas can be taken up in this relatively short time. Drops may get more and more saturated after they have been collected in a precipitation sampler if they still are in contact with the surrounding air. The situation for slightly soluble gases is quite different. The raindrops are almost saturated when they leave the cloud and if the concentration in the air under the cloud is not much different from the concentration in the air in the cloud, they will almost be saturated when they reach the surface. So for those drops it is reasonable to adopt equilibrium. For both highly and slightly soluble gases holds that if the concentration in the air is the same at ground-level and higher up in the atmosphere where clouds are formed, the contribution from in-cloud scavenging is larger than the contribution from below-cloud scavenging. Near relatively strong sources, the concentration in the air below the cloud can become much higher than the background concentration in the atmosphere. Only in this situation the contribution from below-cloud scavenging can become larger than that from in-cloud scavenging.

The over-all effect of in- and below-cloud scavenging can be described empirically by a an overall scavenging ratio:

$$S_{overall} = \frac{c_{pr}}{c_g} \tag{39}$$

where:

c_{pr} = concentration of the compound in precipitation (kg m^{-3})
c_g = concentration of the compound in the air (kg m^{-3})

The philosophy behind this empirical approach is that it is logical to adopt a linear relation between the concentration in precipitation and the concentration in air. $S_{overall}$ is usually found from measured concentrations in precipitation and air at ground-level. As can be see from Figure 17 this is a reasonable assumption for slightly soluble gases if the concentration in air at ground-level is about the same as in air at cloud height. In that case equilibrium can be assumed to exist between the gas and the rain and $S_{overall}$ can be found from the Henry's law coefficient:

$$S_{overall} = \frac{1}{K_H} \tag{40}$$

For highly soluble gases this approach is more tricky. Usually there is no equilibrium between the concentration in the air and precipitation at ground-level, or between the concentration in the air outside the cloud at cloud height and the concentration in precipitation. For highly soluble gases the $S_{overall}$ is often set to about 1×10^6, an upper limit, which depends more on the removal rate of precipitation itself than on the Henry's law coefficient of the gas. Sometimes $S_{overall}$ is also made slightly dependent on the rainfall rate. The rate at which a compound is removed from the atmosphere by scavenging is called scavenging coefficient and is defined by:

$$\Lambda_{overall} = \frac{S_{overall} I}{z_{mix}} \tag{41}$$

where:

$\Lambda_{overall}$ = scavenging coefficient (s^{-1})
I = rainfall rate ($m\ s^{-1}$)
z_{mix} = mixing height (m)

For highly soluble gases and adopting a mixing height of 1000 m this gives removal rates of $2.8\times10^{-4}\ s^{-1}$ at 1 mm hr^{-1} to $2.8\times10^{-3}\ s^{-1}$ at 10 mm hr^{-1}. This means that at a precipitation rate of 1 mm hr^{-1} 64% of the gas is removed from the air after 1 hour with precipitation. At a precipitation rate of 10 mm hr^{-1} more than 99.9% is removed from the air. (This can be calculated with (43)).

Scavenging close to important sources

The situation close to important low-level sources is different form the general situation in that the plume coming from the field on which the pesticide has been applied usually reaches the cloud base height at a distance between 2-10 km from the source. In that case all scavenging is below-cloud scavenging which is not so effective for highly and slightly soluble gases as in-cloud scavenging. Usually no equilibrium will be reached, neither for the highly nor for the slightly soluble gas. There is a limitation to the uptake of a gas: no more gas can be taken up than is transported to the raindrop. This sets an upper limit to the below-cloud scavenging which is reached for highly soluble gases. For slightly soluble gases the below-cloud scavenging is less than this value. The upper limit for convective conditions is given by (Asman, 1995):

$$\Lambda_b = aI^{bav} \tag{42}$$

In this equation a and b depend on the relative humidity and temperature at ground level and the diffusivity of the gas at 25°C (see Appendix 3). In this case I is the rainfall rate in mm hr^{-1}. If the diffusivity of the gas is not known it can be estimated from (15). For non-convective conditions one could e.g. calculate a scavenging coefficient by assuming a temperature of 10°C and a relative humidity of 85%. Figure 18 shows this maximum below-cloud scavenging coefficient of a gaseous pesticide with a molecular weight of 300 as a function of the rainfall rate. Due to the uncertainty in the drop size distribution the uncertainty in the scavenging coefficient is at least a factor of two. For highly soluble gases this gives removal rates of $3.8\times10^{-5}\ s^{-1}$ at 1 mm hr^{-1} to $1.6\times10^{-4}\ s^{-1}$ at 10 mm hr^{-1}. After one hour with precipitation 13 and 44% will be removed at a precipitation rate of 1 and 10 mm hr^{-1} respectively. (see (43)). These rates that are about a factor of 10 lower than for in-cloud scavenging. The fact that the drops that reach the ground are not in equilibrium with the concentration in the air for highly soluble gases can lead to artefacts during sampling of precipitation, because the collected drops on the funnel or in the bottle will still be able to take up gas after the precipitation has stopped.

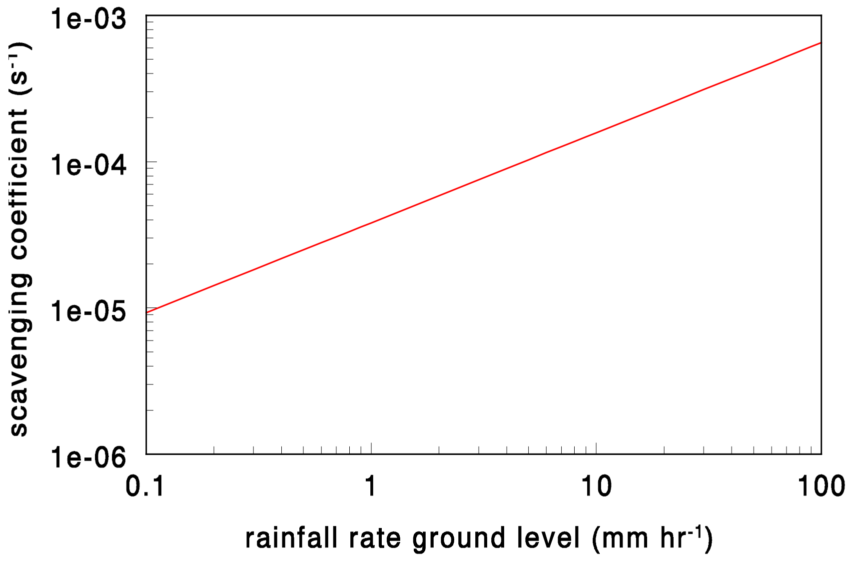


Figure 18
Below-cloud scavenging coefficient for a highly soluble gas with molecular weight of 300 as a function of the rainfall rate at ground level. At ground-level the temperature is 10℃ and the relative humidity is 85%.

Below-cloud scavengingkoefficienten for letopløselig gas med en molekylemasse på 300 som funktion af regnintensiteten i jordniveau. Temperaturen og relativ fugtigheden i jordniveau er henholdsvis 10℃ og 85%.

1.7.4 **Scavenging of particles**

Particles containing pesticides will usually be removed rather efficiently by in-cloud scavenging. Below-cloud scavenging of particles is less efficient and depends on the size distributions of the raindrops and the particles (Slinn, 1983). A scavenging ratio of 1×10^6 can be adopted for an overall-scavenging of particles because scavenging is in general dominated by in-cloud scavenging. Close to sources only below-cloud scavenging is important, the scavenging ratio will often be considerably less and has to be calculated with the appropriate size distributions of raindrops and particles. Rain contains also particles that are only partly dissolved. Pesticides with a low solubility may therefore not only exist in rain as a dissolved gas but also as be part of particles.

Change in concentration in the air due to wet deposition

The concentration left in the air after a precipitation period with length t (s) can be found from:

$$c(t) = c(0)e^{-\Lambda t} \tag{43}$$

where Λ can be the in-cloud scavenging coefficient, below-cloud scavenging coefficient or the overall scavenging coefficient.

Measurements of the wet deposition rate

The wet deposition of pesticides can be measured. It is in principle also possible to derive an overall scavenging coefficient for pesticides from measured concentrations in air and precipitation using (39) and (41). In this case the measured air concentration should be representative for the whole air column, i.e. it should not be measured close to sources.

In-cloud scavenging and properties of the compound

Highly soluble and reactive gases are removed by in-cloud scavenging at a high rate. Almost all gas will be dissolved in the cloud droplet and the concentration in the interstitial air in the cloud will be low. For that reason the scavenging rate does not depend on the Henry's law coefficient, but on the rainfall rate, as almost all gas is dissolved in the cloud drops.

For slightly soluble gases the situation is different: a substantial fraction of the compound is found in the interstitial air in the cloud. The removal rate for these gases will be a function of the Henry's law coefficient and the precipitation rate.

Most particles act as condensation nucleii and will for that reason be removed at a high rate that is determined by the precipitation rate. The removal rate will not depends much on the size of the particles as long as they are hygroscopic.

Below-cloud scavenging and properties of the compound

Highly soluble and reactive gases are removed by below-cloud scavenging at a higher rate than slightly soluble gases, but the removal rate by below-cloud scavenging is less than by in-cloud scavenging (see below). The removal rate for highly soluble gases does in general not depend on the Henry's law coefficient but on the speed at which the gas can diffuse into the drop, which is e.g. a function of the diffusivity of the gas and the raindrop size, which in turn is a function of the precipitation rate. For slightly soluble gases the raindrop is almost saturated with the gas by in-cloud scavenging when the drop reached the air below the cloud. If the air below the cloud has the same concentration no more gas will be taken up. If the air below the cloud has a higher concentration more gas can be taken up. If the air below the cloud has a lower concentration that in the cloud the drops will degas, i.e. dissolved gas will evaporate into the atmosphere.

Particles will in general also be removed by below-cloud scavenging at a lower rate than by in-cloud scavenging. Their removal rate will be a function of their size and the size of the raindrops which is a function of the precipitation rate.

In-cloud scavenging vs. below-cloud scavenging

In case of in-cloud scavenging at a precipitation rate of 1 mm hr^{-1} 64% of a highly soluble gas is removed after 1 hour with precipitation. At a precipitation rate of 10 mm hr^{-1} more than 99.9% is removed from the air after 1 hour.

For highly soluble gases the removal rate by below-cloud scavenging is highest. This gives removal rates of 3.8×10^{-5} s^{-1} at 1 mm hr^{-1} to 1.6×10^{-4} s^{-1} at 10 mm hr^{-1}. After one hour with precipitation 13% and 33% are removed from the air at a precipitation rate of 1 and 10 mm hr^{-1} respectively. In case only below-cloud scavenging is occurring, e.g. close to a low level source, still a considerable fraction of the highly soluble gas remains airborne. The removal rate for slightly soluble gases will be less than for highly soluble gases.
The wet removal rate for particles will also be dominated by in-cloud scavenging and will be the same as for highly soluble gases, at least if the concentration at cloud level is about the same as below the cloud.

Origin of pesticide in precipitation close to an important source

Close to low sources, like fields after application of pesticides, the plume has not yet reached the cloud and for that reason only below-cloud scavenging occurs. As a result the wet deposition near a low source will only be a relatively small fraction of the amount of pesticide volatilised, even in the case of a highly soluble pesticide. It should be noted that in general a background concentration of pesticides will be present in the atmosphere. This background concentration will also exist at cloud level. As in-cloud scavenging is much more efficient than below-cloud scavenging, a larger fraction of the background will be scavenged near the low source than of the released compound from the low source. Only in the case where the low source emits at a relatively high rate or the precipitation period last for a long time, the concentration in precipitation can be dominated by a nearby low source.

Non-soluble particles

Rain contains also particles that are only partly dissolved. Pesticides with a low solubility may therefore not only exist in rain as a dissolved gas but also as be part of particles.

Wet deposition vs. dry deposition

The dry deposition velocity of gases increases in general with the solubility of the gas. The same is the case for removal rates of gases by in-cloud and below-cloud scavenging. For particles the situation is different. Particles with a radius between 0.1 and 1 µm are not removed well from the atmosphere by dry deposition, but are removed well by in-cloud scavenging because they can act as condensation nucleii. As it does not rain that often, their atmospheric lifetime is rather long, of the order of 5 days or longer.

The maximum removal rate by dry deposition is much lower than the maximum removal rate by wet deposition. After 1 hour under Danish conditions only 13% of the a highly soluble gas is removed in the case of cropland and 25% in the case of forests.

The maximum removal rate by precipitation is determined by in-cloud scavenging, if the concentration of the compound in the air at cloud level and below the cloud are the same. It is then 64% hr^{-1} at a precipitation rate of 1 mm hr^{-1} or more than 99.9% hr^{-1} at a precipitation rate of 10 mm hr^{-1}.

So it looks as if wet deposition will be the dominating removal process. This is, however, not necessarily true. The reason for this is that dry deposition occurs all the time, even during precipitation, whereas wet deposition only occurs during precipitation, i.e. during 5-10% of the time. Consequently the average amount dry deposited over a longer period can be of the same order of magnitude as the amount wet deposited, despite the fact that the process is less efficient than dry deposition.

It is very difficult to measure the dry deposition rate and even in the case it can be measured like for highly soluble gases, it is not likely that it will be done continuously. On the contrary it is possible to measure the wet deposition rate.

1.9 Conversion from the gaseous to the particulate phase

As we have seen in section 1.4, dry deposition of particles proceeds at another speed than dry deposition of gases. Pesticides released as gases can be converted to particles and as a result the pesticide will be removed from the atmosphere at another rate than if it were in the gas phase. This process can potentially be important for slightly soluble gases that are not well removed by dry deposition or precipitation scavenging.

It is therefore crucial to know if a pesticide exists in the gas phase or in the particulate phase. Moreover, it is necessary to know at which rate a gaseous pesticide can be converted to its particulate form, so that we e.g. whether the gaseous pesticide is already converted to the particle phase to a substantial extent during the transport over the first 2 km discussed in this report

Ratio particle-gas for

If gaseous pesticides are transformed to particles, they do not form pure *pesticides*

pesticide particles. For thermodynamical reasons it is favourable for gases to condense on existing particles. Junge (1977) found the following relation for the ratio R_{pg} of the concentration of a compound in the particulate phase over the total concentration of the compound in the particulate and gaseous phase:

$$R_{pg} = \frac{c_{zr,p}}{c_{zr,tot}} = \frac{c\varphi}{P^0{}_L + c\varphi} \qquad (44)$$

where:

$c_{zr,p}$ = concentration of the compound in the particulate phase (μg m^{-3}).
$C_{zr,tot}$ = concentration of the compound in the gaseous and particulate phase (μg m^{-3}).
c = a constant, Junge assumed a value of 0.17 (Pa m) for high molecular weight organic compounds.
φ = available particle surface (m^2 $m^{-3}$of air).
$P^0{}_L$ = sub-cooled liquid phase vapour pressure of the compound (Pa).

The typical average background value for φ is 1.5×10^{-4} m^2 m^{-3} (Whitby, 1978). This means that if $P^0{}_L > 2\times10^{-4}$ Pa, over 90% of the compound is in the gaseous phase, whilst at $P^0{}_L < 2\times10^{-6}$ Pa, over 90% of the compound is in the particulate phase (van Pul et al., 1998).

1.10 Photochemical reaction

Gaseous pesticides can be transformed in the atmosphere by photolysis (degradation under influence of sunlight) or by reaction with the following photochemically formed reactive compounds: OH-radical, NO_3-radical and O_3. The rate at which a gaseous pesticide is transformed by the reactive compounds depends on the concentrations of these reactive compounds and the reaction rate of the pesticides with these compounds. The reaction rate of pesticides depends on their chemical structure and will be different for different pesticides. For many pesticides the reaction rates will not be known, but sometimes they can be estimated using some empirical relationships between the structure of the pesticide and its reactivity (Atkinson, 1987, 1988; Winer and Atkinson, 1990). It should be noted here that if a pesticide reacts, reaction products are formed. These reaction products can also be toxic and are in some cases even more toxic than the pesticides themselves. One should in fact also investigate the fate of these reaction products in the atmosphere. This can be rather complicated because usually more than one reaction product is formed. The reaction products can be removed from the atmosphere at different rates than their precursors, because they have different properties.

1.11 Spray drift and other forms of deposition

Different forms of deposition

Pesticide application can lead to different forms for deposition:

a) Deposition of the larger sprayed drops due to sedimentation caused by gravitation. This form of deposition is mainly influenced by the physical properties of the drops (e.g. inertia, which is a function of the size of the droplets) and not by the chemical properties of the pesticide. Moreover, it is influenced by other factors like wind speed, boom height and other meteorological factors.

b) Deposition of sprayed droplets that are so tiny that their movement is not influenced by gravitation, but only by atmospheric turbulence. This is a form of dry deposition. The deposition mechanism is different than for the larger drops previously mentioned, that deposit due to sedimentation. However, in both cases the physical properties of the drops and not the chemical properties of the drops determine the deposition flux to a substantial extent. This form of deposition can be more important than the deposition of sprayed drops due to sedimentation (Peter Kryger Jensen, Danish Institute of Agricultural Sciences, Flakkebjerg, Slagelse, personal communication). For more information on this process see under dry deposition.

c) During spraying, part of the pesticide can evaporate from the droplets before they reach the ground. How much evaporates will depend on the size of the droplets (physical factor), the Henry's law coefficient of the pesticide, properties of the solvent and other related chemical properties. Moreover, it will be influence by meteorological factors like temperature, wind speed and by the height of the boom sprayer over the surface and the type of surface. The evaporated pesticide can later reach the surface in the form of dry and wet deposition.

d) After the spray drops have hit the surface, pesticide can evaporate, and the gaseous pesticide can then later be deposited in the form of dry or wet deposition.

e) Dry deposition. This is deposition of pesticides in gaseous form, or after conversion to particles in particulate form to the surface under influence of atmospheric turbulence. For gases the chemical properties, the meteorological conditions, the concentration in and properties of the surface they deposit onto that determine the deposition flux. For particles (solid or liquid, i.e. also including tiny spray droplets) physical properties, properties of the surface where they deposit on and meteorological processes determine the dry deposition flux.

f) Wet deposition. This is deposition of pesticides that are removed from the atmosphere in gaseous or particulate form by precipitation. For pesticides in gaseous form the chemical properties (Henry's law coefficient) can have a large influence on the wet deposition flux. For pesticides in particulate form the physical properties (which is a function of the size of the particles) has a large influence on the wet deposition flux.

Deposition of sprayed drops due to sedimentation occurs only on the field where the pesticide is applied or up to about 20 m outside this area. All other forms of deposition occur also at longer distances from the field (0 to greater than 500 km). Pesticides are either deposited on the field where they are applied or outside the field. The physical and chemical processes are the same whether they are deposited on the field or not, but for other reasons (agricultural, environmental, political) differentiation between deposition on the field and outside the field is required.

Different definitions of spray drift

There exist apparently different (implicit) definitions of spray drift. One definition of spray drift is that all pesticide deposited outside the target area is spray drift. This is not a very useful definition because it includes the results of many different processes operating on various scales. In the following only spray drift due to sedimentation will be discussed, but it should be kept in mind that this is not the only form of deposition of drops.

Spray drift due to sedimentation: boom sprayers

In this report we will only compare the dry and wet deposition of pesticides as a function of distance to the field onto which pesticides are applied with the spray drift due to sedimentation. Table 5 gives an impression of the deposition caused by spray drift due to sedimentation onto crops caused by conventional boom sprayers (Ganzelmeier, 1995). This results were based on experiments where the fluorescence on crops was measured of a dye that was added to the sprayed drops.

Table 5
Deposition caused by spray drift due to sedimentation as a function of distance to the downward wind edge of a field onto which pesticides are applied (Ganzelmeier, 1995).

Deposition forårsaget af afdrift på grund af sedimentation som funktion af afstanden til kanten af en mark nedstrøms, hvor pesticider er sprøjtet (Ganzelmeier, 1995).

Distance from upwind edge of the field (m)	Deposition caused by spray drift due to sedimentation (% of the applied dose)1)
1	5.0
2	1.8
3	1.4
4	1.0
5	0.7
7.5	0.5
10	0.4
15	0.2
20	0.1

[1)] The applied dose is the amount per surface area applied (e.g. kg ha^{-1}).

1.12 Modelling the deposition close to the source

1.12.1 **K-model**

A two-dimensional K-model (x and z direction) was developed to calculate the diffusion, surface exchange and below-cloud scavenging of a gaseous non-reacting pesticide over a distance of about 2000 m (Figure 19). This model gives the crosswind-integrated concentration/deposition perpendicular to the wind direction, i.e. no diffusion in the y-direction is taken into account. Close to a field where emission occurs the crosswind-integrated concentration is almost equal to the concentration because the spreading of the plume in the y-direction is not important compared to the width of the field in the y-direction. At larger distance from the source this is not any longer the case, unless the width of the field in the y-direction is extremely large. The reason to use a two-dimensional K-model is threefold:

a) Within this project we are interested in generalised information, i.e. not for a particular situation. It is a large, maybe even impossible task, to generalise model results for all possible combinations of shape and size of fields and meteorological conditions (wind direction, wind speed, atmospheric stability etc.). For policy makers it is crucial to know at which distance from the source effects can occur. For that reason it was decided to choose a two-dimensional K-model, which gives the crosswind-integrated concentrations and depositions as a function of the distance to the source.
b) The description of the diffusion of the plume in the y-direction is somewhat more uncertain than the diffusion of the plume in the z-direction.
c) Calculations with a two-dimensional model do not take so much cpu-time as calculations with a three-dimensional model.

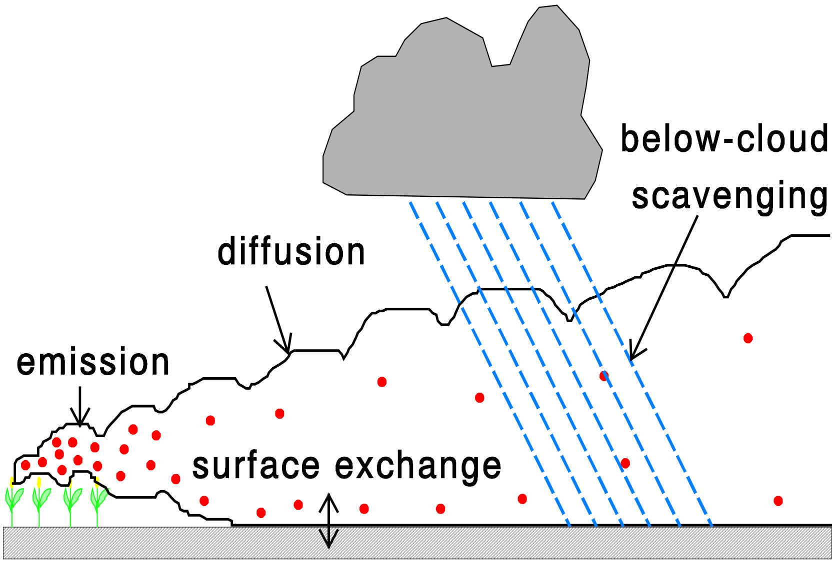


Figure 19
Overview of processes incorporated in the K-model.

Oversigt over de processer, der er indbygget i K-modellen.

Model description

The K-model developed is a steady-state model. The emission in the model for both point sources and area sources can be given by the user, but for area sources there is the possibility that the user supplies a surface concentration and that the model generates then the emission from the surface concentration and the meteorological conditions. As a result the model can the emission of pesticides in a more realistic way. In the work reported here a point source was only used to compare model results with measurements. All other runs were made with emissions that are generated from a surface concentration. The surface exchange was described with an exchange velocity (16), the vertical diffusion with a an eddy diffusivity coefficient (12), the wind speed was made a function of height (6). Scavenging was only taken into account in one case, where a maximum below-cloud scavenging coefficient for highly soluble gases with a molecular weight of 300 g mol^{-1} was applied (42). In-cloud scavenging was not taken into account, because the plume will in general not have reached the cloud level at 2 km from the source. Photochemical reaction and conversion from the gaseous phase to the particulate phase can also be taken into account. For all calculations 40 logarithmically spaced vertical layers were used, except for the calculation of the long-range transport for which 10 layers were used. A more detailed description of this type of model can be found in Asman (1998).

1.12.2 **Verification of the vertical diffusion calculated with the model**

Tracer experiment

The vertical diffusion part of the model was tested against the results of a tracer experiment in the U.S.A., where the tracer was also release from a low-level source, just as pesticides are. In this experiment sulphur dioxide was released from a 0.46 m high point source (van Ulden, 1978). The concentrations were measured at a height of 1.5 m at distances of 50, 200 and 800 from the source. The surface roughness length for the observations was 0.008 m. It appeared that the model overestimated the crosswind-integrated concentrations at 800 m from the source, especially for stable and unstable atmospheres. This phenomenon was also observed by other modellers (Gryning et al., 1983; Brown et al., 1993). They guess that part of the observed differences can be explained by the fact that sulphur dioxide is dry depositing to a minor extent. But they mention also other reasons.

Such experiments are very expensive and for that reason there are not many experimental data to verify the diffusion.

Adjusting the vertical eddy diffusivity

It was decided to increase the vertical eddy diffusivity in the model by 30% to get better results. In Figure 20 the concentrations modelled in this way were compare with measurements. At 50 m from the source the model underpredicts the concentrations by 9%, at 200 m it overpredicts the. concentrations by 7% and at 800 m it overpredicts the concentrations by 23%. Taking into account the uncertainty in the measurements this is a very reasonable result. In all following calculations the eddy diffusivity was increased by 30%.

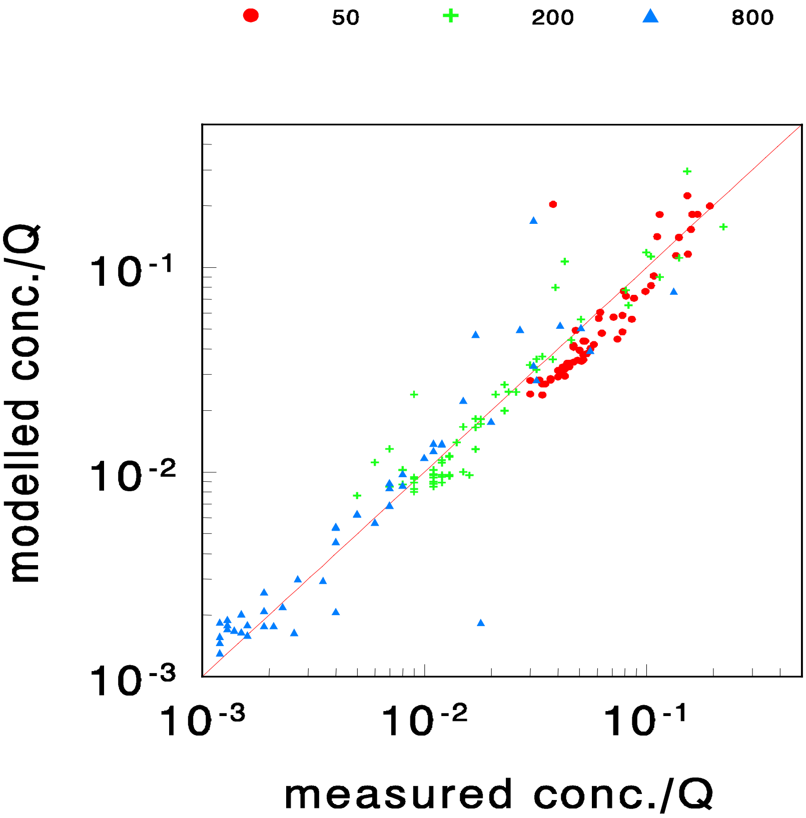


Figure 20
Modelled vs. measured crosswind-integrated concentration divided by the source strength for three downwind distances: 50, 200 and 800 m.

Modelleret vs. målt koncentration på tværs af vinden divideret med kildestyrken for tre nedstrøms afstande: 50, 200 and 800 m.

1.12.3 **Situation modelled in all further model calculations**

Model area

All the calculations made in the following are made for a field of 250 m length in the x-direction (wind direction) where pesticide has been applied and emission occurs (“emission field”) followed by an area where only deposition can occur of 1750 m in the x-direction (“deposition area”). The only exception is the calculations of the possible long-range transport where the deposition up to about 1000 km from the field are calculated (see section 1.12.10).

Emission modelled using

The emission of the field is calculated assuming a constant crosswind-

a surface concentration integrated gas concentration in the surface (here arbitrarily set to 1 kg m^{-2}). It does not matter that the surface concentration is arbitrary in this case, because in the following the deposition is always expressed as an accumulated fraction of the emission, or cases are compared where one parameter is varied, but where the surface concentration is the same. In the present model concept it is only possible to use sources at the ground when using the surface concentrations to describe the emission. There is, however, not a large difference in the results between situations where a ground source or a source at e.g. 1 m height is used. This was verified for point sources, for which the model can take sources at all heights into account. The model does not take into account that this surface concentration usually will decrease as a function of time due to loss processes (volatilisation, leaching, degradation, uptake by plants etc.). The reason is that this was beyond the scope of this project. Moreover, by not varying the surface concentration, the results can be generalised.

Relative changes important The absolute concentration or flux is not important in the calculations shown in the following, only relative differences between runs for different conditions are important. The main purpose of the following sections is to show how the emission and deposition can vary as a function of e.g. the friction velocity/wind speed, the atmospheric stability or the surface roughness length. For the results where the accumulated fraction of the emission deposited is shown, the absolute numbers are important.

Values model parameters used Variations of the conditions with respect to a "base case" are studied. In the base case both the field and the deposition area have a surface roughness length of 0.1 m (crops of about 1 m high), a friction velocity of 0.3 m s^{-1} and a neutral atmosphere (characterised by a Monin-Obukhov length of 2000 m) and a mixing height of 400 m. The atmosphere is most often neutral in Denmark, but the atmosphere can also be unstable or stable. It should be noted that the mixing height only influences the calculated concentrations and depositions if pesticides have been mixed up to the mixing height. This is not the case for transport up to about 2000 m from the low source. But the mixing height has an influence on the calculated concentrations and depositions during long-range transport that is shown in one case. The wind speed at 10 m height adopted in the calculations is 3.97 m s^{-1}, which is about the average wind speed in Denmark. It is assumed that the pesticide is gaseous and has a molecular mass of 300 g mol^{-1}. It is assumed that no atmospheric reaction occurs or conversion from the gaseous to the particulate phase. In all cases, except the case where the surface resistance has been varied, a surface resistance for both the emission and deposition area of 0 s m^{-1} has been adopted. This gives both a maximum emission and dry deposition rate. This is done to calculate the "worst case situation". In reality it is likely that at least the deposition rate is much lower than adopted in the calculations here. Apart from the results presented in one section only dry deposition is taken into account and not wet deposition.

1.12.4 Influence of friction velocity/wind speed

Figure 21 shows the influence of the variation of the friction velocity (which influences the wind speed) on the horizontal flux of the pesticide vertically integrated over the whole mixing layer as function of the distance to the upwind edge of the emission field. This gives information on much of the pesticide is airborne. The case with a friction velocity of 0.30 m s^{-1} is the base case. The wind speed at 10 m height is 1.98, 3.97 and 7.93 m s^{-1} for friction velocities of 0.15, 0.30 and 0.60 m s^{-1}.

The emission (occurring in the first 250 m) increases linearly with wind speed. The accumulated fraction of the emission dry deposited as a function of distance from the downwind edge of the emission field is, however, the same for all cases (these results are the same as presented for the neutral case in Figure 23 in the next section). As mentioned before the calculations are made with a surface resistance of zero. If the surface resistance is not 0, i.e. e.g. for moderately and slightly the accumulated fraction deposited as a function of distance to the downwind edge of the emission area will decrease the friction velocity/wind speed if the surface concentration is 0 (Asman, 1998).

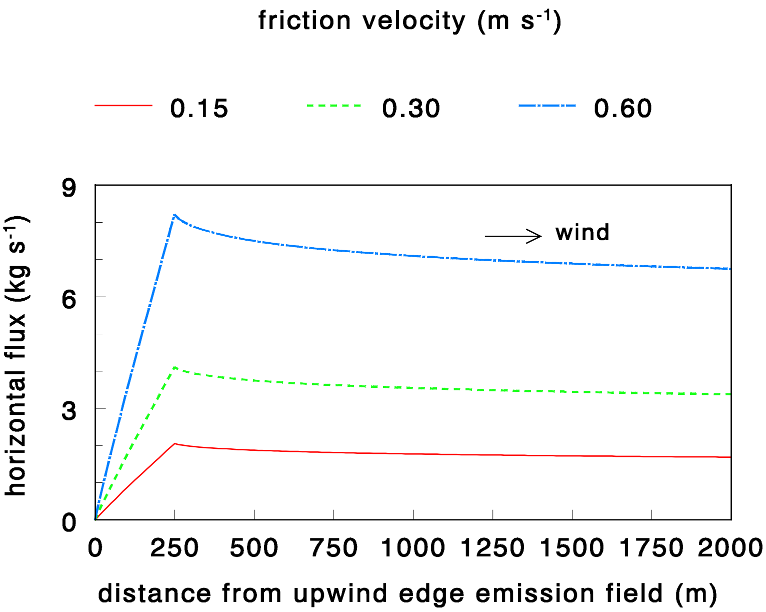


Figure 21
Modelled horizontal flux vertically integrated over the whole mixing layer for different friction velocities as a function of distance from the upwind edge of the emission field. This flux indicates how much airborne material integrated over the whole mixing height passes by per unit of time.

Modelleret horisontal flux vertikalt integreret over hele blandingshøjden for forskellige friktionshastigheder som funktion af afstanden til kanten af marken opstrøms, hvor fordampning finder sted. Denne flux er et mål for hvor meget materiale der passerer forbi pr. tidsenhed, integreret over alle højder.

1.12.5 **Influence of atmospheric stability**

In this section the influence of the atmospheric stability on the model results is discussed. For the stable atmosphere (characterised by a Monin-Obukhov length of 20 m) a friction velocity of 0.08 m s^{-1} was chosen and a mixing height of 400 m. The wind speed at 10 m height is 1.58 m s^{-1} in this case. For the unstable atmosphere (characterised by a Monin-Obukhov length of -17 m) a friction velocity of 0.28 m s^{-1} was chosen and a mixing height of 400 m. The wind speed at 10 m height is 3.03 m s^{-1} in this case. All these situations including the conditions during the neutral atmosphere are chosen to be “typical” of such conditions. In reality the meteorological conditions show a wide variation and during a particular event where pesticides are applied none of those “typical” conditions may occur.

Figure 22 shows the crosswind-integrated concentration as a function of distance from the source for different atmospheric conditions. The concentrations are higher everywhere under stable conditions than under neutral or unstable conditions. The reason for this is twofold. In stable conditions the friction velocity is less which leads to both a reduced wind speed and a reduced vertical diffusion.

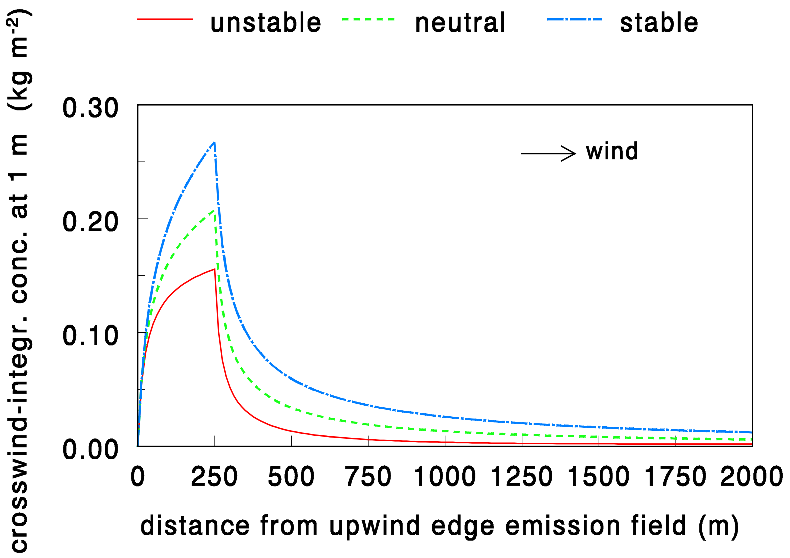


Figure 22
Modelled crosswind-integrated concentration for different atmospheric stabilities as a function of the distance from the upwind edge of the emission field.

Modelleret koncentration på tværs af vinden for forskellig atmosfærisk stabilitet som funktion af afstanden fra kanten af marken opstrøms, hvor fordampning finder sted.

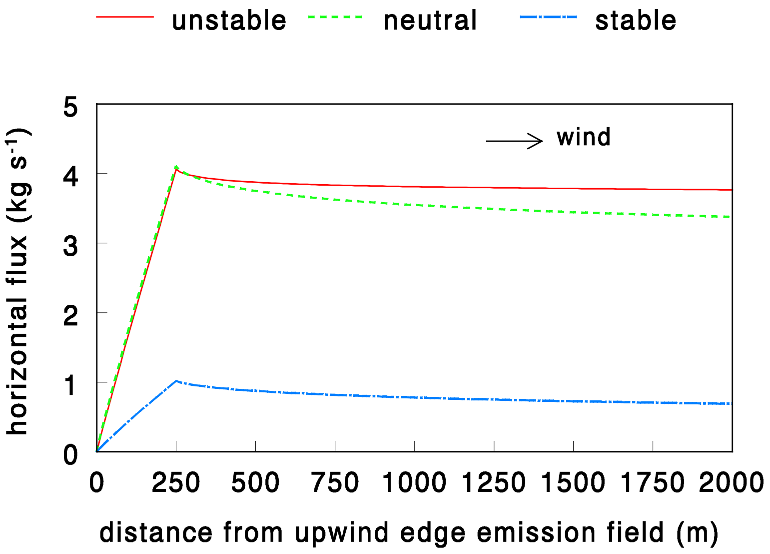


Figure 23
Modelled horizontal flux vertically integrated over the whole mixing layer for different atmospheric stabilities as a function of distance from the upwind edge of the emission field. This flux indicates how much airborne material integrated over the whole mixing height passes by per unit of time.

Modelleret horisontal flux vertikal integreret over hele blandingshøjden for forskellig atmosfærisk stabilitet som funktion af afstanden til kanten af marken *opstrøms, hvor fordampning finder sted. Denne flux er et mål for hvor meget materiale der passerer forbi pr. tidsenhed, integreret over alle højder.*

Emission rate

Figure 23 shows the horizontal flux (vertically integrated over the whole mixing height) as a function of the distance from the upwind edge of the field where pesticides are applied. The horizontal flux indicates how much pesticide is airborne. This gives information on how much pesticide is airborne. During the first 250 m the horizontal flux increases because the air is transported over the emitting field. Then the horizontal flux decreases slowly due to dry deposition and that the largest part of the emitted pesticide is still airborne at 2000 m from the upwind edge of the field. It should be stressed here, that the dry deposition is set to its maximum value in these calculations by assuming a surface resistance of 0 s m^{-1}.

Variation in the emission rate with atmospheric stability

The emission rate varies with the atmospheric conditions. During neutral and unstable conditions the emission rate is relatively large due to the larger turbulence. During stable conditions the emission rate is much lower due to the lower turbulence. Figure 24 shows the accumulated fraction of the emission (i.e. fraction of the horizontal flux at the end of the emission field) that is deposited as a function of the distance from the downwind edge of the emission field. This figure shows clearly that the deposition is largest for stable conditions where the concentration near the surface is relatively large due to reduced vertical mixing and wind speed. For neutral and stable conditions the fraction deposited is smaller.

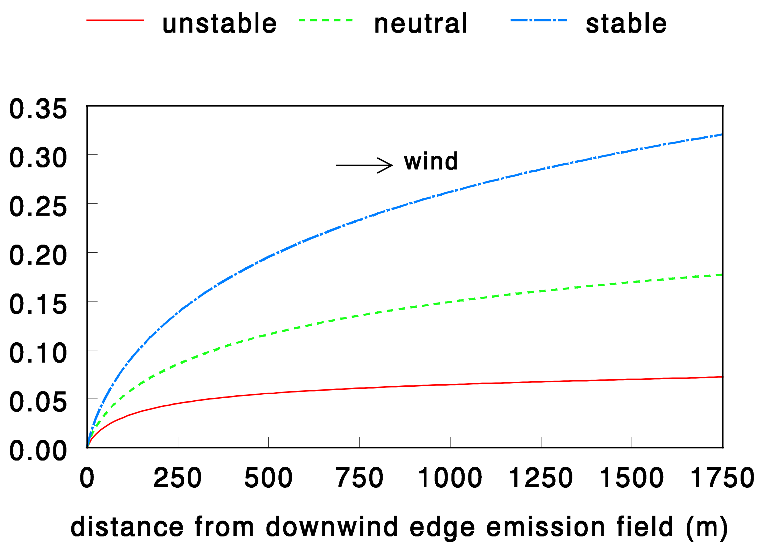


Figure 24
Modelled accumulated fraction of the emission dry deposited for different atmospheric stabilities as a function of distance from the downwind edge of the emission field.

Modelleret akkumuleret fraktion af emissionen, som er tørdeponeret ved forskellig atmosfærisk stabilitet som funktion af afstanden til kanten af en mark nedstrøms, hvor fordampning finder sted.

Crosswind-integrated concentration at 1 m height

Figure 24 shows the crosswind-integrated concentration at 1 m height as a function of the distance from the upwind edge of the field. This clearly shows that the concentration under stable conditions is larger than under neutral and unstable conditions. This is, as mentioned before, a result of the reduced vertical mixing and wind speed. The concentration decreases very sharply after the deposition area has been reached. This is mainly due to vertical mixing and not to dry deposition.

1.12.6 **Vertical concentration profiles**

Vertical profiles on the emission field

Figure 25 shows the vertical concentration profiles in the lowest 50 m of the atmosphere at different distances from the upwind edge of the emission field. The profiles at 12.5 and 250 m belong to the emission field. The concentrations at 250 m from the upwind edge of the emission field are at all heights higher than at 12.5 m from the upwind edge of the emission field. This is caused by the fact that the concentration at 250 m distance is the result of a much larger emitting area upwind than the concentration at 12.5 m distance.

Vertical profiles in the deposition area

At 500 m from the source, i.e. 250 m in the deposition area the concentration decreases with height in the lowest metres. This is caused by dry deposition, that removes material faster than turbulence can replenish from higher up in the atmosphere. At the 2000 m point the concentration is still lower in the lowest metres, but all concentrations are lower than at the 500 m point, except at 40-50 m height. This is mainly caused by the fact that the pesticide has been mixed over a greater height. At 40-50 m height the concentration is higher at 2000 m from the upwind edge of the emission field than at 500 m from that edge. The reason for that is that at 500 m, mixing has not yet been able to transport so much material upward as at 2000 m.

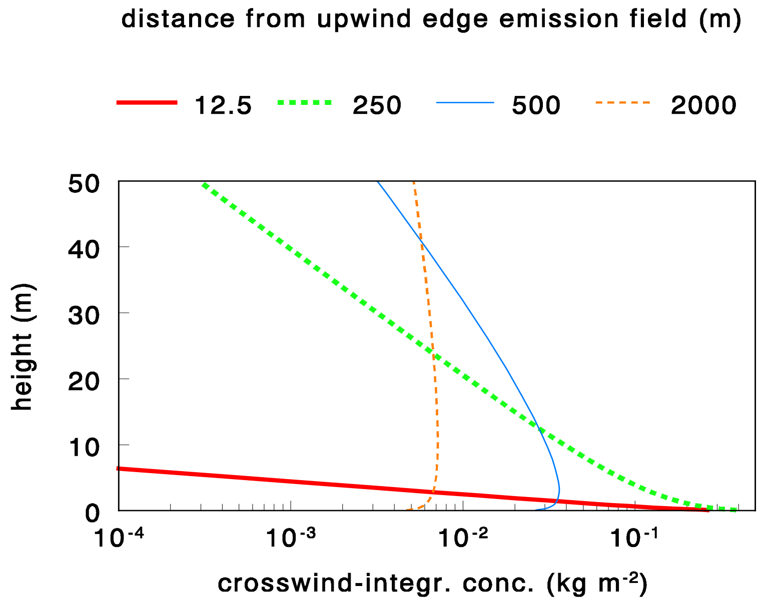


Figure 25
Modelled vertical concentration profiles as a function of the distance to the upwind edge of the emission field.

Modellerede vertikale koncentrationsprofiler som funktion af afstanden til kanten af den mark nedstrøms, hvor fordampningen finder sted.

1.12.7 Reduction of the emission rate on the emission field due to upwind emissions

Figure 26 shows how the net emission rate (resulting from the upward emission flux and the downward deposition flux) on the emission field decreases as a function of distance from the edge of the emission field for neutral atmospheric conditions (base case). This is caused by the fact that the net emission rate depends on the difference ($c_{g,surf}$ - $c_{g,air}$); $c_{g,surf}$ is take constant in the model, but the air concentration $c_{g,air}$ increases with distance to the upwind edge of the emission field due to the emission in from the upwind area. The increased $c_{g,air}$ concentration reduces the net emission rate. This effect is not very substantial, but noticeable and will increase with the size of the emission field in the wind direction (x-direction). In the model $c_{g,surf}$ is taken constant. In reality this is not the case and $c_{g,surf}$ will mainly decrease as a function of time as a result of different loss processes (volatilisation, leaching, degradation, uptake by plants etc.). But the main message of the results presented in Figure 26 is that the average net emission rate of a field also to a minor extent will depend on the size of the field in the wind direction for the same pesticide application rate (kg ha^{-1}).

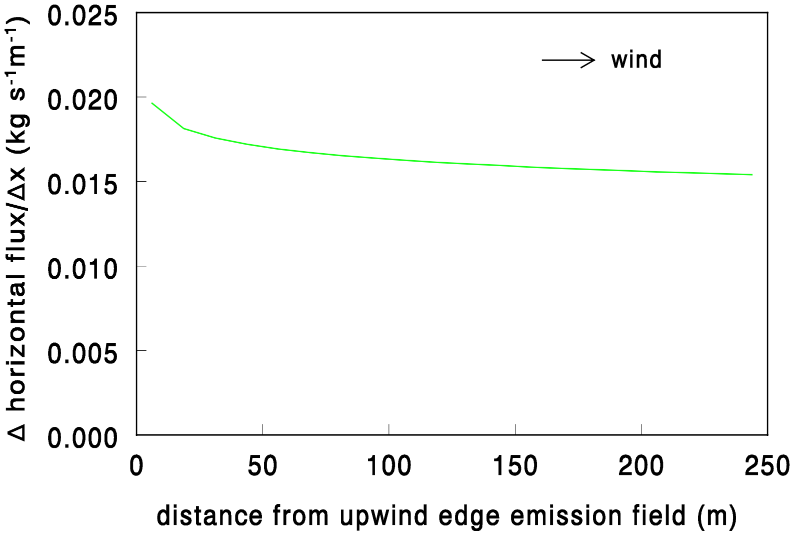


Figure 26
Modelled change in net emission flux on the emission field a function of the distance to the upwind edge of the field.

Modelleret ændring i netto emissionsfluxen på den mark hvorpå fordampningen finder sted som funktion af kanten af marken opstrøms.

1.12.8 Effect of surface roughness

In the base case a surface roughness length (z_{0m}) of 0.1 m is adopted, being representative of crops of about 1 m high. Sometimes, however, pesticides are applied when there are almost no crops. The surface roughness is then about 0.006 m. The friction velocity itself is also influenced by the surface roughness. This means that we cannot use the base case friction velocity of 0.3 m s^{-1} in the calculation for the case with the lower surface roughness.

Method to estimate the friction velocity for another surface

One way to tackle this problem is to find the wind speed at 60 m height for the base case using (6) and then to find friction velocity for the low surface roughness case from this wind speed using the same equation. This can be done because the wind speed at 60 m does not any longer depend on the local surface roughness, but on the surface roughness of an area of about 5x5 km^2 (Wieringa and Rijkoort, 1983). By doing this it is assumed that the average surface roughness of this area does not vary and that we only go down from 60 m height to another part of the area with a lower surface roughness. This method is to some extent arbitrary, but at least the friction velocity becomes more realistic in this way. With this method a friction velocity of 0.21 m s^{-1} is found.

Figure 27 shows the horizontal flux (vertically integrated over the whole mixing height). This is just the amount of pesticide that is airborne. Figure 27 shows that the emission rate is much less for the lower surface roughness. This is caused by reduced turbulence (characterised by a lower friction velocity). Figure 28 shows that the accumulated fraction of the emission that is dry deposited does not vary much with surface roughness. The reason for this is presumably that in the case of the lower surface roughness not only the deposition velocity is reduced, but also the vertical diffusion. A reduced vertical diffusion leads to higher concentrations near the surface and this may compensate for the lower dry deposition rate. It should be noted here that it is more difficult to model the case where the emission area has a different surface roughness than the deposition area because an internal boundary layer is formed at the boundary between the two roughnesses.

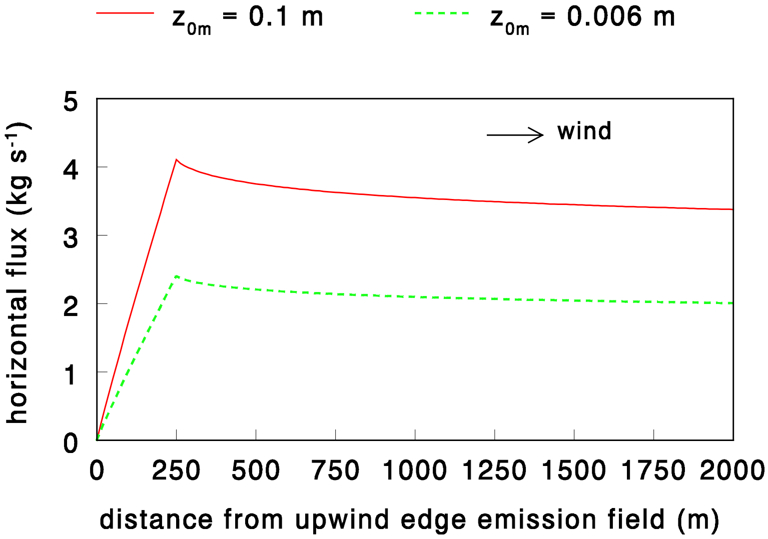


Figure 27
Modelled horizontal flux for different surface roughnesses as a function of distance from the upwind edge of the emission field. This flux indicates how much airborne material integrated over the whole mixing height passes by per unit of time.

Modelleret horisontal flux vertikal integreret over hele blandingshøjden for forskellige ruhedshøjder som funktion af afstanden til kanten af marken opstøms, hvor fordampning finder sted. Denne flux er et mål for hvor meget materiale der passerer forbi pr. tidsenhed, integreret over alle højder.

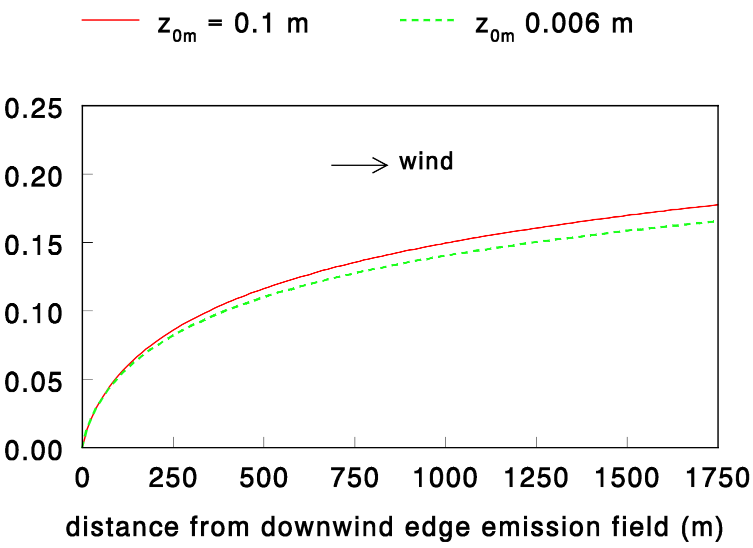


Figure 28
Modelled accumulated fraction of the emission dry deposited for different surface roughnesses as a function of distance from the downwind edge of the emission field.

Modelleret akkumuleret fraktion af emissionen som er tørdeponeret ved forskellige ruhedshøjder som funktion af afstanden til kanten af en mark nedstrøms, hvor fordampning finder sted.

1.12.9 **Effect of surface resistance**

Until now we have only discussed the extreme case where the surface resistance (r_c) is 0 and a maximum exchange/dry deposition velocity occurs. This is in reality only the case for high soluble and very reactive compounds like gaseous nitric acid (HNO_3). Without modelling the processes in the soil and in and on the crops it is difficult to know what the surface resistance is for pesticides, but some examples for well known air pollutants can maybe give an impression of possible implications of a non-zero surface resistance.

Figure 29 shows the effect of variations in the surface resistance. The following surface resistances r_c were chosen: 0, 100 and 1000 s m^{-1}. This reflects the situation for a highly soluble gas like HNO_3 ($r_c = 0$), a moderately soluble gas like SO_2 ($r_c = 100$) and a slightly soluble gas like NO ($r_c = 1000$) For a highly dry deposited gas the accumulated fraction of the emission deposited at the end of the deposition area is 0.1775. For a moderately soluble gas this is 0.0741 and for a slightly soluble gas this is 0.0118. This means that moderately and slightly soluble gases are being transported over much longer distances than highly soluble gases, if they are not depleted relatively fast by other processes.

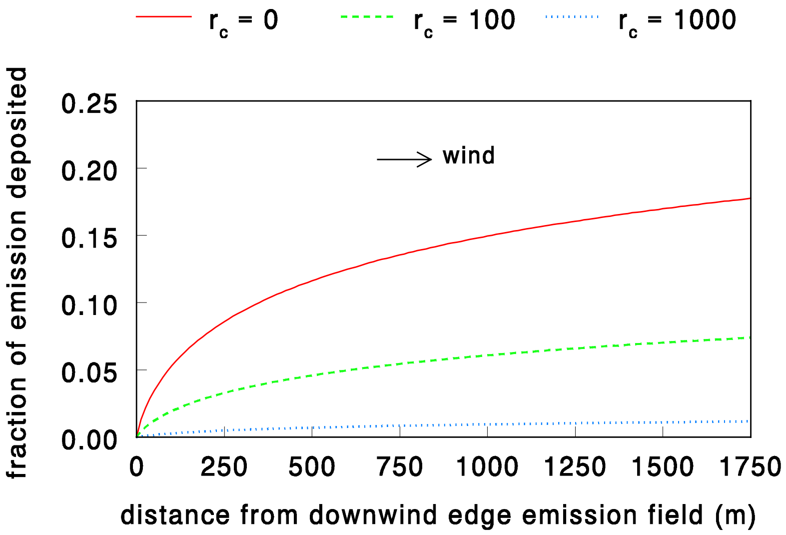


Figure 29
Modelled accumulated fraction of the emission dry deposited for different surface resistances as a function of distance from the downwind edge of the emission field.

Modelleret akkumuleret fraktion af emissionen som er tørdeponeret for forskellige overflademodstande som funktion af afstanden til kanten af en mark nedstrøms, hvor fordampning finder sted.

1.12.10 **Possibility of long-range transport**

Figure 30 gives the accumulated fraction of the emission dry deposited as a function of distance from the upwind edge of the emission field for a compound with zero surface resistance, i.e. with the maximum possible dry deposition velocity like for gaseous HNO_3. The calculations are in this case made for distances up to 1000 km from the downwind edge of the emission field.

Even in this extreme case about half of the released compound is still airborne after 100 km. As pesticides generally are less soluble and reactive as HNO_3, it is likely that they can be transported over considerable distances before they are deposited. As it is only raining 5-10% of the time, incorporation of rain events will not change the overall picture much. Some pesticides that are not very water soluble and do not react can have atmospheric lifetimes of at least several years (e.g. lindane) and are then found everywhere (Wania and Mackay, 1995).

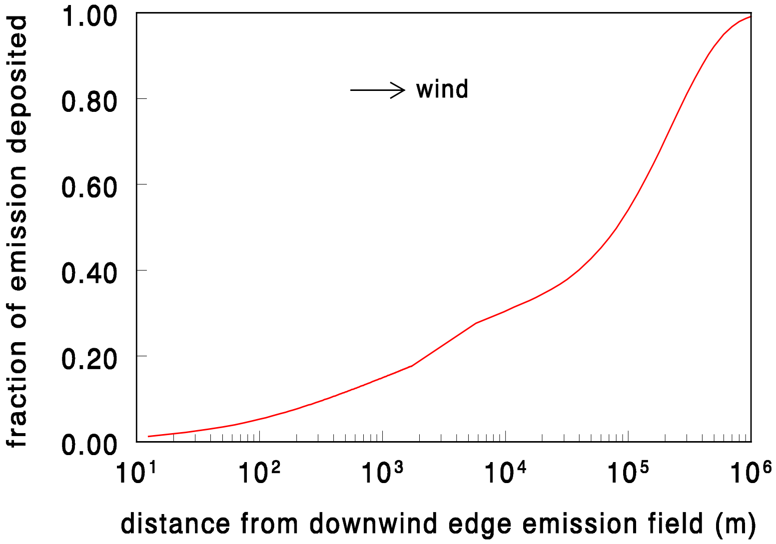


Figure 30
Modelled accumulated fraction of the emission dry deposited as a function of distance from the downwind edge of the emission field.

Modelleret akkumuleret fraktion af emissionen som er tørdeponeret som funktion af afstanden til kanten af en mark nedstrøms, hvor fordampning finder sted.

1.12.11 Maximum sum of dry and wet deposition

Usually pesticides are not applied during rain events or if rain is expected to occur in the near future. It is, however, useful to know how much wet deposition could maximally be compared to the maximum dry deposition (i.e for the case the surface resistance is 0). In all cases it is assumed that it is only raining in the deposition area and not in the emission field. It is also assumed that only below-cloud scavenging occurs, which is a reasonable assumption because the pesticide plume will not have been diffused to a height where there can be clouds (350-400 m on the average, see Table 4).

In Figure 31 three cases are presented. The first case is the base case where only dry deposition occurs. In the second case not only dry deposition occurs, but also wet deposition at a rainfall rate of 1 mm hr^{-1} in the deposition area only. In the third case the rain fall rate is increased to the rather high value of 10 mm hr^{-1}. In these calculations it is assumed that the surface resistance is zero (maximum dry deposition velocity) and that the raindrops cannot be saturated, i.e. that all gaseous pesticide reaching the raindrop surface is absorbed (maximum below-cloud scavenging rate).

Maximum sum of dry and wet deposition

In this situation less than 25% of the emitted pesticide is deposited within 1750 m from the downwind edge of the emission field. This percentage could be higher in case the wind speed is higher than about 4 m s^{-1} (used in the base case), which is about the average wind speed in Denmark. It is, however, unlikely that farmers will apply pesticides at high wind speeds.

Wet deposition vs. dry deposition

Figure 31 shows that the contribution from wet deposition, also for the relatively high rainfall rate of 10 mm hr^{-1} is much less than the contribution from dry deposition. This is the case for highly soluble gases. For other gases the ratio wet vs. dry deposition can be different.

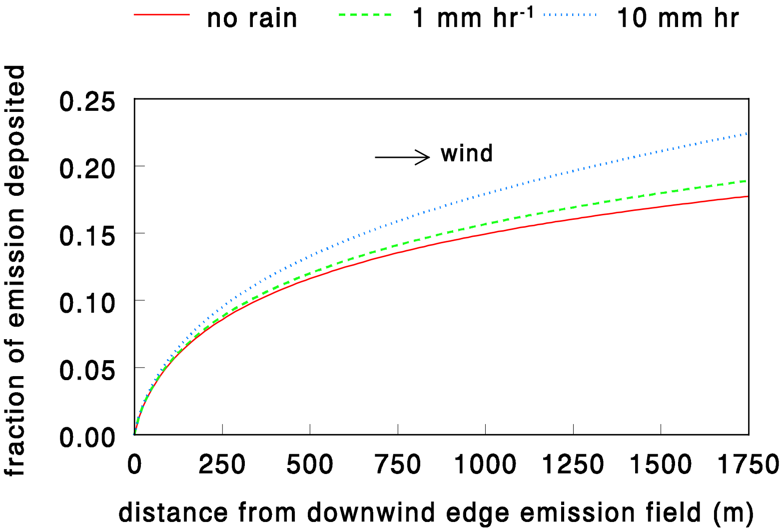


Figure 31
Modelled accumulated fraction of the emission dry deposited for different rainfall rates as a function of distance from the downwind edge of the emission field.

Modelleret akkumuleret fraktion af emissionen som er tørdeponeret for forskellige regn-intensiteter som funktion af afstanden til kanten af en mark nedstrøms, hvor fordampning finder sted.

1.12.12 **Comparison of dry and wet deposition with spray drift due to sedimentation**

Deposition

So far this report has been focused on how much of the emitted pesticide can be dry and wet deposited in the deposition area, i.e. the accumulated fraction of the emission deposited in the area of 0-1750 m from a field onto which pesticides are applied. The amount of pesticide emitted is only a fraction of the total amount of pesticide applied per unit area (dose).

Spray drift due to sedimentation

Deposition caused by spray drift due to sedimentation is usually expressed as a percentage of the dose and not the accumulated deposition due to spray drift as a function of distance to the downwind edge of the field is given (which was reported previously), but the deposition at each distance. This means that the dry and wet deposition results presented previously have to be expressed as the deposition for each distance and that assumptions have to be made on the fraction of the dose that volatilises in order to compare the dry and wet deposition with the deposition caused by spray drift due to sedimentation.

Dry and wet deposition flux expressed as percentage of the emission flux

Figure 26 shows the dry and wet deposition fluxes for each downwind distance expressed as a percentage of the average emission flux on the field onto which pesticides are applied. The emission flux, however, is not the same everywhere on the field. For that reason the dry and wet deposition fluxes were expressed as a function of the average emission flux on the field. The calculations were made for the case with the maximum sum of dry and wet deposition (surface resistance $r_c = 0$ and a high rainfall rate of 10 mm hr^{-1}) presented in the previous section. Such high deposition fluxes occur only for highly soluble gases (such as HNO_3). Gaseous pesticides will usually not have such extremely high solubilities. For that reason also results are presented for moderately soluble ($r_c = 100$) and slightly soluble ($r_c = 1000$) gaseous pesticides. The problem is that it was not possible to develop a model for below-cloud scavenging of moderately or slightly soluble gases within this project. So only information is available on the dry deposition of these compounds and not on the wet deposition. Moreover, if it had been possible to model the below-cloud scavenging of these compounds, another problem would arise: the scavenging of such compounds depends also on the concentration in raindrops before they reach the air below the cloud and this concentration should then be set arbitrarily. For that reason it was decided only to include dry deposition in the results presented here. Figure 32 shows that the flux is highest for the highly soluble gas and can be 38% of the emission flux at a distance of 1 m from the field. For other gases, the flux is lower, but can still be 1% of the emission flux close to the field.

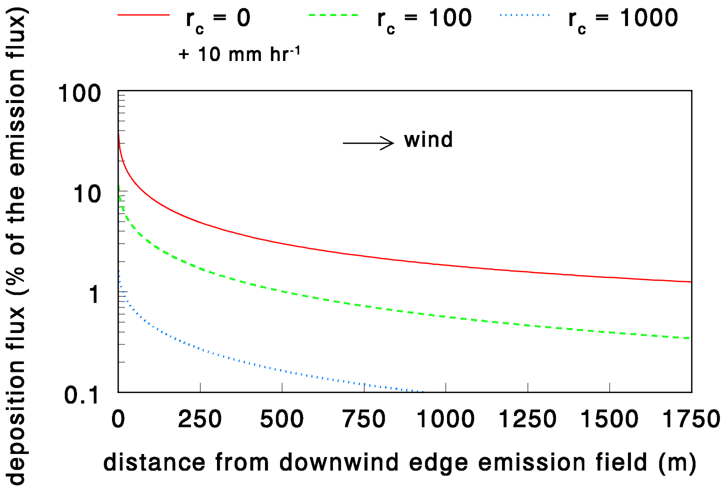


Figure 32
Modelled deposition flux expressed as percentage of the average emission flux on the field as a function of distance from the downwind edge of the emission field. The results are given for 3 cases: a) a surface resistance of 0 s m^{-1} and a rainfall rate of 10 mm hr^{-1}, b) a surface resistance of 100 s m^{-1} and no rain and c) a surface resistance of 1000 s m^{-1} and no rain.

Modelleret depositionsflux udtrykt som procentdel af den gennemsnitlige emission flux på marken, som funktion af afstanden til kanten af en mark nedstrøms, hvor fordampning finder sted. Resultaterne er givet for 3 situationer. a) en overflademodstand på 0 s m^{-1} og en regnintensitet på 10 mm i timen, b) en overflademodstand på 100 s m^{-1} og c) en overflademodstand på 1000 s m^{-1}.

Emission factor of 20% of the applied dose assumed

As has been mentioned previously, not all pesticide that has been applied volatilises. In order to be able to compare the dry/wet deposition with the spray drift an emission factor has to be assumed, i.e. the percentage of the applied pesticide that volatilises. Pesticides with an emission factor of 20% are not uncommon. For that reason such a factor was chosen for the example below. The estimated deposition caused by spray drift due to sedimentation was taken from Ganzelmeier (1995).

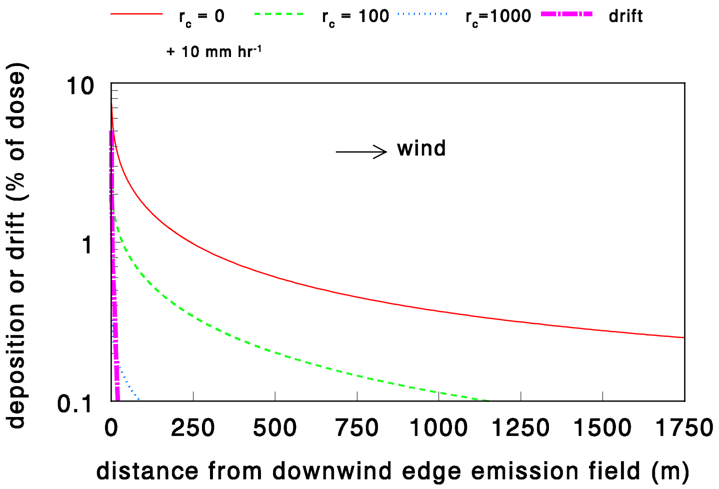


Figure 33
Modelled dry/wet deposition flux and estimated deposition flux caused by spray drift due to sedimentation expressed as percentage of the applied dose as a function of distance from the downwind edge of the field onto which the pesticide is applied. The results are given for 4 situations: a) dry and wet deposition with a surface resistance of 0 s m^{-1} *and a rainfall rate of 10 mm hr*$^{-1}$*, b) dry deposition with a surface resistance of 100 s m*$^{-1}$ *and no rain, c) dry deposition with a surface resistance of 1000 s m*$^{-1}$ *and no rain and d) deposition caused by spray drift due to sedimentation.*

Modelleret tør/våddepositionsflux og den estimerede afdriftsflux pga. sedimentation udtrykt som procentdel af den anvendte dosis på marken, som funktion af afstanden til kanten af en mark nedstrøms, hvor pesticidet er sprøjtet. Resultaterne er givet for 4 situationer. a) tør- og våddeposition med en overflademodstand på 0 s m^{-1} *og en regnintensitet på 10 mm i timen, b) tørdeposition med en overflademodstand på 100 s m*$^{-1}$ *c) tørdeposition med en en overflademodstand på 1000 s m*$^{-1}$ *og d) deposition forårsaget af afdrift pga. sedimentation.*

Importance of dry and wet deposition of s pesticidecompared to deposition due to spray drift

Figure 33 shows the deposition (derived from Figure 32 by assuming 20% volatilisation) and spraydrift flux expressed as a percentage of the dose. Figure 34 is in principle the same as Figure 33, but shows only results at the first 50 m. The main conclusion is that for highly soluble gases the deposition is everywhere larger than the spray drift (for an emission factor of 20%). Also for moderately and slightly soluble gases the deposition is appreciable and is larger than the spray drift at distances larger than 2 m (moderately soluble gases) or 15 m (slightly soluble gases) from the downwind edge of the field. From Figure 33 it can be noted that deposition due to spray drift decreases much faster with distance than the dry/wet deposition. This is mainly due to the fact that the relatively large spray droplets have fall velocities that are relatively large and hence cannot be transported over large distances.

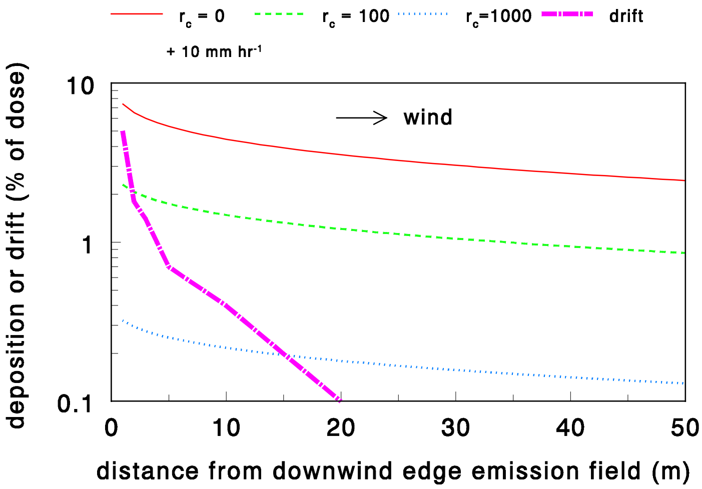


Figure 34
Modelled dry/wet deposition flux and estimated deposition flux due to spray drift expressed as percentage of the applied dose as a function of distance from the downwind edge of the field onto which the pesticide is applied. The results are given for 4 situations: a) dry and wet deposition with a surface resistance of 0 s m^{-1} and a rainfall rate of 10 mm hr^{-1}, b) dry deposition with a surface resistance of 100 s m^{-1} and no rain, c) dry deposition with a surface resistance of 1000 s m^{-1} and no rain and d) deposition due to spray drift.

Modelleret tør/våddepositionsflux og den estimerede afdriftsflux udtrykt som procentdel af den anvendte dosis på marken, som funktion af afstanden til kanten af en mark nedstrøms, hvor pesticidet er sprøjtet. Resultaterne er givet for 4 situationer. a) tør- og våddeposition med en overflademodstand på 0 s m^{-1} og en regnintensitet på 10 mm i timen, b) tørdeposition med en overflademodstand på 100 s m^{-1} c) tørdeposition med en en overflademodstand på 1000 s m^{-1} og d) deposition forårsaget af afdrift.

1.13 Intermezzo: conclusions on the model results

Only the influence of meteorological factors on the emission rate reported

In the following the emission rate is discussed. In principle this report deals only with the meteorological factors influencing the emission. Other factors will, however, also influence the emission rate. These factors are e.g. the properties of the surface (plant, soil) and the processes going on in and on the surface (see section 1.6. for a brief discussion). A basic conclusion is, that it depends on the properties of the compounds and the surface how important the meteorological influence on the emission rate is. Here only the effect of meteorological factors on the emission rate are discussed.

Results are mainly given for a highly soluble gas: gives maximum deposition

Unless indicated otherwise the results presented are for a highly soluble gas. This is done because the deposition is highest in that case. In this way an estimate is obtained on the maximum possible deposition close to a field onto which pesticides are applied. This was one of the main objectives of the project.

Emission rate as a function of wind speed

The emission rate of pesticides applied to a field increases with wind speed.

Dry deposition as a

In case of highly soluble gases, when the surface resistance is 0, the accu-

function of the wind speed mulated fraction of the emission dry deposited as a function of distance to the downwind edge of the field will be independent of the wind speed. For moderately or slightly soluble a surface resistance has a higher value than 0. In that case the accumulated fraction of the emission dry deposited will decrease with wind speed, at least if the surface concentration is 0. In other words: moderately and slightly soluble gases will in that case be transported over longer distances at higher wind speed.

Emission as a function of atmospheric stability Calculations were made for typical atmospheric conditions for different stability classes. The emission rate is higher during neutral and stable atmospheric conditions than during stable conditions.

Dry deposition as a function of atmospheric stability The accumulated fraction of the emission dry deposited is larger in the following order: for stable < neutral < unstable atmospheric conditions.

Emission rate as a function of field size The (net) emission rate (kg m^{-2} s^{-1}) decreases with the size of the field. This is, however, a minor effect. In the calculations a constant surface concentration was adopted, that was the same everywhere. The surface concentration will in reality decrease with time due to depletion caused by the emission and for that reason it is likely that the observed effect is negligible in reality.

Emission rate as a function of the surface roughness The emission rate will increase with the surface roughness, if the wind speed is the same at greater height (60 m). This is due to increased turbulence. For that reason the emission rate form a crop will be higher than from bare soil (for the same compound under the same conditions).

Deposition as a function of the surface roughness The accumulated fraction of the emission dry deposited increases only slightly with surface roughness. It should be noted, however, that the emission itself increases much with surface roughness.

Variation in the emission rate due to variations in the meteorological conditions The variation in the emission rate due to variations in the friction wind speed and the atmospheric stability can easily be more than a factor 4 for those pesticides for which the emission rate is governed by meteorological processes. In practise the variation can be even greater because the gas phase concentration in the soil is highly temperature dependent, because the Henry's law coefficient is a function of temperature.

Minimum long-range transport Results for a highly soluble gas indicate that about half of the emitted amount will still be airborne after a transport distance of 100 km. For less soluble gases and for particles containing pesticides much more than half of the emitted amount will be airborne after 100 km. Often half of it will still be airborne after 1000 km.

Rapidly decreasing air concentrations with distance does not necessarily mean a short transport distance Measurements close to sources will show that the concentration in the air at ground-level decreases rapidly with distance to the source. It is tempting to conclude then that the pesticide is not travelling over long distances. In fact, the opposite is true. The concentration at ground-level decreases rapidly with distance because the compound is being mixed rapidly to greater heights, where it is not subject to removal by dry deposition. As a result it can be transported over long distances, at least when it is not removed by rain.

Influence of precipitation Within 2 km from a source most of the emitted pesticide has not yet reached the clouds and only wet removal by the less efficient below-cloud scavenging process occurs. For a highly soluble gas the wet deposition in this area is much less than the dry deposition. The ratio wet to dry deposition depends e.g. on the meteorological conditions including the precipitation rate. The ratio wet to dry deposition will in general be different for different compounds. For gases both the dry and the wet removal rate increase with solubility, indicating lower dry and wet removal rates for these gases. For most particulate pesticides the wet removal rate will be much larger than the dry removal rate, because particles are not dry deposit at a high rate, but are removed very efficiently by precipitation (see section 1.5).

Maximum accumulated fraction of the emission deposited within 2 km from the source

Under average Danish conditions less than 25% of the emission of a highly soluble gas will be removed by dry and wet deposition within 2 km from the source area. For less soluble gases and for particulate pesticides much less than 25% will be deposited within 2 km from the source. If only dry deposition occurs, a very rough estimate will be that 7% of a moderately soluble gas and 1% of a slightly soluble gas will be deposited within 2 km from the source. These very rough estimates are highly uncertain and indicate merely the right order of magnitude. For less soluble gases processes in the surface (soil, plant) are very important and no good model results can be obtained for these gases unless the concentrations in and on the surface (soil, plant) is modelled as well.

Deposition vs. spray drift due to sedimentation

Dry and wet deposition of highly soluble gaseous pesticides at distances of 1-20 m from the field onto which pesticides are applied can be more important than deposition caused by spray drift due to sedimentation for pesticides of which 20% or more volatilises. For moderately soluble or slightly soluble gaseous pesticides the dry and wet deposition can be as important as deposition caused by spray drift due to sedimentation for these pesticides at distances greater than 2 m (moderately soluble gases) or 15 m (slightly soluble gases). Another form of spray drift, i.e. the spray drift caused by small droplets is not investigated much, but can be potentially more important than spray drift due to sedimentation.

2 Discussion and conclusions

In section 1.5 the main conclusions on meteorology and surface exchange are presented. In section 1.8 the main conclusions on wet deposition are presented including a comparison with dry deposition. In section 1.13 the main conclusions on the model results are presented. These conclusions will not be repeated in this section, which mainly deals with overall conclusions on the atmospheric behaviour of pesticides and not at least with recommendations for future research.

Important pesticide properties

The atmospheric behaviour of pesticides is to a large extent governed by their properties, amongst which the solubility in water (Henry's law coefficient) and the vapour pressure are most important. For possible reactions in the atmosphere their chemical structure, which also determines their solubility and vapour pressure, are important.

Uncertainty in crucial properties

Modelling the atmospheric behaviour of pesticides is handicapped by the fact that information on crucial properties of pesticides is not available or is uncertain. E.g. a factor of 10 uncertainty in a crucial variables as the Henry's law coefficient or the vapour pressure is not uncommon.

Difficult to generalise

Pesticides are compounds that have in common that they are biologically active and that they often are organic compounds. That is about the only properties they have in common. The properties that are of crucial importance to their behaviour in the environment, in particular in the atmosphere, can vary up to 5 orders in magnitude. This in combination with a large variety of possible surfaces with again different properties, gives a huge number of different possible combinations. For that reason it is difficult to generalise. It is even more difficult to generalise the atmospheric behaviour because we have not enough knowledge presently. This in turn is also the challenge. Summarising it could be stated that pesticides have one more property in common: they are different.

It should be noted here, that many hundreds of pesticides are used or have been used in the past. Some pesticides have been abandoned, but are still in the environment, others are novel. They have all in common that the information provided by the manufactures for the official approval procedure is not enough to predict their atmospheric behaviour. For that reason improvement of the approval procedure is needed and research should be conducted to find easy but effective methods to screen the potential of pesticides to cause any harm via the atmospheric pathway.

Processes related to the surface should be included

Surface exchange (emission, dry deposition) of gaseous pesticides depends not only on atmospheric processes, but also on the properties of the surface (soil, plant) and on the processes that take place in the surface. The atmospheric behaviour of pesticides cannot be modelled without taking these processes into account. Important processes with that respect are transport into the surface and degradation in the surface. For many gaseous pesticides dry deposition will be determined more by these processes than by atmospheric processes. Emission of pesticides from soil depends also to a large extent on soil processes. It should be noted here, that even if the pesticides are applied onto plants, part of the applied amount reaches the soil, either directly or after having been washed down by precipitation.

Moreover, heating of the surface and evaporation of water from the surface determines to some extent the friction velocity and the atmospheric stability and has therefore influence on vertical diffusion and surface exchange. Water and heat are also important for the surface exchange (emission, dry deposition) of pesticides from the soil. Water is important for soil processes because it can replace pesticides adsorbed onto soil particles and can be carrier of dissolved pesticides. Heat is important, because the evaporation of water depends on it and because the vapour pressure and Henry's law coefficient are temperature dependent. In that way atmospheric processes and processes in the soil and on plants (evaporation of water) are interrelated. In stead of treating atmospheric and surface processes separately in models they should be integrated, otherwise model results will be less realistic.

Stable atmospheric conditions

During the development and testing of the model it was noted that the diffusion under very stable conditions modelled with a K-model can be much less than the diffusion modelled with the OML-model, a Gaussian plume model. This illustrates probably the uncertainty in the diffusion during these conditions. The dry deposition close to the source modelled with a K-model can then become extremely high. In such model situations the wind speed near the ground is extremely low. Moreover, the vertical mixing is highly reduced. As a result the pesticide is "hanging around". In such situations with a very low wind speed most diffusion models are not any longer correct, because the air flow is in such cases more determined by height differences in the terrain, spatial differences in the heat flux etc. than by the wind. These situations occur, however, quite frequently in the evening when the surface cools down. Under these conditions the emission is also very much reduced. It should for that reason be investigated what this lack of knowledge means for conclusions on the atmospheric behaviour of pesticides, e.g. can it be assumed that the emission and consequently the dry deposition is negligible during these conditions.

Dry deposition of slightly soluble gaseous pesticides from laboratory experiments

For slightly soluble gaseous pesticides is it possible to obtain information on the uptake rate by dry deposition from laboratory experiments. It would be useful to consider the possibility to obtain information from laboratory measurements for these gaseous pesticides in the future.

Dry deposition close to a source has never been measured

It was shown, that at maximum less than 25% of the emission of pesticides can be dry deposited within 2 km from the source. This in case of highly soluble gases. In case of moderately soluble gases this will be of the order of 7% and for slightly soluble gases this will be of the order of 1%. In these calculations knowledge on atmospheric diffusion and dry deposition of gases are combined. The model for atmospheric diffusion has been verified with measurements and the model used here for dry deposition has been verified at some distance from sources for other compounds than pesticides. The modelled dry deposition as a function of distance from the source relatively close to a source has never been measured, although in extreme cases about 20% of the emission could be dry deposited within a few hundred metres from the source. It would therefore be useful to measure this for a highly soluble gas that is easy to measure. This could be used to obtain an upper estimate of the deposition close to a source.

Scavenging ratio can be measured

By measuring concentrations in air and precipitation simultaneously the scavenging ratio for both gaseous and particulate pesticides can be determined. This can only be done at such a distance from important sources that the pesticide has been mixed in such a way that the concentration measured at ground-level is representative of the concentration of the air that enters the cloud. The scavenging coefficient, i.e. the rate at which material is removed from the atmosphere can then be calculated if the mixing height is known. For slightly soluble gases the scavenging ratio should be the same as calculated from the Henry's law coefficient with (40).

Partitioning

It is important to determine how much of a pesticide is in the gas phase and how much in the particulate phase and to obtain information on the size of the particles. The reason for this is that the rate at which pesticides are removed from the atmosphere depend to a large extent on the form or size (particles) in which they are present. It would be useful to try to measure this partitioning. Moreover, it would be useful to have more information on the conversion rate from the gaseous to the particulate phase and the factors that have an influence on it.

Photochemical reactions and conversion from the gaseous to the particulate phase are important

In this report it is assumed, that photochemical atmospheric reactions of pesticides and conversion of pesticides from the gaseous to the particulate phase are not important within 2 km from a source. This is likely, but by no means proven.

Pesticides are removed from the atmosphere by dry and wet deposition. Both the dry and wet removal rate of gaseous pesticides increase with the solubility in water. For not very soluble gases this means that they can be transported over very long distances, if there are no other processes that can contribute to their removal. It is here that photochemical reactions and conversion from the gaseous to the particulate phase play a role. These processes do not remove compounds from the atmosphere. They do, however, lead to other products, that may be removed more efficiently from the atmosphere. E.g. slightly soluble pesticides associated with particles are generally removed rather efficiently from the atmosphere by precipitation than the same pesticides in the gas phase.

This illustrates that it is very important to have information on the photochemical reactions and the conversion from the gaseous to the particulate phase (and vice versa), because these processes limit the long-range transport of many pesticides.

Need for mechanistic emission models

Some preliminary methods exist to estimate the maximum or cumulative emission of pesticides (see section 1.6). These methods are based on a statistical correlation of measured emission fluxes with properties of the pesticide and not on a mechanistic description of the processes that are going on. Although these preliminary methods can be useful to estimate emissions in screening procedures for pesticides, it is less useful to apply them to generate emissions in atmospheric transport and deposition models used to calculate the deposition as a function of distance to the emission field. The principal reason for this is that emissions, diffusion and dry deposition depend on the same meteorological factors (turbulence, heat flux, water vapour flux). And this is not taken into account if emissions, diffusion and dry deposition are calculated separately, e.g. if the emission is calculated for average atmospheric conditions and the atmospheric conditions are far from average. Recent calculations for ammonia have shown that if the meteorological conditions are such that they lead to increased emission, they also favour long-range transport (Asman et al., 1998). It is only possible to reveal this type of interactions if mechanistic models are applied with the same meteorology to describe both the emission, diffusion and dry deposition processes. More mechanistic models should be developed to describe the emission of pesticides and their results should be verified with already existing or new laboratory and field experiments.

Difference in information needed for screening and atmo-

The information presented in the previous section illustrates the fact that in general information that is sufficient for screening procedures in connection with the approval of a pesticide not necessarily is sufficient to describe the *spheric transport models* processes needed to quantify fluxes with atmospheric transport and deposition models.

Measurements for different purposes

There are different reasons to measure pesticides. The first reason is to monitor, e.g. to get an impression of the compounds present and to know whether the concentration is so high that it could lead to effects. Moreover, this type of measurements can be used to verify the results of atmospheric transport and deposition models. This type of measurements is necessary, but it is a kind of reaction on the action performed by the pesticide manufacturers and farmers.

Another reason to measure pesticides is to obtain information on processes that occur, e.g. processes that could be part of a model. This model could be an emission model, a deposition model or even an integrated atmospheric transport and deposition model. Such models can be used for various purposes for which it is difficult or impossible to use monitoring:

- Prediction of the behaviour of compounds that are not yet on the marked.
- Estimation of import and export of pesticides.
- Interpolation of measurements in space and time.
- Description of historical situations for which no monitoring data are available.
- Design of experiments to obtain information on processes or to design of the locations of stations in a monitoring network.
- Study of the effect of different scenarios, e.g. different possibilities to apply pesticides, so that the best pesticide or conditions can be chosen for a given purpose.

Field experiments, model experiments and laboratory experiments

It should be noted here that models never can replace measurements entirely, but can provide best estimates. A good way to apply models is to design experiments. The results of the experiments can then lead to an improvement of the model, which in turn can lead an improved measurement strategy.

The analysis of pesticides is time consuming and difficult, partly because concentrations are so low. For that reason they are also very expensive. This means that experiments should be planned with much more care than usually is done in atmospheric science. It is here that models can play a crucial role. Also laboratory experiments can be a relative good investment, e.g. for emission, uptake by plants, photochemical reactions etc. Laboratory experiments are useful, because it is possible to study processes under controlled conditions and it gives the possibility of just varying one factor, whereas in the real world many factors vary at the same time, so that it is difficult to get insight in different processes that occur at the same time. It is, however, never possible to rely fully on laboratory experiments. One reason is that it is very difficult to create the same turbulence in the laboratory as in the atmosphere as in the field. An good research strategy should have an optimal balance between field experiments, laboratory experiments and model development and calculations.

Process research

Pesticides come in the atmosphere by emission, are diffused, react and deposit (in that order). There is not so much known on the atmospheric behaviour of pesticides. It would for that reason be advisable to start exploring their behaviour by studying separate processes and not the result of more than one process. It would also be advisable to pay much attention to the emission process, because studies of the other processes would benefit from information on the first process in the chain. Moreover, it is useful to know whether or not the pesticide is emitted to the atmosphere. If not, further atmospheric research is not necessary.

Spray drift

The deposition of tiny spray droplets that do not deposit due to sedimentation should be investigated.

Time perspective It took about 20 years before atmospheric scientists had enough knowledge to understand the atmospheric behaviour of sulphur dioxide. It took then only about 10 years before the more complicated behaviour of nitrogen oxides were understood, because knowledge gained during research on sulphur dioxide could be used. These compounds occur in concentrations that are a factor of 1000 higher than pesticides. Much attention was paid to just a few compounds. There are hundreds of pesticides around in the atmosphere, they have very different properties and they occur in very low concentrations. For that reason it is a far from easy task to study them, and the study will therefore take much time.

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Appendix I

D_g^*: the apparent diffusivity of the gas in the gas phase

$$D_g^* = \frac{D_g}{1 + \dfrac{4D_g}{r\alpha_g \overline{v_g}}}$$

where:

D_g^* = apparent diffusivity of the gas in the gas phase ($m^2\ s^{-1}$).

D_g = diffusivity of the gas in the gas phase ($m^2\ s^{-1}$).

α_g = accomodation coefficient (dimensionless) which gives the probability that the gas molecule that hits the surface of the drop is absorbed and $\overline{v_g}$ is the average speed of the gas molecules ($m\ s^{-1}$) defined by:

$$\overline{v_g} = \sqrt{\frac{8RT}{\pi M_g}}$$

where:

R = gas constant (8.317 J °K^{-1} mol^{-1})

T = temperature (°K)

M_g = molecular mass of the gas (kg mol^{-1})

If α_g is larger than about 0.01, D_g^* is approximately equal to D_g.

Appendix II

Characteristic time and distance of absorption

The characteristic time and distance of absorption can be calculated from Table A2-1 and the Henry’s law coefficient using equations (34) or (38).

τ_{abs} can be found from:

$$\tau_{abs} = \frac{\text{factor1}}{K_H}$$

Δ_{abs} can be found from:

$$\Delta_{abs} = \frac{\text{factor2}}{K_H}$$

where K_H = Henry’s law coeffcient (c_{gas}/c_{water}) (dimensionless).

Table A2-1
Properties of drops and factors that can be used to find the characteristic time constant of absorption τ_{abs} *and the characteristic distance of absorption* Δ_{abs}*. The molecular mass of the gas is 300, which gives an estimated diffusivity in air of* 6.062×10^{-6} m^2 s^{-1}.

Egenskaber for dråber og faktorer som kan anvendes til at finde den karakteriske tidskonstant for absorption τ_{abs} *og den karakteristiske afstand for absorption* Δ_{abs}*. Gassens molekylmasse er 300, som giver en estimeret diffusivitet i luft på* 6.062×10^{-6} m^2 s^{-1}.

Radius (m)	Terminal velocity v_t (m s^{-1})	f_g (dim.less)	factor1 = $r^2/(3f_gD_g)$ (s)	factor2 = $(r^2v_t/(3f_gD_g)$ (m)
1×10^{-6}	1.328×10^{-4}	1.000	5.499×10^{-8}	7.303×10^{-12}
2×10^{-6}	5.118×10^{-4}	1.000	2.199×10^{-7}	1.126×10^{-10}
3×10^{-6}	1.137×10^{-3}	1.000	4.948×10^{-7}	5.626×10^{-10}
4×10^{-6}	2.008×10^{-3}	1.000	8.796×10^{-7}	1.766×10^{-9}
5×10^{-6}	3.126×10^{-3}	1.000	1.374×10^{-6}	4.295×10^{-9}
6×10^{-6}	4.489×10^{-3}	1.001	1.978×10^{-6}	8.880×10^{-9}
7×10^{-6}	6.099×10^{-3}	1.001	2.691×10^{-6}	1.641×10^{-8}
8×10^{-6}	7.955×10^{-3}	1.002	3.513×10^{-6}	2.795×10^{-8}
9×10^{-6}	1.006×10^{-2}	1.002	4.443×10^{-6}	4.469×10^{-8}
1×10^{-5}	1.237×10^{-2}	1.003	5.480×10^{-6}	6.778×10^{-8}
2×10^{-5}	4.834×10^{-2}	1.026	2.144×10^{-5}	1.036×10^{-6}
3×10^{-5}	1.043×10^{-1}	1.084	4.565×10^{-5}	4.763×10^{-6}
4×10^{-5}	1.745×10^{-1}	1.187	7.409×10^{-5}	1.293×10^{-5}
5×10^{-5}	2.539×10^{-1}	1.327	1.036×10^{-4}	2.630×10^{-5}
6×10^{-5}	3.390×10^{-1}	1.473	1.344×10^{-4}	4.557×10^{-5}
7×10^{-5}	4.273×10^{-1}	1.620	1.663×10^{-4}	7.107×10^{-5}

8×10^{-5}	5.173×10^{-1}	1.768	1.991×10^{-4}	1.030×10^{-4}
9×10^{-5}	6.081×10^{-1}	1.916	2.325×10^{-4}	1.414×10^{-4}
1×10^{-4}	6.991×10^{-1}	2.064	2.664×10^{-4}	1.862×10^{-4}
2×10^{-4}	1.587	3.516	6.255×10^{-4}	9.930×10^{-4}
3×10^{-4}	2.438	4.933	1.003×10^{-3}	2.446×10^{-3}
4×10^{-4}	3.247	6.314	1.393×10^{-3}	4.524×10^{-3}
5×10^{-4}	3.983	7.633	1.801×10^{-3}	7.173×10^{-3}
6×10^{-4}	4.608	8.854	2.236×10^{-3}	1.030×10^{-2}
7×10^{-4}	5.135	9.987	2.698×10^{-3}	1.385×10^{-2}
8×10^{-4}	5.616	1.107×10^{1}	3.178×10^{-3}	1.785×10^{-2}
9×10^{-4}	6.060	1.212×10^{1}	3.675×10^{-3}	2.227×10^{-2}
1×10^{-3}	6.468	1.313×10^{1}	4.188×10^{-3}	2.709×10^{-2}
1×10^{-3}	7.982	1.758×10^{1}	7.036×10^{-3}	5.616×10^{-2}
2×10^{-3}	8.723	2.106×10^{1}	1.044×10^{-2}	9.109×10^{-2}
2×10^{-3}	8.976	2.378×10^{1}	1.445×10^{-2}	1.297×10^{-1}
3×10^{-3}	9.010	2.603×10^{1}	1.901×10^{-2}	1.713×10^{-1}
3×10^{-3}	9.006	2.804×10^{1}	2.402×10^{-2}	2.163×10^{-1}

Note: This example is for a gas with a molecular mass of 300. If a gas with a molecular mass of 200 were chosen f_g would have been the same for small drops and about 7% less for the larger drops; factor1 and factor2 would have been 13-19% less. If a gas with a molecular mass of 400 were chosen, f_g would have been the same for small drops and about 5% larger for the larger drops; factor1 and factor2 would have been 10-15% larger. The conclusion is that these factors do not depend so much on the diffusivity D_g.

Appendix III

Parametrization of the below-cloud scavenging coefficient for highly soluble gases

Asman (1995) made a detailed model for below-cloud scavenging under convective conditions that includes the evaporation of the droplets. The model can handle different descriptions of the raindrop size distribution. The results of this model for the raindrop size distribution of Best (1950) were parameterized with the drop size distribution in such a way that they easily could be incorporated in atmospheric transport models. The only input parameters necessary are the rainfall rate, temperature and relative humidity at ground-level and the diffusivity of the gas at 25°C. The parameterization of the below-cloud scavening coefficient is:

$$\Lambda_b = aI^{bav}$$

where:

Λ_b = below cloud scavenging coefficient (s^{-1})

I_{mm} = rainfall rate at ground level (mm hr^{-1})

In this equation a and bav are coefficients that are functions of the relative humidity at ground level (rh(0), in %) and the temperature at ground level (T(0), in °K) and of the diffusivity of the gas at 25°C and 1 atm (D_g in $m^2\ s^{-1}$). If D_g is not known it can be estimated from the molecular weight of the gas and (15).

The value of a is found from the following set of equations:
$a = aa + bb\, D_g$
where:
$aa = a0 + a1\, rh(0)$
$bb = b0 + b1\, rh(0)$
with the following values of the coefficients:
$a0 = 4.476x10^{-5} - 1.347x10^{-7}T(0)$
$a1 = -3.004x10^{-7} + 1.498x10^{-9}T(0)$
$b0 = 8.717 - 2.787x10^{-2}T(0)$
$b1 = -5.074x10^{-2} + 2.894x10^{-4}T(0)$

The value of bav is found from the following set of equation:
$bav = bav0 + bav1\, rh(0)$
where:
$bav0 = 9.016x10^{-2} + 2.315x10^{-3}T(0)$
$bav1 = 4.458x10^{-3} - 2.115x10^{-5}T(0)$

The functions are here given with greater accuracy than actually known, to avoid any rounding off. This parameterization is made for below-cloud scavenging under convective conditions. This parameterization can, however, also be used to get an estimate of the below-cloud scavenging coefficient under non-convective conditions.

Pesticides in precipitation

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Table of contents

Summary

Pesticides in precipitation

The concentration of pesticides in precipitation was investigated during the period May 1996 - December 1998 at three sites on Zealand in Denmark (Gadevang, Gisselfeld and Lorup). These sites had not been directly affected by local emissions. The samples were analysed for isoproturon (including 2 metabolites), the phenoxyalkanoic acid herbicides MCPA, mecoprop, and dichlorprop plus bentazone (including 2 metabolites), and DNOC.

Effects of pesticides

Pesticides in precipitation when applicated

This project was part of a larger project, which studied the effects of pesticides in precipitation on plants and plant ecosystems. The highest measured concentrations were 0.9µg/L for isoproturon and 0.6µg/L for phenoxyalkanoic acid herbicides. In most cases the concentrations in precipitation were found at times when the pesticides were known to be applied to crops. Combined samples for these three sites for the period September 1996 - November 1997 were analysed for 44 compounds. Concentrations over the detection limit were only found for isoproturon, metamitron, DNOC (2-methyl-4,6-dinitrophenol), mecoprop, methabenzthiazuron, 2-hydroxyterbuthylazine, terbuthylazine and 2,4-D.

DNOC in precipitation caused by photochemical reactions

Unexpectedly high concentrations of DNOC (0.38 - 4.5µg/L) were found during the whole sampling period. Although DNOC has not been applied in Denmark since 1986, it has been detected in other investigations in the top layers of the ground water and in streams. Current literature indicates that DNOC is likely to be formed by photochemical reactions of toluene and nitrogen oxides in the atmosphere probably from traffic pollution. The atmospheric deposition of DNOC, mecoprop and isoproturon is respectively 7.5-, 0.3- and 0.3g/ha/year.

Generally, pesticides will be transported over distances of more than several hundred kilometers before they are deposited, unless they are (photochemically) degraded in the atmosphere at a high rate.

Dansk sammendrag

Den danske nedbørs eventuelle indhold af pesticider er undersøgt ved opsamling af regnvandsprøver fra lokaliteter, som er beliggende således, at et lokalt bidrag er minimeret.

Pesticider i nedbør fra skovlysninger

Der er udtaget nedbørsprøver fra lysninger i skove på 3 sjællandske lokaliteter Gadevang, Gisselfeld og Lorup, som i perioden 1996-1997 er blevet analyseret for phenoxysyrerne: MCPA, mechlorprop og dichlorprop samt for isoproturon. I 1998 er analyseprogrammet udvidet, idet bentazon og 2 metabolitter heraf, DNOC samt 2 metabolitter af isoproturon er medtaget.

Pesticider fundet i sprøjtesæsonen

Den højeste koncentration af phenoxysyrerne var på 0,6µg/L. For isoproturons vedkommende var den maksimale koncentration 0,9µg/L. I langt de fleste tilfælde var der sammenfald mellem det tidspunkt, hvor herbiciderne blev påvist i nedbøren og anvendelsestidspunktet. DNOC er påvist i alle de vandprøver, der er udtaget i 1998 i koncentrationsområdet fra 0,04µg/L til 0,87µg/L.Phenoxysyrerne forekommer på alle tre lokaliteter forår og efterår 1996. I 1997 er der kun fundet mechlorprop i en enkelt prøve i sprøjteperioden om efteråret og i 1998 er der ikke påvist phenoxysyrer. Isoproturon er påvist efterår 1996 og 1997 på alle tre lokaliteter og forår og efterår 1998 på alle tre lokaliteter. Det er ikke tilladt at anvende isoproturon om foråret i Danmark, så der kan være tale om langtransport fra lande, hvor sprøjtning er tilladt eller eventuelt sprøjtning i Danmark uden for efterårsperioden, hvor det har været tilladt.

DNOC i nedbør stammer fra atmosfæriske processer

Derudover er der i perioden september 1996 til november 1997 udtaget 13 prøver til analyse for de 44 stoffer, som indgår i DMU´s analysemetode, heraf er de 8 påvist. Det er følgende pesticidkemikalier: isoproturon, metamitron, DNOC (2-methyl-4,6-dinitrophenol), mechlorprop, methabenzthiazuron, 2-hydroxyterbuthylazin, terbuthylazin og 2,4-D. Det, der især overraskede, var indholdet af DNOC, som blev fundet igennem hele perioden og i et forholdsvis højt koncentrationsområde fra 0,38µg/l til 4,5µg/l. Stoffet har ikke været anvendt i Danmark de sidste 10 år, så her er formentlig tale om en mere global forurening, sandsynligvis stammende fra atmosfærekemiske processer forårsaget af traffikkens forurening. Beregnes belastningen i g pr. ha i ovennævnte periode, er belastningen af DNOC 7,5 g pr. ha, mechlorprop og isoproturon tilfører begge ca. 0,3 g pr. ha svarende til henholdsvis 88% og 8% af den totale belastning.

1 Introduction and background

Transport of pesticides in the atmosphere depends on atmospheric lifetime

Pesticides that evaporate can be transported in the atmosphere before they are deposited on the surface again. How far a substance can be transported depends on its atmospheric lifetime, which is determined by how fast the compound is removed from the atmosphere caused by reaction, dry deposition, and wet deposition.

In a co-operation project within the framework of Nordic Council of Ministers from 1992 to 1994, rainwater samples from 2 places in Denmark, respectively from Ulborg plantation 10 km from the Jutlandic west coast (56° 17’ N , 8° 26’ E) and from Gadevang in Gribskov were gathered. The content of the samples was analysed for the following 10 pesticides: propiconazole, prochloraz, lambda-cyhalothrin, cypermethrin, esfenvalerate, deltamethrin, atrazine, mecoprop, dichlorprop and MCPA. Only phenoxyalkanoic acid herbicides were found. The maximum concentrations were 0.4µg/L (Kirknel and Felding, 1995).

Lindane in precipitation

In 1990-1991, the National Environmental Institute in Denmark measured the contents of α-HCH and γ-HCH (lindane) in rainwater on 2 localities in Denmark Husby (56° 17’ N , 8° 8’ E) and Ulborg in West Jutland respectively. Three localities, Ulborg, Bagenkop and Anholt, respectively were tested in 1992. The maximum concentration found was 0.1µg/L, The conclusion was, that findings of lindane was due to their use in countries South and West of Denmark (Cleemann et al., 1995).

Wet deposition of pesticides investigated

In the present study, wet deposition of pesticides was investigated. Precipitation samples have been gathered over a period of 3 years from 1996-1998 from 3 localities on Zeeland: Gadevang, Gisselfeld and Lorup, which have been analysed for the phenoxyalkanoic acid herbicides: MCPA, mecoprop and dichlorprop together with isoproturon. In 1998 the program was expanded, when bentazone and 2 of its metabolites, DNOC, and 2 metabolites of isoproturon were included.

44 pesticides in analytical programme

13 water samples, taken in the period from September 1996 to November 1997, from the 3 above mentioned localities, were analysed for 44 different pesticide compounds.

2 International findings

A short summary about the findings of specific pesticides in precipitation in different countries is given below.

Chlorinated insecticides in USA

USA (U.S. Geological Survey, 1995). U.S. Geological Survey has gathered the results from 132 studies of pesticide findings in air and in precipitation in the United States during 30 years in a summary report. The studies show:

- that most of the pesticides being analysed for were found and that the findings represent many different chemical groups of pesticides,
- that pesticides have been found in the atmosphere in all regions in the United States,
- that the highest concentrations of pesticides are found in the spraying season,
- and that certain slowly degradable pesticides are found throughout the year in low concentrations in the atmosphere. The most frequently found pesticides are the insecticides; DDT, HCH, heptachlor and dieldrine. The annual wet deposition of pesticides is generally found to be less than 1% of the amount of pesticides used in the region concerned.

Phenoxyacid herbicides in Norway, Sweden and Finland

Norway (Lode et al., 1995). In Norway during 1992-1993, 520 tests of rainwater were conducted. Phenoxyalkanoic acid herbicides MCPA and dichlorprop were analysed among others. The maximum concentrations found were respectively 0.32 µg/L and 0.25 µg/L. Pesticides have been found in every tenth sample. Regarding phenoxyalkanoic acid herbicides a correlation was found between the findings of the pesticides in the precipitation and the spraying season.

Sweden (Kreuger et al., 1995). From 1990 to 1992, 18 pesticides were detected. Phenoxyalkanoic acid herbicides were found most frequently (MCPA in 35% of the samples, max. concentration 0.24 µg/L). For MCPA the load in g/ha/year was from 0.0001- 0.092.

Finland (Hirvi et al., 1995). From 1991-1992, the largest measured concentration of phenoxyalkanoic acid herbicides in 22 samples, were 0.19µg/L for dichlorprop.

Isoproturon, atrazine, lindane terbuthylazine and others in Germany

Germany (Hüskes and Levsen, 1997). In 1992, 40 samples were gathered from the area around Hannover, and they were analysed for 59 pesticides, 11 pesticides were found in more than 10 of the samples. The highest concentrations were due to terbuthylazine. There is a correlation between the findings in the samples and the spraying season as demonstrated in other projects. In 1995, Bester et al. also detected terbuthylazine. In 1994, Siebers et al., published a study from North-Germany, where they analysed for 11 pesticides: isoproturon, atrazine, lindane and terbuthylazine, and others. The pesticides were mainly detected in the spraying season. The highest concentrations found were about 0.7µg/L. The load of isoproturon on the soil amounts to about 0.1g/ha/år. Jeaschke et al. also found IPU in samples taken in the area around Frankfurt in 1995.

MCPA in Italy

Italy (Trevisan et al.,1993). In 1988, 166 air and precipitation samples were gathered and analysed for 11 pesticides; MCPA among others, (max. concentration 0.3µg/L), in 49 of the 166 samples at least one of the 11 pesticides was present.

Lindane in India

India (Dua et al., 1994). In the period from January to September 1992, samples were analysed for HCH, which constitutes 55% of the pesticide consumption (1984 figures). The average concentration was 0.077µg/L. The largest concentrations were measured in the spraying season.

Japan (Suzuki 1996). From 1989-1992, samples were analysed for 9 pesticides, most of them were only found in the spraying season.

3 Materials and methods

The localities were chosen so they were at some distances from agricultural areas. They are all situated in a clearing in a forest.

Three localities away from agricultural areas

The Gadevang locality (12°16.29´Ø, 55°58.01´N) is placed about 1 km West, 5 km South, 5 km East and more than 10 km North of the nearest agricultural area. The Lorup locality (11°29.86´Ø, 55°23.24´N) is situated about 0.5 km in all directions from smaller fields, but 2-3 km from larger connected agricultural areas in all directions. The Gisselfeld locality (11°55.20´Ø,55°15.50´N) is placed about 1 km West, 3 km East and 2,5 km North of sprayed areas. Samples were taken in March/April, when the first spraying is conducted and until November/December, when the last spraying is done before it begins to freeze.

3.1 Sampling and analysis of rainwater

2 weeks collection periods

The rainwater is sampled through a glass funnel (20 cm in diameter), which is placed about 2 meters above ground. From the funnel, the water runs through a Teflon tube into a 2 liter glass bottle, which is insulated to prevent fluctuations in the temperature and photochemical reactions. Four bottles were placed at each locality, each collects water from two funnels to get a sample that is large enough for analysis. The bottles were acidified to avoid/delay microbiological degradation of whatever pesticides, collected with the rainwater. The samples were normally collected after 2 weeks. In the laboratory the samples were kept at approximately –18^{o}C until sample preparation and analysis.

With the described experimental design it was not possible to avoid degradation of the pesticides from the time they were collected in the bottle to the time they arrived in the laboratory. Pesticide residues due to rainfall in the beginning of the collection period will result in lower concentrations due to degradation compared to pesticides from rainfall happening just before the samples are collected and brought to the laboratory.

Minimum concentrations depending on storage periodes on locations

Therefore the concentrations listed in the tables in the result section, are minimum concentrations. Stability tests were performed to study the keeping qualities of the rainwater samples when they were frozen before extraction. The amount of pesticides being degraded at -18°C, is negligible compared to the amount degraded in the collection period.

Solid phase extraction followed by gas- or liquid chromatography with mass spectrometric detection

The method for analysing isoproturon in the samples is based on a pre-concentration by solid phase extraction. The phenoxyalkanoic acid herbicides in the samples are also determined by a concentration step with solid phase extraction followed by derivatization with pentafluorobenzylbromide, which produces the corresponding pentafluorobenzylesters. The samples are analysed with GC-MS in SIM and SCAN mode (see appendix I-III). The water samples collected in 1998 are analysed with the use of LC-MS (see appendix IV). With this method it is not necessary to derivatize the phenoxyalkanoic acid herbicides. The detection limit in using the LC-MS has been 0.01μg/L. Together with the rainwater samples, samples spiked with the pesticides concerned, were analysed.

For the GC-MS-analysis, several water samples were spiked in the concentration range 0.05µg/L-1.00µg/L, r^2 values were ≥0.95 and the detection limits differed from 0.01µg/L and 0.09µg/L. The detection limits were set (Miller and Miller, 1988), every time a set of samples was analysed by quantifying the spiked samples together with the collected rain water samples. The samples were scanned to identify, if it was isoproturon, mecoprop, MCPA or dichlorprop etc. The results from the tests were transferred to SAS, which calculates the detection limits and the concentrations of pesticides in the samples based on the calibration data.

3.2 The pesticides

MCPA, dichlorprop, mecoprop and isoproturon

The phenoxyalkanoic acid herbicides; MCPA, dichlorprop and mecoprop together with isoproturon were chosen in the beginning as model substances. The phenoxyalkanoic acid herbicides were extensively used both in the spring and in the autumn when the project began in 1996. In the beginning of 1997 the Danish Environmental Protection Agency announced that products containing phenoxyalkanoic acid herbicides in general were prohibited for autumn use henceforward and only allowed for spring for a few applications.

In 1996, isoproturon was approved for use both in the spring and in the autumn, but from 1997 only the autumn application was permitted.

The substances have been found in precipitation from neighbouring countries (Kirknel and Felding, 1996)

DNOC in 1998

In 1998, the analysis program was extended to include bentazone and 2 of its metabolites, DNOC, and 2 metabolites of isoproturon. DNOC has not been used in Denmark during the last 10 years, but was included because it was found in the samples that were analysed at DMU in 1997.

4 Results

The results are from the period of May 1996 until December 1998. The samples from 1996 and 1997 are analysed with GC-MS, whereas the rainwater samples from 1998 have been analysed with LC-MS.

Table 1
Concentration in µg/L (95% confidence limit) of phenoxyalkanoic acids herbicides in rainwater from Gadevang 1996 and 1997.

Koncentration i µg/L (95% konfidensinterval) af phenoxysyrer i regnvand fra Gadevang 1996 og 1997.

Locality	**Collection period**	**Mecoprop µg/L**	**MCPA µg/L**	**Dichlor prop µg/L**
Gadevang	10/5-20/5-1996	Nr	Nr	Nr
Gadevang	20/5-28/5-1996	Nr	Nr	Nr
Gadevang	28/5-10/6-1996	Nr	Nr	Nr
Gadevang	10/6-20/6-1996	Nr	Nr	Nr
Gadevang	20/6-5/7-1996	Nr	Nr	Nr
Gadevang	5/7-21/7-1996	Nr	Nr	Nr
Gadevang	21/7-19/8-1996	Nr	Nr	Nr
Gadevang	19/8-3/9-1996	Nr	Nr	Nr
Gadevang	3/9-16/9-1996	Nr	Nr	Nr
Gadevang	16/9-2/10-1996	Nr	Nr	Nr
Gadevang	2/10-21/10-1996	0.087(0.086;0.089)	Nr	Nr
Gadevang	21/10-31/10-1996	0.081(0.080;0.082)	Nr	Nr
Gadevang	31/10-12/11-1996	0.020(0.019;0.022)	Nr	Nr
Gadevang	12/11-25/11-1996	Nr	Nr	Nr
Gadevang	16/4-5/5-1997	Nr	Nr	Nr
Gadevang	5/5-21/5-1997	Nr	Nr	Nr
Gadevang	21/5-3/6-1997	Nr	Nr	Nr
Gadevang	3/6-24/6-1997	Nr	Nr	Nr
Gadevang	24/6-2/7-1997	Nr	Nr	Nr
Gadevang	2/7-29/29-1997	Nr	Nr	Nr
Gadevang	29/7-11/8-1997	Nr	Nr	Nr
Gadevang	11/8-1/9-1997	Nr	Nr	Nr
Gadevang	1/9-15/9-1997	Nr	Nr	Nr
Gadevang	15/9-6/10-1997	Nr	Nr	Nr
Gadevang	6/10-15/10-1997	Nr	Nr	Nr
Gadevang	15/10-03/11-1997	¤	¤	¤
Gadevang	03/11-14/11-1997	Nr	Nr	Nr
Gadevang	14/11-02/12-1997	Nr	Nr	Nr

Nr = no respons
¤ = only for IPU

Table 2
Concentration in µg/L of phenoxyalkanoic acid herbicides and other acidic herbicides in rain from Gadevang 1998.

Koncentration i µg/L af phenoxysyrer og andre sure herbicider i regnvand fra Gadevang 1998.

Locality	**Collection period**	**Bentazone µg/L**	**6-Hydroxy-bentazone µg/l**	**8-Hydroxy-bentazone µg/L**	**DNOC µg/L**	**Meco-prop µg/L**	**2,4-D µg/L**	**Dichlor-prop µg/L**	**MCPA µg/L**
Gadevang	24/3-6/4-98	n.d.	n.d.	n.d.	0.40	n.d.	n.d.	n.d.	n.d.
Gadevang	6/4-23/4-98	n.d.	n.d.	n.d.	0.59	n.d.	n.d.	n.d.	n.d.
Gadevang	23/4-11/5-98	n.d.	n.d.	n.d.	0.24	n.d.	n.d.	n.d.	n.d.
Gadevang	11/5-29/5-98	n.d.	n.d.	n.d.	0.23	n.d.	n.d.	n.d.	n.d.
Gadevang	29/5-11/6-98	n.d.	0.011	n.d.	0.38	n.d.	n.d.	n.d.	n.d.
Gadevang	11/6-25/6-98	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.
Gadevang	25/6-3/7-98	n.d.	0.019	n.d.	0.09	n.d.	n.d.	n.d.	n.d.
Gadevang	3/7-28/7-98	n.d.	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	n.d.
Gadevang	28/7-18/8-98	n.d.	n.d.	n.d.	0.29	n.d.	n.d.	n.d.	n.d.
Gadevang	18/8-7/9-98	n.d.	n.d.	n.d.	0.17	n.d.	n.d.	n.d.	n.d.
Gadevang	7/9-28/9-98	n.d.	n.d.	n.d.	0.22	n.d.	n.d.	n.d.	n.d.
Gadevang	28/9-13/10-98	n.d.	n.d.	i.a.	0.28	n.d.	n.d.	n.d.	n.d.
Gadevang	13/10-21/10-98	n.d.	n.d.	n.d.	0.20	n.d.	n.d.	n.d.	n.d.
Gadevang	21/10-28/10-98	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.
Gadevang	28/10-11/11-98	n.d.	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	n.d.
Gadevang	11/11-3/12-98	n.d.	n.d.	n.d.	0.25	n.d.	n.d.	n.d.	n.d.
Gadevang	3/12-21/12-98	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.

n.d.: Not detected. Detection limit is 0.01µg/L.

All phenoxyalkonic acid herbicides in 1996

Only mecoprop in 1997

The results for the phenoxyalkanoic acid herbicides and other acidic substances are listed in table 1-6. At the Gadevang locality only mecoprop was detected in the period from October 1996 until Mid-November 1996. At the Lorup and Gisselfeld localities, all 3 phenoxyalkanoic acid herbicides were detected in 1996. In 1997, only mecoprop was found in one sample from Lorup, the sample was collected during November.

The products available on the market in 1996 containing phenoxyalkanoic acid herbicides were prohibited the July 1st 1997, but hereafter manufacturers could apply for new permits for other products containing phenoxyalkanoic acid herbicides. This is the reason why it is still possible to find a number of products containing phenoxyalkanoic acid herbicides, which are permitted for weed control in herbage seed, grass lawns, and for control of root weeds in cereals in the late spraying growth stages. The permits are based on the coverage of the crop, i.e. the demand of a maximum of a 100 g (for dichlorprop 60 g) depositing on the soil surface.

Table 3
Concentration in µg/L (95% Confidence limits) of phenoxyalkanoic acid herbicides in rainwater from Lorup 1996 and 1997.

Koncentration i µg/L (95% konfidensinterval) af phenoxysyrer i regnvand fra Lorup 1996 og 1997.

Locality	**Collection period**	**Mecoprop µg/L**	**MCPA µg/L**	**Dichlorprop µg/L**
Lorup	14/5-20/5-1996	Nr	Nr	Nr
Lorup	20/5-28/5-1996	0.018(0.017;0.019)	0.075(0.072;0.077)	0.632(0.623;0.642)
Lorup	28/5-10/6-1996	Nr	0.102(0.099;0.104)	0.148(0.146;0.150)
Lorup	10/6-20/6-1996	Nr	0.124(0.119;0.130)	0.204(0.200;0.207)
Lorup	20/6-5/7-1996	Nr	Nr	Nr
Lorup	5/7-21/7-1996	Nr	0.092(0.087;0.097)	0.202(0.199;0.205)
Lorup	21/7-19/8-1996	Nr	Nr	Nr
Lorup	19/8-3/9-1996	Nr	Nr	Nr
Lorup	3/9-16/9-1996	Nr	Nr	Nr
Lorup	16/9-2/10-1996	Nr	Nr	Nr
Lorup	2/10-21/10-1996	0.143(0.142;0.145)	Nr	Nr
Lorup	21/10-31/10-1996	0.145(0.144;0.147)	Nr	Nr
Lorup	31/10-12/11-1996	0.064(0.060;0.068)	Nr	Nr
Lorup	12/11-25/11-1996	0.031(0.027;0.034)	Nr	Nr
Lorup	3/4-14/4-1997	Nr	Nr	Nr
Lorup	15/4-5/5-1997	Nr	Nr	Nr
Lorup	5/5-21/5-1997	Nr	Nr	Nr
Lorup	21/5-3/6-1997	Nr	Nr	Nr
Lorup	3/6-24/6-1997	Nr	Nr	Nr
Lorup	24/6-2/7-1997	Nr	Nr	Nr
Lorup	2/7-29/29-1997	Nr	Nr	Nr
Lorup	29/7-11/8-1997	Nr	Nr	Nr
Lorup	11/8-1/9-1997	Nr	Nr	Nr
Lorup	1/9-15/9-1997	Nr	Nr	Nr
Lorup	15/9-6/10-1997	¤	¤	¤
Lorup	6/10-15/10-1997	¤	¤	¤
Lorup	15/10-03/11-1997	¤	¤	¤
Lorup	03/11-14/11-1997	0.086(0.084;0.089)	Nr	Nr
Lorup	14/11-02/12-1997	Nr	Nr	Nr

Nr = No response
¤ = Only for IPU

Table 4
Concentrations in μg/L of phenoxyalkanoic acid herbicides and other acidic herbicides in rain water from Lorup 1998.

Koncentration i μg/L af phenoxysyrer og andre sure herbicider i regnvand fra Lorup 1998.

Locality	**Collection period**	**Bentazone μg/L**	**6-Hydroxy-bentazone μg/L**	**8-Hydroxy-bentazone μg/L**	**DNOC μg/L**	**Mecoprop μg/L**	**2,4-D μg/L**	**Dichlorprop μg/L**	**MCPA μg/l**
Lorup	24/3-6/4-98	n.d.	n.d.	n.d.	0.32	n.d.	n.d.	n.d.	n.d.
Lorup	6/4-23/4-98	0.019	n.d.	n.d.	0.87	n.d.	n.d.	n.d.	n.d.
Lorup	23/4-11/5-98	n.d.	n.d.	n.d.	0.60	n.d.	n.d.	n.d.	n.d.
Lorup	11/5-29/5-98	n.d.	n.d.	n.d.	0.27	n.d.	n.d.	n.d.	n.d.
Lorup	29/5-11/6-98	n.d.	n.d.	n.d.	0.40	n.d.	n.d.	n.d.	n.d.
Lorup	11/6-25/6-98	n.d.	n.d.	n.d.	0.15	n.d.	n.d.	n.d.	n.d.
Lorup	25/6-3/7-98	n.d.	n.d.	n.d.	0.19	n.d.	n.d.	n.d.	n.d.
Lorup	3/7-28/7-98	n.d.	n.d.	n.d.	0.23	n.d.	n.d.	n.d.	n.d.
Lorup	28/7-18/8-98	n.d.	n.d.	n.d.	0.29	n.d.	n.d.	n.d.	n.d.
Lorup	18/8-7/9-98	n.d.	n.d.	n.d.	0.25	n.d.	n.d.	n.d.	n.d.
Lorup	7/9-28/9-98	n.d.	n.d.	n.d.	0.23	n.d.	n.d.	n.d.	n.d.
Lorup	28/9-13/10-98	n.d.	n.d.	i.a.	0.30	n.d.	n.d.	n.d.	n.d.
Lorup	13/10-21/10-98	n.d.	n.d.	n.d.	0.32	n.d.	n.d.	n.d.	n.d.
Lorup	21/10-28/10-98	n.d.	n.d.	n.d.	0.19	n.d.	n.d.	n.d.	n.d.
Lorup	28/10-11/11-98	n.d.	n.d.	n.d.	0.14	n.d.	n.d.	n.d.	n.d.
Lorup	11/11-3/12-98	n.d.	n.d.	n.d.	0.18	n.d.	n.d.	n.d.	n.d.
Lorup	3/12-21/12-98	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.

n.d.: not detected. The detection limit is 0.01μg/L

Table 5

Concentrations in µg/L (95% confidence limits) of phenoxyalkanoic acid herbicides in rainwater from Gisselfeld 1996 and 1997.

Koncentration i µg/L (95% konfidensinterval) af phenoxysyrer i regnvand fra Gisselfeld 1996 og 1997.

Locality	**Collection period**	**Mecoprop µg/L**	**MMCPA µg/L**	**DDichlorprop µg/L**
Gisselfeld	15/5-20/5-1996	Nr	0.081(0.077;0.084)	0.351(0.346;0.356)
Gisselfeld	20/5-28/5-1996	0.089(0.082;0.097)	0.143(0.136;0.151)	0.220(0.214;0.226)
Gisselfeld	28/5-10/6-1996	Nr	Nr	0.106(0.103;0.108)
Gisselfeld	10/6-20/6-1996	Nr	Nr	Nr
Gisselfeld	20/6-5/7-1996	Nr	Nr	Nr
Gisselfeld	5/7-21/7-1996	Nr	Nr	Nr
Gisselfeld	21/7-19/8-1996	Nr	Nr	Nr
Gisselfeld	19/8-3/9-1996	Nr	Nr	Nr
Gisselfeld	3/9-16/9-1996	Nr	Nr	Nr
Gisselfeld	16/9-2/10-1996	Nr	Nr	Nr
Gisselfeld	2/10-21/10-1996	0.073(0.072;0.074)	Nr	Nr
Gisselfeld	21/10-31/10-1996	0.033(0.032;0.034)	Nr	Nr
Gisselfeld	31/10-12/11-1996	Nr	Nr	Nr
Gisselfeld	12/11-25/11-1996	Nr	Nr	Nr
Gisselfeld	3/4-15/4-1997	Nr	Nr	Nr
Gisselfeld	15/4-5/5-1997	Nr	Nr	Nr
Gisselfeld	5/5-21/5-1997	Nr	Nr	Nr
Gisselfeld	21/5-3/6-1997	Nr	Nr	Nr
Gisselfeld	3/6-24/6-1997	Nr	Nr	Nr
Gisselfeld	24/6-2/7-1997	Nr	Nr	Nr
Gisselfeld	2/7-29/29-1997	Nr	Nr	Nr
Gisselfeld	29/7-11/8-1997	Nr	Nr	Nr
Gisselfeld	11/8-1/9-1997	Nr	Nr	Nr
Gisselfeld	1/9-15/9-1997	Nr	Nr	Nr
Gisselfeld	15/9-6/10-1997	¤	¤	¤
Gisselfeld	6/10-15/10-1997	Nr	Nr	Nr
Gisselfeld	15/10-03/11-1997	¤	¤	¤
Gisselfeld	03/11-14/11-1997	Nr	Nr	Nr
Gisselfeld	14/11-02/12-1997	Nr	Nr	Nr

Nr = no response
¤ = Only for IPU

Table 6
Concentrations in µg/L of phenoxyalkanoic acid herbicides and other acidic herbicides in rainwater from Gisselfeld 1998

Koncentration i µg/L af phenoxysyrer og andre sure herbicider i regnvand fra Gisselfeld 1998.

Locality	**Collection period**	**Benta-zone µg/L**	**6-Hydroxy-bentazone µg/L**	**8-Hydroxy-bentazone µg/L**	**DNOC µg/L**	**Mecoprop µg/L**	**2,4-D µg/L**	**Dichlor-prop µg/L**	**MCPA µg/L**
Gisselfeld	24/3-6/4-98	n.d.	n.d.	n.d.	0.10	n.d.	n.d.	n.d.	n.d.
Gisselfeld	6/4-23/4-98	n.d.	n.d.	n.d.	0.74	n.d.	n.d.	n.d.	n.d.
Gisselfeld	23/4-11/5-98	n.d.	n.d.	n.d.	0.16	n.d.	n.d.	n.d.	n.d.
Gisselfeld	11/5-29/5-98	n.d.	n.d.	n.d.	0.13	n.d.	n.d.	n.d.	n.d.
Gisselfeld	29/5-11/6-98	n.d.	n.d.	n.d.	0.32	n.d.	n.d.	n.d.	n.d.
Gisselfeld	11/6-25/6-98	n.d.	n.d.	n.d.	0.13	n.d.	n.d.	n.d.	n.d.
Gisselfeld	26/6-3/7-98	n.d.	n.d.	n.d.	0.17	n.d.	n.d.	n.d.	n.d.
Gisselfeld	3/7-28/7-98	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.
Gisselfeld	28/7-18/8-98	n.d.	n.d.	n.d.	0.19	n.d.	n.d.	n.d.	n.d.
Gisselfeld	18/8-7/9-98	n.d.	n.d.	n.d.	0.10	n.d.	n.d.	n.d.	n.d.
Gisselfeld	7/9-28/9-98	n.d.	n.d.	n.d.	0.24	n.d.	n.d.	n.d.	n.d.
Gisselfeld	28/9-13/10-98	n.d.	n.d.	i.a.	0.48	n.d.	n.d.	n.d.	n.d.
Gisselfeld	13/10-21/10-98	n.d.	n.d.	n.d.	0.40	n.d.	n.d.	n.d.	n.d.
Gisselfeld	21/10-28/10-98	n.d.	n.d.	n.d.	0.18	n.d.	n.d.	n.d.	n.d.
Gisselfeld	28/10-11/11-98	n.d.	n.d.	n.d.	0.23	n.d.	n.d.	n.d.	n.d.
Gisselfeld	11/11-3/12-98	n.d.	n.d.	n.d.	0.39	n.d.	n.d.	n.d.	n.d.
Gisselfeld	3/12-21/12-98	n.d.	n.d.	n.d.	0.13	n.d.	n.d.	n.d.	n.d.

n.d.: Not detected. The detection limit is 0.01µg/L
i.a.: not analysed

Up to 0.87 µg/L DNOC

The results for DNOC in table 2,4 and 6 are corrected for 60% recovery at the sample preparation. The rest of the data is not corrected, because the recovery rates were close to 100%. DNOC was detected in all the samples in concentrations ranging from 0.04 µg/L to 0.87µg/L.

In 1996, the phenoxyalkanoic acid herbicides; respectively; mecoprop, MCPA and dichlorprop, were detected in the following concentrations; from 0.02 µg/L to 0.15 µg/L, from 0.08 µg/L to 0.14 µg/L and from 0.11µg/L to 0.63 µg/L. There is an obvious connection between findings in the rainwater and the time of spraying (Felding, 1998).

No phenoxyalkanoic acid herbicides were detected in 1997 at the Gadevang locality, with exception of the period from the 15/10 to the 3/11 where no samples were collected. In Lorup, none of the samples from the period 15/9 to 3/11, were analysed for phenoxyalkanoic acid herbicides, but in the following period mecoprop was detected in the samples. At the Gisselfeld locality, no phenoxyalkanoic acid herbicides were found in 1997, however, here are 2 periods without samples, from the 15/9 to the 6/10 and again from the 15/10 to the 3/11.

No phenoxyalkanoic

In 1998, no phenoxyalkanoic acid herbicides were detected at the three *acid herbicides in 1998*

locations, which show that the limitation in the use of the phenoxyalkanoic acid herbicides had a remarkably effect on the findings in precipitation. It also shows that it is not possible to trace transport of phenoxyalkanoic acid herbicides from other countries without limitations in the use of these specific pesticides.

DNOC in all samples

With the exception of two findings of trace amounts of hydroxybentazone, bentazone and hydroxy compounds were not detected in the samples taken in 1998. On top of that, DNOC was detected in all samples from 1998, and most of the samples contained DNOC in concentrations between 0.1 and 0.4µg/L.

Isoproturon detected on all localities

The results for isoproturon are listed in table 7-12, where the compound is detected in rainwater from all three localities in the autumn 1996, 1997 and 1998 as well as in the spring 1998 at all three localities. Concentrations of isoproturon vary from 0.01-to 0.86µg/L.

The concentrations of pesticides shown in the tables are to be regarded as minimum concentrations, because of the degradation of the pesticides that are certain to arise from the time the rain event has occurred, and until the sample is collected and brought to the laboratory about 2 weeks later, even though the water is preserved.

Table 7
Concentrations in µg/L (95% confidence limits) of isoproturon in the rainwater from Gadevang in 1996 and 1997.

Koncentration i µg/L (95% konfidensinterval) af isoproturon i regnvand fra Gadevang i 1996 og 1997.

Locality	**Collection period**	**Isoproturon in µg/L**
Gadevang	10/5-20/5-1996	Nr
Gadevang	20/5-28/5-1996	Nr
Gadevang	28/5-10/6-1996	Nr
Gadevang	10/6-20/6-1996	*
Gadevang	20/6-5/7-1996	Nr
Gadevang	5/7-21/7-1996	*
Gadevang	21/7-19/8-1996	Nr
Gadevang	19/8-3/9-1996	Nr
Gadevang	3/9-16/9-1996	Nr
Gadevang	16/9-2/10-1996	Nr
Gadevang	2/10-21/10-1996	0.257(0.223;0.292)
Gadevang	21/10-31/10-1996	Nr
Gadevang	31/10-12/11-1996	Nr
Gadevang	12/11-25/11-1996	Nr
Gadevang	16/4-5/5-1997	Nr
Gadevang	5/5-21/5-1997	Nr
Gadevang	21/5-3/6-1997	Nr
Gadevang	3/6-24/6-1997	Nr
Gadevang	24/6-2/7-1997	Nr
Gadevang	2/7-29/7-1997	Nr
Gadevang	29/7-11/8-1997	Nr
Gadevang	11/8-1/9-1997	Nr
Gadevang	1/9-15/9-1997	Nr
Gadevang	15/9-6/10-1997	0.073(0.071;0.075)
Gadevang	6/10-15/10-1997	0.039(0.038;0.04)
Gadevang	15/10-03/11-1997	0.859(0.846;0.873)
Gadevang	03/11-14/11-1997	Nr
Gadevang	14/11-02/12-1997	Nr

Nr = No response   * = Only for phenoxyalkanoic acid herbicides

Table 8

Concentrations in µg/L of isoproturon and 2 metabolites in rainwater from Gadevang 1998.

Koncentration i µg/L af isoproturon og 2 metabolitter i regnvand fra Gadevang 1998.

Locality	**Collection period**	**Isopropyl-phenylurea µg/L**	**Isopropyl-phenylmethylurea µg/L**	**Isoproturon µg/L**
Gadevang	24/3-6/4-98	n.d.	n.d.	n.d.
Gadevang	6/4-23/4-98	n.d.	n.d.	0.037
Gadevang	23/4-11/5-98	n.d.	n.d.	0.015
Gadevang	11/5-29/5-98	n.d.	n.d.	0.014
Gadevang	29/5-11/6-98	n.d.	n.d.	n.d.
Gadevang	11/6-25/6-98	n.d.	n.d.	n.d.
Gadevang	25/6-3/7-98	n.d.	n.d.	n.d.
Gadevang	3/7-28/7-98	n.d.	n.d.	n.d.
Gadevang	28/7-18/8-98	n.d.	n.d.	n.d.
Gadevang	18/8-7/9-98	n.d.	n.d.	n.d.
Gadevang	7/9-28/9-98	n.d.	n.d.	n.d.
Gadevang	28/9-13/10-98	n.d.	n.d.	0.033
Gadevang	13/10-21/10-98	n.d.	n.d.	0.048
Gadevang	21/10-28/10-98	n.d.	n.d.	0.011
Gadevang	28/10-11/11-98	n.d.	n.d.	n.d.
Gadevang	11/11-3/12-98	n.d.	n.d.	n.d.
Gadevang	3/12-21/12-98	n.d.	n.d.	n.d.

n.d.: Not detected. The detection limit is 0.01µg/L

Table 9
Concentrations in µg/L of isoproturon (95% confidence limits) in rainwater from Lorup 1996 and 1997.

Koncentration i µg/L (95% konfidensinterval) af isoproturon i regnvand fra Lorup i 1996 og 1997.

Locality	**Collection period**	**Isoproturon in µg/L**
Lorup	14/5-20/5-1996	Nr
Lorup	20/5-28/5-1996	Nr
Lorup	28/5-10/6-1996	*
Lorup	10/6-20/6-1996	*
Lorup	20/6-5/7-1996	Nr
Lorup	5/7-21/7-1996	*
Lorup	21/7-19/8-1996	Nr
Lorup	19/8-3/9-1996	Nr
Lorup	3/9-16/9-1996	Nr
Lorup	16/9-2/10-1996	0.011(0.010;0.012)
Lorup	2/10-21/10-1996	0.171(0.142;0.201)
Lorup	21/10-31/10-1996	0.080(0.071;0.088)
Lorup	31/10-12/11-1996	0.030(0.024;0.036)
Lorup	12/11-25/11-1996	Nr
Lorup	3/4-14/4-1997	Nr
Lorup	15/4-5/5-1997	Nr
Lorup	5/5-21/5-1997	Nr
Lorup	21/5-3/6-1997	Nr
Lorup	3/6-24/6-1997	Nr
Lorup	24/6-2/7-1997	Nr
Lorup	2/7-29/7-1997	Nr
Lorup	29/7-11/8-1997	*
Lorup	11/8-1/9-1997	Nr
Lorup	1/9-15/9-1997	Nr
Lorup	15/9-6/10-1997	0.099(0.098;0.100)
Lorup	6/10-15/10-1997	Nr
Lorup	15/10-03/11-1997	Nr
Lorup	03/11-14/11-1997	Nr
Lorup	14/11-02/12-1997	Nr

Nr = No response *= Only for phenoxyalkanoic acid herbicides

Table 10

Concentrations in µg/L of isoproturon and 2 metabolites in rainwater from Lorup 1998.

Koncentration i µg/L af isoproturon og 2 metabolitter i regnvand fra Lorup 1998.

Locality	**Collection period**	**Isopropyl-phenylurea µg/L**	**Isopropyl-phenylmethyl-urea µg/L**	**Isoproturon µg/L**
Lorup	24/3-6/4-98	n.d.	n.d.	n.d.
Lorup	6/4-23/4-98	n.d.	n.d.	0.021
Lorup	23/4-11/5-98	n.d.	n.d.	0.015
Lorup	11/5-29/5-98	n.d.	n.d.	n.d.
Lorup	29/5-11/6-98	n.d.	0.011	n.d.
Lorup	11/6-25/6-98	n.d.	n.d.	n.d.
Lorup	25/6-3/7-98	n.d.	n.d.	n.d.
Lorup	3/7-28/7-98	n.d.	n.d.	n.d.
Lorup	28/7-18/8-98	n.d.	n.d.	n.d.
Lorup	18/8-7/9-98	0.082	n.d.	n.d.
Lorup	7/9-28/9-98	0.074	n.d.	n.d.
Lorup	28/9-13/10-98	n.d.	n.d.	0.019
Lorup	13/10-21/10-98	n.d.	0.016	0.061
Lorup	21/10-28/10-98	n.d.	n.d.	0.046
Lorup	28/10-11/11-98	n.d.	n.d.	0.042
Lorup	11/11-3/12-98	n.d.	n.d.	n.d.
Lorup	3/12-21/12-98	n.d.	n.d.	n.d.

n.d.: Not detected. The Detection limit is 0.01µg/L

Table 11
Concentrations in µg/L of isoproturon (95% confidence limits) in rainwater from Gisselfeld 1996 and 1997.

Koncentration i µg/L (95% konfidensinterval) af isoproturon i regnvand fra Gisselfeld i 1996 og 1997.

Locality	**Collection period**	**Isoproturon in µg/L**
Gisselfeld	15/5-20/5-1996	Nr
Gisselfeld	20/5-28/5-1996	Nr
Gisselfeld	28/5-10/6-1996	*
Gisselfeld	10/6-20/6-1996	*
Gisselfeld	20/6-5/7-1996	Nr
Gisselfeld	5/7-21/7-1996	*
Gisselfeld	21/7-19/8-1996	Nr
Gisselfeld	19/8-3/9-1996	Nr
Gisselfeld	3/9-16/9-1996	Nr
Gisselfeld	16/9-2/10-1996	Nr
Gisselfeld	2/10-21/10-1996	0.383(0.346;0.428)
Gisselfeld	21/10-31/10-1996	0.081(0.075;0.087)
Gisselfeld	31/10-12/11-1996	0.044(0.038;0.050)
Gisselfeld	12/11-25/11-1996	Nr
Gisselfeld	3/4-15/4-1997	Nr
Gisselfeld	15/4-5/5-1997	Nr
Gisselfeld	5/5-21/5-1997	Nr
Gisselfeld	21/5-3/6-1997	Nr
Gisselfeld	3/6-24/6-1997	Nr
Gisselfeld	24/6-2/7-1997	Nr
Gisselfeld	2/7-29/7-1997	Nr
Gisselfeld	29/7-11/8-1997	*
Gisselfeld	11/8-1/9-1997	Nr
Gisselfeld	1/9-15/9-1997	Nr
Gisselfeld	15/9-6/10-1997	Nr
Gisselfeld	6/10-15/10-1997	Nr
Gisselfeld	15/10-03/11-1997	0.398(0.392;0.404)
Gisselfeld	03/11-14/11-1997	Nr
Gisselfeld	14/11-02/12-1997	Nr

Nr = No response * = Only for phenoxyalkanoic acid herbicides

Table 12
Concentrations in µg/L of isoproturon and 2 metabolites in rainwater from Gisselfeld 1998.

Koncentration i µg/L af isoproturon og 2 metabolitter i regnvand fra Gisselfeld 1998.

Locality	**Collection period**	**Isopropyl-phenylurea µg/L**	**Isopropyl-phenylmethylurea µg/L**	**Isoproturon µg/L**
Gisselfeld	24/3-6/4-98	n.d.	n.d.	n.d.
Gisselfeld	6/4-23/4-98	n.d.	n.d.	0.138
Gisselfeld	23/4-11/5-98	n.d.	n.d.	0.031
Gisselfeld	11/5-29/5-98	n.d.	n.d.	0.015
Gisselfeld	29/5-11/6-98	n.d.	n.d.	n.d.
Gisselfeld	11/6-25/6-98	n.d.	n.d.	n.d.
Gisselfeld	26/6-3/7-98	n.d.	n.d.	n.d.
Gisselfeld	3/7-28/7-98	n.d.	n.d.	n.d.
Gisselfeld	28/7-18/8-98	n.d.	n.d.	n.d.
Gisselfeld	18/8-7/9-98	n.d.	n.d.	n.d.
Gisselfeld	7/9-28/9-98	n.d.	n.d.	n.d.
Gisselfeld	28/9-13/10-98	n.d.	n.d.	0.037
Gisselfeld	13/10-21/10-98	n.d.	n.d.	0.048
Gisselfeld	21/10-28/10-98	n.d.	n.d.	0.027
Gisselfeld	28/10-11/11-98	n.d.	n.d.	0.012
Gisselfeld	11/11-3/12-98	n.d.	n.d.	n.d.
Gisselfeld	3/12-21/12-98	n.d.	n.d.	n.d.

n.d.: Not detected. The detection limit is 0.01µg/L

Isoproturon metabolites only in 4 samples

The samples from 1998 were tested for isoproturon and two of its metabolites. Metabolites were only detected in four samples from Lorup, with a maximum concentration of isopropyl-phenylurea at 0.082 µg/L.

Samples analysed for 44 pesticides

During the autumn of 1997 it was possible to analyse some frozen samples for up to 44 different pesticides. Samples from September 1996 until November 1997 were defrosted and mixtures from the three localities were made. The analyses were performed by National Environmental Research Institute, Department for Environmental Chemistry. The pesticides analysed, are listed in table 13.

Table 13
List of pesticides and metabolites contained in the analysis program at DMU.

Liste over pesticider og nedbrydningsprodukter i DMU's analyseprogram

Components in the analysis at DMU
Atrazine
Atrazine-2-hydroxy
BAM(2,6-Dichlorobenzamide)
Carbofuran
Chloridazon
Cyanazine
Deethyl-terbuthylazine
Deethylatrazine
Deisopropylatrazine
Dimethoate
Diuron
Hexazinone
Hydroxy-carbofuran
Isoproturon
Linuron
Metamitron
Methabenzthiazuron
Metribuzin
Pirimicarb
Prochloraz
Propiconazole
Propyzamide
Simazine
Terbuthylazine,2-hydroxy
Terbuthylazine
Triadimenol
2,4-D
2,4-dichlorophenol
Benazolin
Bentazone
Bromoxynil
Chlorsulfuron
DNOC
Dicamba
Dichlorprop
Dinoseb
Flamprop
Fluazifop
Ioxynil
MCPA
Mecoprop
Metsulfuron-methyl
Triasulfuron
Thifensulfuron-methyl

8 different pesticides detected

In table 14 the concentrations of the 8 different pesticide chemicals which were found in the sample mixture are listed. In addition to herbicides mecoprop and isoproturon, which were also detected in the samples mentioned above, the following substances were detected in relatively low concentrations from 2 to 5 times during the period. These are; metamitron, methabenzthiazuron, 2-hydroxyterbuthylazine, terbuthylazine and 2,4-D. DNOC on the other hand, was found in rainwater during the entire sampling period in concentrations from 0.38- to 4.5µg/L.

Table 14

Concentrations of pesticides in rainwater samples collected in the period from September 1996 until November 1997. The samples are in most cases sample mixtures from Lorup, Gisselfeld and Gadevang, and they typically represent a period of 2-3 weeks which gives results once or twice a calendar month. All together there was analysed for 44 pesticide chemicals at DMU. Results in µg/L

Koncentration af pesticider i regnvandsprøver opsamlet fra september 1996 til november 1997. Prøverne er i de fleste tilfælde blandingsprøver fra Lorup, Gisselfeld ogGadevangog repræsenterer 2-3ugers nedbør, hvilket giver et eller to resultater per kalenermåned.. Alle er analyseret for 44 pesticidkemikalier af DMU. Resultater i µg/L.

Collected	**IPU**	**Metamitron**	**DNOC**	**Mecoprop**	**Methabenz-Thiazuron**	**2-Hydroxy-terbuthylazine**	**Terbuthylazine**	**2,4-D**
Sept. **96**	0.007		0.61	0.005				
October	0.20	0.019	4.5	0.23				
October	0.054	0.039	0.69	0.07				
Novem.	0.017	0.038	0.89	0.07				
Novem.			0.77	0.030	0.013			
April **97**			0.82	0.016	0.008	0.096		
May			0.31	0.015		0.098	0.008	
June			0.57	0.012			0.009	
August		0.024	1.6					
Sept.			0.38	0.005				0.046
Sept.	0.17	0.088	1.3	0.068		0.015	0.008	0.059
October			0.44	0.016				0.013
October	0.29		0.47	0.076				

In table 15 the measured concentration of pesticide chemicals -from table 14- are converted from µg/L to g/ha. As shown in the table, DNOC supplies the ground with roughly 90% of the total amount of pesticides (7,5g of 8,5g), detected by the extended analysis.

Table 15
Concentrations of pesticides and metabolites in g pr. ha.

Koncentration af pesticider og metabolitter i gram per ha.

Collected	**IPU**	**Metamitron**	**DNOC**	**Meco-prop**	**Methabenz-thiazurone**	**2-Hydroxy-terbuthylazine**	**Terbuthy-lazine**	**2,4-D**
Sept. **96**	0.007		0.632	0.005				
October	0.050	0.005	1.132	0.058				
October	0.053	0.038	0.676	0.069				
Novem.	0.018	0.040	0.944	0.074				
Novem.			0.657	0.026	0.011			
April **97**			0.640	0.012	0.006	0.075		
May			0.271	0.013		0.086	0.007	
June			0.356	0.007			0.006	
August		0.014	0.920					
Sept.			0.077	0.001				0.009
Sept.	0.072	0.037	0.548	0.029		0.006	0.003	0.025
October			0.454	0.017				0.013
October	0.116		0.188	0.030				
Total	*0.316*	*0.134*	*7.496*	*0.341*	*0.017*	*0.167*	*0.016*	*0.048*

5 Discussion and conclusion

Connection between spraying and findings

Especially in the case of the phenoxyalkanoic acid herbicides and isoproturon, there is an obvious connection between findings in the rainwater and the time of spraying. The same pattern is repeated in the foreign papers, that describe analysis of rainwater. From the previous European research it appears, that the load of pesticides is of the same magnitude as in Denmark. A compound as lindane is also frequently seen in foreign literature, here the compound is normally detected in precipitation all year around.

Limitations in use reduced content in precipitation

The highest measured concentrations were 0.9 µg/L for isoproturon and 0.6 µg/L for phenoxyalkanoic acid herbicides. Phenoxyherbicides were in 1996 detected in the spraying periods in spring and autumn (autumn only mecoprop, which is the only phenoxyherbicide used for autumn application). In 1997 only mecoprop was detected and solely on one location in November, while in 1998 no phenoxyalkanoic acid herbicides were detected on the three localities. This displays that the limitations in the use of these herbicides have greatly reduced their appearance in precipitation.

Isoproturon was from 1997 until 1999 only allowed for autumn application. The compound was detected on all the three localities in the spraying period in 1996 and 1997, while in 1998 it was detected in the spring as well as in the autumn. This might be a result of long term transport from other countries or illegal use of the pesticide in Denmark.

High DNOC concentrations

DNOC formation in the atmosphere

The concentration of DNOC is high, and the compound is also detected in rainwater collected in periods were spraying is normally not performed. This indicates that either there are other sources of DNOC, or that the half-life of DNOC is very long (months) so that it can be transported over long distances from areas where application is still allowed. DNOC has been detected in the rainwater from September 1996 to November 1997 and in all samples collected in 1998. It is therefore most likely that the findings of DNOC are caused by formation of the compound in the atmosphere. Nojima and Isogami (1994), Grosjean (1985), Nojima et al., (1983) and Atkinson and Aschmann (1994) describe the formation of DNOC in the atmosphere probably from a reaction between toluene and nitrous oxides caused by the sunlight. The limiting factor is most likely toluene which might come from the traffic. The amount of DNOC, about 7,5g, added to the area, is a rather modest amount compared to the amount of DNOC which was used in the eighties, about 2 kg a.i. pr. ha.

DNOC measured abroad

DNOC has also been measured abroad. In cloud water in England concentrations at 0.26-2.13µg/L were found (Lüttke and Levsen, 1997), and in Germany at 0.9-12.5µg/L (Richartz *et al.*, 1990). Results from Switzerland shows concentrations at 0.95-1.6µg/L for rainwater samples (Leuenberger *et al.*, 1988). The concentrations detected in the rain in Denmark are of the same size as concentrations found in England, Germany and Switzerland.

10 years since DNOC used in Denmark

DNOC is the only one of the 8 detected pesticides, which is no longer used in Denmark, it is about 10 years since the compound was used. In 1996, DNOC was still used in a few countries in Europe and probably also outside Europe.

DNOC has been detected in groundwater close to the soil surface and in streams in Denmark (Spliid *et al.,* 1996).

Rainfalls in beginning of collection periods gave unstable samples

Analysis of control samples placed at the three localities have shown that the samples are not adequately stable especially in the summer season if the rain falls in the beginning of the collection period. In forthcoming rainwater projects it is therefore necessary to use more advanced sampling equipment where the samples for example are cooled during the collection period.

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Appendix I

Gaschromatography Mass Spectrometry

GC-MS:	Hewlett Packard model 5890A gas chromatograph connected to a Hewlett Packard mass selective detector model 5970
Tube:	capillary tube HP 5 (5% diphenyl-95% dimethylsiloxan), 25 m 0,2 mm inner diameter and 0.33 µm coating

Program for IPU detection SIM and SCAN

Injection temperature: 260°C

Oven temperature: temp. 1: 60°C (1 min.), rate 1: 10°C/min.
temp. 2: 130°C, rate 2: 6°C/min.
temp. 3: 175°C, rate 3: 20°C/min.
temp. 4: 290°C (5 min.)

Transfer line temperature: 290 °C
Carrier gas: helium, 15 psi
Injection: 1 µl splitless (1.0 min. purge)
Solvent delay 8 min., dwell time 100 ms mass^{-1}, electron multiplier -2200V
SIM ion 146

Program for detection of phenoxyalkanoic acid herbicides SIM and SCAN

Injection temperature: 280°C

Oven temperature: temp. 1: 60°C (1 min.), rate 1: 10°C/min.
temp. 2: 130°C, rate 2: 6°C/min.
temp. 3: 260°C, rate 3: 10°C/min.
temp. 4: 290°C (5 min.)

Transfer line temperature: 290 °C
Carrier gas: helium, 15 psi
Injection: 1 µl splitless (1.0 min. purge)
Solvent delay 20 min., dwell time 100 ms mass^{-1}, electron multiplier -2200V
SIM ion 181

Appendix II

Method for analysis of isoproturon (IPU)

50 ml preservation solution is added to the rainwater pr. 2 L bottle before it is placed at the collection site. When the water samples arrive at the laboratory the pH value is checked. It is supposed to be 1.
The rainwater is filtered via büchner funnels through a glass micro fibre filter, this is done before a possible freezing of the water, which is parted into 1 L pr. bottle.

Extraction:

5 ml methanol / L water is added.
The RDX-tubes are pre-treated with:

1. 10 ml acetonitrile
2. 10 ml methanol
3. 20 ml milli-Q water

The fluid is sucked slowly through every time.
It is very important that the tubes are not running dry.

The water samples are fitted with a vacuum suction at about 8 mm Hg.
1 L sample is sucked through each column, 2 L from each locality is extracted and the two fractions are treated together (same registry number).
The columns are air dried with maximum suction in further 20 minutes.
Each column is eluted with 5 ml methanol.
First 1 ml is eluted. Then 2 minutes standing and the rest of the methanol is passed through the column. The elution is repeated with further 5 ml methanol.

Preconcentration:

The methanol fraction is evaporated to dryness under a gentle stream of nitrogen at ambient temperature.
The residue is redissolved in 1 ml ethylacetate in an ultra sonication bath for 5 minutes.
The ethylacetate fraction is filtered through 0,2 µm filter and evaporated to exactly 300 µl and is now ready for analysis. The vial is kept at –18°C until analysis.

Appendix III

Analysis of phenoxyalkanoic acid herbicides:

50 ml preservation solution is added to the rainwater pr. 2 L bottle before it is placed at the collection site. When the water samples arrive at the laboratory the pH value is checked. It is supposed to be 1.
The rainwater is filtered via büchner funnels through a glass micro fibre filter, this is done before a possible freezing of the water, which is parted into 1 L pr. bottle.

Extraction:

A C8- Empore-disc is placed on the glass filter for millipore filtration. The filter is treated with 10 mL CH_2Cl_2. After 3 minutes standing the solvent is slowly sucked through the filter. The filter is dried by further suction for one minute. The filter is then treated with 10 mL methanol. The filter must not go dry before the water sample is passed through the filter. The filter is air dried by further suction during 15 minutes. The C8-filter is eluted with 10 mL CH_2Cl_2, and the elution is repeated.

Further 10 ml CH_2Cl_2 is used for transfer of the solutes and rinsing of the flask. The extracts are transferred to a separation funnel.
50 mL 1% NaOH is added and the funnel is shaken for 2 minutes. After 10 minutes standing the CH_2Cl_2 fraction is discarded. 3 mL 24 % H_2SO_4 is added to the separation funnel, pH less than 1. The funnel is shaken 2 min with 20 mL CH_2Cl_2. The dichloromethane-fraction is after 10 minutes standing transferred to a round bottom flask equipped with a funnel with anhydrous sodium sulphate on glass wool. The extraction is repeated twice. Na_2SO_4 is washed with 5-10 mL dichloromethane. The dichloromethane is evaporated on a rotoevaporator at 38-40 ^{o}C at -0,4 bar. The evaporation is stopped when about 500µL is left and 2 ml acetone is added. The acetone fraction is filtered through a 0.2 µm filter into a 20 mL test tube. Further 2x2 mL acetone is used for rinsing of the flask and the filter.

Derivatisation:

25 µL 1% pentafluorbenzylbromide solution and 20 mg incinerated K_2CO_3 is added to the acetone fraction.
The test tube is closed an shaken for 5 sec. on a Whirley mixer and is then standing over night at ambient temperature. The liquid phase is transferred to a new test tube while the precipitate is cleaned with 1 mL acetone which is transferred to the test tube.
2 mL isooctane is added to the test tube and the volume is reduced to about 1 ml under a gentle stream of nitrogen. This step is repeated twice and the residual volume is transferred to an amber glass vial passing a 0,2 µm filter.

The test tube is rinsed twice with max. 6 drops of isooctane which is transferred to the vial. The volume is reduced to exactly 300 µL under a gentle stream of nitrogen. The vial is closed with a teflon coated cap and is kept at –18 ^{o}C until analysis.

Appendix IV

Principles for analysis of water samples collected in 1998:

The water sample is passed through a solid phase extraction column (SPE-column) and the retained compounds are eluted with an organic solvent. The solvent is evaporated in a vacuum centrifuge and the residue is redissolved in a suitable solvent for HPLC. The compounds are separated on a HPLC column and detected in a mass spectrometer after electrospray ionisation (ESI)

Chemicals, solutions and standards:

Methanol, HPLC grade (Rathburn)
Acetonitril, gradient grade (Merck)
Acetic acid 100 %, p.a. (Merck),
1,2-propanediol (propylene glycol), (Sigma),
Konc. HCl rauchend, 37 %, (Merck),
Precervation solution for rain water: 60,0 ml konc. HCl – op to 1000 ml with milli-Q-treated water.
Deionised water from central osmose plant further cleaned in Milli-Q system (Millipore). Ammonium acetate, p.a. (Merck).
Standards from Dr Ehrendorfer or Riedel de Häen.

Stock solutions, standards and internal standards:
Stock solutions are made by weighing of 50 mg standard, which is dissolved in 50 ml acetonitril. Stock solutions are stored in refrigerator and are registered in a stock solution record.
Standards are made by dilution in acetonitril and final dilution in A-eluent or in a solvent comparable to HPLC-start conditions. Standard concentrations should cover the concentration range for the samples after preconcentration, for instance 10, 50 ,100 and 200 µg/L.
^{13}C- or ^{2}H-labelled internal standards are recommended for adding to the samples before preconcentration to checking recovery.

HPLC-Eluents:
For analysis of isoproturon the following gradient system is used:
A1-eluent: methanol/10 mM Ammonium acetate in milliQ-water 10/990,
B1-eluent: methanol/10 mM ammonium acetate 90/10,

For phenoxyalkanoic acid herbicides and other acidic compounds:
A1-eluent: methanol/ 20 mM acetic acid 10/90,
B1-eluent: 20 mM acetic acid in methanol.
The eluents are filtered through 0.2 µm millipore filter (type Fluropore, FG), Millipore.

LC-conditions

The LC-MS system was composed by a Hewlett-Packard LC-MSD 1100 system with a binary gradient pump system.
The HPLC-column was a Hypersil BDS 250 x 2.1 mm column.
The same linear gradient profile were used for both acidic compounds and isoproturon compounds with different eluents, as described above:

Time, min	B-solvent, %
0	0
3	50
30	100
33	100
36	0
45	0

Injection volume: 50 µl.
Flow: 0,2 ml/min
Column temperature: 30 °C.

Mass spectrometry:

Phenoxyalkanoic acid herbicides, bentazon and – metabolites together with DNOC was detected by MS with electrospray inlet (ESI), negative mode and selected ion monitoring (SIM):

Drying gas temperature: 350 °C
Drying gas flow: 10,0 L/min.
Nebulizer pressure: 40 psig
Capillary voltage: 4000 V.
The following masses were measured (*m/z*): 197, 199, 201, 213, 215, 233, 235, 239, 255, 380,
Dwell time 146 ms.
Fragmentor voltage 80 V.

Isoproturon and degradation products were detected by MS with electrospray inlet (ESI),positive mode and selected ion monitoring (SIM):

Drying gas temperature: 350 °C
Drying gas flow: 10,0 l/min.
Nebulizer pressure: 40 psig
Capillary voltage: 4000 V.
The following masses were measured (*m/z*): 136, 179, 193, 207.
Dwell time 146 ms.
Fragmentor voltage 80 V.

Sample preparation:

50 ml preservation solution is added to the sample flasks before they are placed on the locations.
The samples are stored at 4 °C if sample preparation takes places within a few days. Otherwise the samples are frozen at –18 °C until sample preparation will take place.

The sample volume is registered and eventually internal standard is added
The sample is passed through a glass fibre prefilter and a glass fibre filter and the filters are rinsed with 5 ml methanol.
The filtrate or 250 ml water sample (+ 1,25 ml Methanol) (+ 6,25 ml preservation solution to recovery and blanks) are added to Porapak Rdx solid phase extraction columns, which are preconditioned with 10 ml acetonitril, 10 ml Methanol and 20 ml Milli-Q water. The water sample is applied under vacuum pressure with a flow about 10-20 ml/min. The columns must never run dry during the application.
Afterwards the columns are air dried with vacuum suction in further 20 min.

The columns are eluted with 5 ml methanol/acetonitril 1/1 in the following way: 1 ml is passed through the column, 2 minutes standing and the rest of the solvent is passing without vacuum into a vial with 50 µL propylene glycol as keeper.
The sample volume is reduced to 50 µl in a vacuum centrifuge. The propylene glycol residue is diluted with 500 µl 10% methanol and is ready for HPLC-analysis.

Effects of herbicides in precipitation on plants and plant communities

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Indhold

Summary

In several European studies pesticides have been found in precipitation. The potential risk of adverse effects of herbicides in precipitation on plants and plant communities in the agro-ecosystem and adjacent ecosystem can be assessed if the No Observable Effect Level (NOEL) is known. In this project NOEL was defined as the dose required to reduce fresh or dry weight by 10% (ED_{10}). Mecoprop-P was selected as model pesticide and the ED_{10} dose was determined on a number of susceptible plant species at different growth stages. In addition, the competition indeces between selected species grown in binary mixtures were compared without herbicide treatment and following application of mecoprop-P doses close to $ED_{10.}$ The ED_{10} dose of the most susceptible plant species included in this study was more than 3 times higher than the maximum yearly deposition of mecoprop in Danish rain water. In the study, different methods were applied to assess effects of the low doses of mecoprop-P. The results showed that biomass production was as susceptible a parameter as seed production. The substitution rate between plant species with similar competitive ability but different susceptibility to mecoprop was not significantly influenced of doses close to ED_{10}.

Sammendrag

I såvel internationale som danske undersøgelser er der påvist forekomst af pesticider i nedbør. For at kunne vurdere hvorvidt disse forekomster udgør en risiko i økotoksikologisk sammenhæng, er der behov for viden om hvor lave koncentrationer af pesticider, der kan forventes at resultere i målbare effekter i naturen. Af hensyn til den statistiske bearbejdning af resultaterne har vi valgt at definere NOEL (No Observable Effect Level), som den dosering, der resulterer i 10% reduktion af frisk- eller tørvægten på de behandlede planter (=ED_{10}). Mechlorprop-P er anvendt som modelstof ,og ED_{10} doseringen af dette herbicid er bestemt overfor en række følsomme plantearter (Agersennep, Pengeurt, Hyrdetaske, Agertidsel, Haremad, Hvidmelet gåsefod og Fuglegræs). Bestemmelsen er foretaget ved behandling på forskellige udviklingstrin, ved forskellige høsttidspunkter og ved måling af biomasse og frøproduktion. Desuden er det undersøgt, om konkurrenceevnen af en følsom art overfor en mindre følsom art påvirkes ved behandling med doseringer af mechlorprop-P omkring ED_{10}. Resultaterne viste, at der ikke er målbare effekter af de mængder af mechlorprop-P, som er fundet i opsamlede regnvandsprøver , idet ED_{10} doseringen på den mest følsomme planteart var ca. 10 gange højere end det maksimale fund i en enkelt udtagning og 3 gange højere end den gennemsnitlige årlige deponering pr. arealenhed. Undersøgelsen har desuden vist, at hverken frøproduktion eller konkurrenceevnen er mere følsomme parametre end biomasseproduktion.

1 Introduction

Several European studies have revealed that pesticides can occur in precipitation (Sibers et al., 1995; Jaeschke et al., 1995, Lode et al., 1995; Kreuger, 1995). In the years 1992-94 rain water collected at two locations in Denmark was analysed for the content of 10 pesticides but only phenoxyalkanoic acid herbicides were found and this group of herbicides occured at concentrations up to 0.4 mg/l (Kirknel & Felding, 1995). For this study we therefore selected mecoprop as model herbicide. Mecoprop was extensively used in Denmark in 1996 when the project was initiated, however in the following year the usage of phenoxyalkanoic acid herbicides was severely restricted resulting in a 80-85% reduction in the consumption from 1996 to 1997.

It seems probable that herbicides in precipation can affect the growth and reproductivity of terrestrial plants. However no attempts have been made so far to assess the possible effects of herbicides in precipitation on plants and plant communities in the agro-ecosystems and adjacent ecosystems.

The objective of this part of the project was to assess the potential risk of adverse effects of mecoprop-P present in precipitation on plants and plant communities in the agro-ecosystem.

The No Observable Effect Level (NOEL) is a recognized ecotoxicological term designating the highest dose having no effects on the growth of the test organism. As the experimental design and number of replications can have a marked influence on the estimation of NOEL it is more convenient to define NOEL as the dose required to reduce growth by 5 or 10%. In this project the dose resulting in a 10% reduction in growth of the test plants (ED10) has been used as a measure for NOEL.

2 Materials and methods

The effects of low doses of mecoprop were examined in two different types of experiments:

1. The ED_{10} dose of mecoprop-P was determined on a number of susceptible plant species
2. The competition indeces between selected species grown in binary mixtures were compared following no application of herbicide and application of mecoprop-P doses close to the ED_{10}.

2.1 Experiments for determining ED_{10} doses

Test plants

The ED_{10} doses of mecoprop-P were determined on Capsella bursa-pastoris, Thlaspi arvense, Sinapis alba, Circium arvense, Lapsana communis Chenopodium album and Stellaria media. All species are known to be very susceptible to phenoxyalkanoic acid herbicides.

The experiments were carried out in a glasshouse in the period from April 15 to October 15. Seeds were sown in 2 L pots in a soil/ sand/ peat mixture (2:1:1 w/w) containing all necessary macro and micro nutrients. After emergence the number of plants per pot was reduced to a similar number.

Application and doses

The treatments with mecoprop were carried out on different growth stages of the plants varying from two to eight leaves. In one experiment *Thlaspi arvense* was also exposed to mecoprop-P at the flowering stage. Mecoprop-P was applied using a laboratory pot sprayer equipped with two Hardi 4110-14 nozzles in a spray volume varying between 130 and 165 L ha^{-1}. Each plant species was treated with 7 to 10 doses of mecoprop-P (Duplosan MP, 600 g L^{-1} mecoprop-P). In order to obtain responses from 0 to 100% effect the doses were varied between plant species and growth stages. Each treatment was replicated three times using a completely randomised layout

Plants were harvested 3-4 weeks after treatment and fresh and dry weights were collected. In one experiments the influence of time of harvest was examined by harvesting at two different time intervals (2 respectively 4 weeks) after treatment. This experiment included also a comparison of the effect of mecoprop-P on seed *versus* biomass production.

Model used for estimating dose response curves

For each plant species and growth stage dose response curves were estimated using non-linear regressions. A four parameter logistic model was used to describe the relationship between plant weight and dose :

$$U = \frac{D - C}{1 + \exp(2b(\log(ED_{10}) - 1.099/b - \log(z)))}$$

In this model U is the fresh- or dry weight of the plants, D denotes the upper limit of plant biomass at zero dose, C the lower limit at high doses, b is the slope, z the dose and ED_{10} is the dose resulting in 10% reduction of growth.

The regression model was evaluated by a test for lack of fit comparing the sum of residuals from the regression and variance analyses.

2.2 Competition experiments

Test plants

In the competition experiments different densities of *C. bursa-pastoris* and *G. dissectum* were grown in monoculture and in binary mixtures varying the ratio and density of the two species.

At the 1-2 leaf stage plants of the two species were transplanted to 40 by 40 cm polystyren boxes (growth area 35 by 35 cm) filled with a soil/sand/peat mixture (2:1:1 w/w) containing all necessary micro- and macro nutrients.

Experimental design

The experiments were based on a complete additive design as proposed by Cousens (1991). Plants were transplanted in a geometric series of plant densities using regular patterns (Figure 1). The density of each plant species varied between 1 and 32 plants per box covering scenarios from no competition to high competition intensity. For each plant species, 5 different densities were used giving 25 different combinations. In addition a high density (64 plants per box) of each species alone was included in order to assess the intraspecific competition at a high density.

The plants were placed in a glasshouse and watered daily. The boxes were placed in blocks according to the total number of plants in the boxes. One block included boxes with less than 20 plants, another included boxes with 20 to 40 plants and in the last block boxes with more than 40 plants were placed.

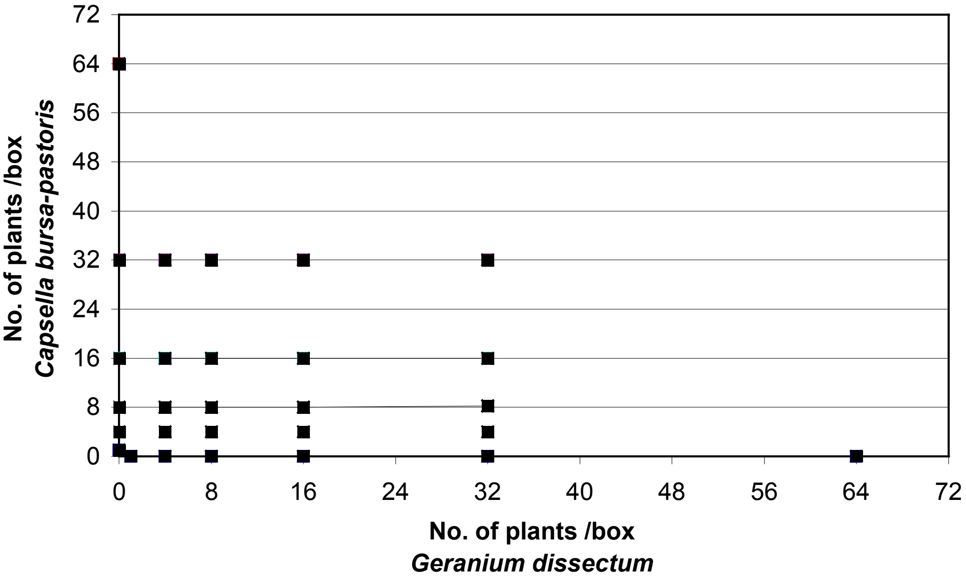


Figure 1
Composition of two component mixtures of G. dissectum *and* C. bursa-pastoris *in the experiments. The axes show the number of plants per box (growth area 35 by 35 cm).*

Sammensætning af to-komponent blandinger af G. dissectum *og* C. bursa-pastoris *i forsøgene. Akserne viser antallet af hver planteart pr. kasse (vækstareal 35 x 35 cm).*

Application and doses

Mecoprop-P was applied to the plants at the 6-8 leaves stage. Each combination of plant densities and ratios were represented by an untreated and one or two doses of mecoprop-P close to the expected ED_{10} dose of *C. bursa-pastoris*. Each treatment was replicated twice. Mecoprop-P was applied using a laboratory pot sprayer equipped with two Hardi 4110-14 flat fan nozzles producing a spray volume of 150 L ha^{-1}.

Concurrently with the competition experiments the ED_{10} doses of each of the two plant species were estimated in pot experiments.

The plants were harvested 3 weeks after treatment. The outer 5 cm of the boxes was not harvested. The number of plants of each species was counted and harvested separately. Fresh- and dry weights were collected.

The biomass per plant y_1 and y_2 of species 1 (*C. bursa-pastoris*) and species 2 (*G. dissectum*) can be calculated when the number of plants n_1 and n_2 and the total plant biomass x_1 and x_2 are known.

$$y_1 = \frac{x_1}{n_1} \quad y_2 = \frac{x_2}{n_2}$$

Competition model

If however we wish to describe the biomass y_1 as a function of n_1 and n_2 the invers linear model suggested by Spitters (1983) can be used:

$$\frac{1}{y_1} = B_0 + B_1 n_1 + B_2 n_2$$

In this model B_0, B_1 and B_2 are unknown parameters. As y_1 and y_2 are the most relevant factors in this context the equation was rewritten as:

$$y_1 = \frac{1}{B_0 + B_1 n_1 + B_2 n_2}$$

Madsen et al. (1995) reparameterized this equation in order to give all parameters a biological meaning:

$$y_1 = \frac{A}{1 + \frac{A}{B}(n_1 + Cn_2 - n_0)}$$

y_1 is now the biomass per plant of species 1 when grown in a binary mixture containing n_1 plants of species 1 and n_2 plants of species 2 per box. *A* is the biomass per plant at an arbitrar zero density (n_0), which in the analyses was set to 8. *B* denotes the maximum yield per box at infinite plant densities and *C* is the substitution rate. If plants compete for the same resources *C* can be used to decribe the competition rate of species 2 against species 1. If $C > 1$ species 2 is more competitive than species 1 and *vise versa*. The arbitrary value for n_o is used to avoid extrapolation to non-observed densities as well as devoting a welldefined biological explanation for *B* (Fredshavn, 1994).

When the substitution rate *C* is known the effective density n_e can be calculated:

ne = n1 + Cn2

3 Results and discussion

3.1 Determining ED_{10} doses

Susceptibility of different plant species

Table 1 shows the estimated ED_{10} doses. The most susceptible species were *S. alba* and *C. bursa-pastoris* with ED_{10} doses lower than 1 g a.i. ha^{-1} while the ED_{10} doses of *T. arvense*, *C. album* and *C. arvense* were 3 to 4 g a.i. ha^{-1}. *L. communis* and *S. media* were the most tolerant species with ED_{10} doses higher than 5 g a.i. ha^{-1}. One would expect the ED_{10} dose to increase with growth stage, however as the experiments were carried out at different times of the year factors other than growth stage could have an influence on the susceptibility of the plants.

Table 1
Estimated ED_{10} doses of mecoprop on different species and growth stages. The figures in parentheses are minimum and maximum of the estimated mean values.

Estimerede ED10 doseringer af mechlorprop på forskellige arter og udviklingstrin. Tallene i parentes er minimum og maximum af de estimerede værdier.

Plant species	Growth stage	ED_{10} (g a.i.ha^{-1})	Number of trials
1.1.1 *Sinapis alba*	2-3 leaves	0.6 (0.5; 0.7)	3
	4-5 leaves	0.8	1
1.1.2 *Thlaspi arvense*	2-3 leaves	3.0	1
	4-5 leaves	2.8	1
	6-8 leaves	3.2 (0.9;7.3)	3
	9-10 leaves	3.3 (1.8; 4.3)	3
Capsella bursa-pastoris	4-5 leaves	1.2 (1.1; 1.3)	3
	6-8 leaves	0.6 (0.4; 0.8)	2
	9-10 leaves	0.5	1
Circium arvense	2-3 leaves	5.0 (1.2; 9.3)	5
Lapsana communis	2-3 leaves	12.6 (8.5; 16.6)	2
	4-5 leaves	5.0 (2.4; 7.5)	2
Chenopodium album	4-5 leaves	2.6 (0.5; 5.3)	3
1.1.3 *Stellaria media*	4-5 leaves	6.5 (5.5; 7.6)	2
	6-8 leaves	5.6 (2.6; 8.5)	2

Deposition of mecoprop by rain

The maximum yearly deposition of mecoprop calculated on basis of the analysis of the rain samples was 0.2 g mecoprop ha^{-1} (Table 3.15). Consequently, the ED_{10} dose of the most susceptible species was more than 3 times higher than the maximum yearly deposition by rain and 10 times the maximum concentration found in one sample.

Influence of time of harvest

In the experiments shown in Table 1 the plants were harvested approximately 3 weeks after treatment. In practise plants will often grow for a longer period after exposure to herbicides which raises the question whether they will gradually recover. Here the influence of the time of harvest on the final effect was determined in one experiment where plants were harvested at different time intervals after treatment. In addition the susceptibility to mecoprop-P at the flowering stage as well as the effect on seed production was examined. The results are shown in Table 2.

Table 2

The influence of growth stage at treatment and time of harvest on ED_{10} doses of Thlaspi arvense *estimated on biomass and seed production, respectively. Figures in parentheses are standard errors.*

Betydning af udviklingstrin på behandlingstidspunktet og høsttidspunkt for e ED_{10} doseringer på Thlaspi arvense *beregnet udfra henholdsvis biomasse og frøproduktion. Tallene i parentes er standardafvigelser.*

Growth stage	Interval between treatment and harvest	ED_{10} dose (g.a.i. ha^{-1})	
		Biomass	Seed production
8-10 leaves	2 weeks	3.9 (2.5)	
	4 weeks	1.8 (1.4)	
	> 15 weeks		10.7 (4.6)
Flowering	2 weeks	1.3 (0.6)	
	> 15 weeks		3.5 (2.3)

When treated at the 8 to 10 leaves stage no significant differences were found between harvest 2 and 4 weeks after treatment. Surprisingly biomass production was inhibited more when plants were exposed to mecoprop-P at the flowering stage compared to the 8 to 10 leaves stage. At both growth stages the ED_{10} doses estimated on basis of seed production were significantly higher than those estimated on basis of biomass production.

3.2 Competition experiments

Characteristics of test plants

Three competition experiments were carried out. The purpose of the first experiment was to determine plant species and densities to be used in the subsequent experiment (results not shown). *C. bursa-pastoris* and *G. dissectum* were selected as two plant species possessing the same competitive ability but differing in susceptibility to mecoprop. The growth habit of these two plant species differ widely. *C. bursa-pastoris* is a relative small plant which elongate at an early stage where as *G. dissectum* forms a vigorous roset at an early growth stage. *C. bursa-pastoris* is known to be much more susceptible to mecoprop than *G.dissectum.*

Susceptibility to

In subsequent experiments, the competition between the two species without *mecoprop*

herbicide and after treatment with 1 or 2 doses of mecoprop-P was determined. In one trial a dose of 3 g a.i. ha^{-1} of mecoprop-P was applied while in the second trial 0.5 and 2.0 g a.i. ha^{-1} were applied. The ED$_{10}$ doses estimated on the pot-grown plants grown in monoculture revealed that the ED$_{10}$ doses of mecoprop-P on *C. bursa-pastoris* and *G. dissectum* were respectively 0.4 g a.i. ha^{-1} and 8.2 g a.i. ha^{-1}.

Susceptibility of A and B parameters

Table 3 shows the estimated parameters in the two competition experiments. In both experiments the *A* parameter (weight per plant at n_0=8 plants per box) of *C. bursa-pastoris* was significantly higher than the *A* parameter of *G. dissectum*. In experiment 1, the applied dose of mecoprop-P was much higher than the ED$_{10}$ dose of *C. bursa-pastoris* and the *A* parameter of *C. bursa-pastoris* was significantly reduced while no effect was found on *G. dissectum*. A tendency to a reduction of the *B* parameter of *C. bursa-pastoris* (the maximum production per box) was also seen.

In experiment 2 the *A* and *B* parameters were unaffected of the lowest dose of mecoprop-P while on *C. bursa pastoris* both parameters tended to decrease with increasing dose. The *B* parameter of *G. dissectum* also tended to decrease with increased dose.

Susceptibility of C parameter

The influence of herbicide treatments on the interspecific competition can be assessed by the *C* parameter. No significant differences in *C* parameters were found between the species and doses indicating that the interspecific competition was equal. In experiment 1, the estimated *C* parameters on *G. dissectum* was 1.7 for untreated and 0.9 after treatment with 3 g a.i. ha^{-1}. Consequently, 1 plant of *C. bursa-pastoris* can be replaced by 1.7 and 0.9 plants of *G. dissectum* respectively. Based on the *C. bursa-pastoris* data the results showed that when untreated 1 plant of *G.dissectum* could be replaced by 1.4 plants of *C. bursa-pastoris* while the substitution rate after treatment with 3 g a.i. ha^{-1} of mecoprop was 1. Herbicide treatment halves the substitution rate of *G. dissectum* while the change of the substitution rate of *C.bursa-pastoris* was lower indicating that the applied mecoprop dose had more influence on the growth of *C. bursa-pastoris* than of *G. dissectum*. However, as none of the estimated *C* parameters differed significantly from 1 and as they were not significantly affected by the applied doses it can be concluded that the competitiveness of the species was not significantly influenced by the applied mecoprop-P dose.

In experiment 2 the *C* parameter of *G. dissectum* tended to decrease when 0.5 g a.i. mecoprop was applied confirming that *C. bursa-pastoris* was more susceptible than *G. dissectum.* Similarly the number of *G. dissectum* plants necessary to substitute one *C. bursa-pastoris* plant was lower after herbicide treatment. However when the dose was increased to 5 times the ED$_{10}$ dose the *C* parameter tended to increase, which we can not explain. None of the differences were significant.

Figure 2 shows the observed and predicted *A* values (biomass per plant) as a function of n_e (effective plant density). The curves of *C. bursa-pastoris* are more steep than the corresponding curves of *G. dissectum*, indicating that *C. bursa pastoris* was more susceptible to increasing plant density than *G. dissectum.* This was not reflected as a difference in the competition ability because intraspecific competition played a major role with *C. bursa-pastoris*.

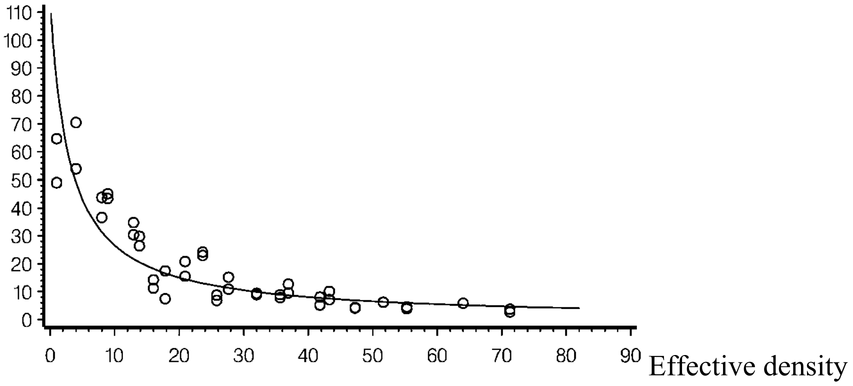
In the competition experiments, the two selected plant species, although differing widely in growth habits, were expected to possess the same competition ability whereas the susceptibility to mecoprop differed. Following application of a mecoprop-P dose that would influence the growth of the most susceptible species, one would expect a change in the competition index favourizing the most tolerant species. However, no significant differences in the competitive ability of *C. bursa-pastoris* and *G. dissectum* were observed when applying a mecoprop-P dose close to the ED_{10} dose of *C. bursa-pastoris* or a dose 5 times higher. Therefore it can be concluded that when using the experimental design adopted in this study competition was not a more susceptible factor to study than biomass production.

Table 3
Estimated parameters in the competition experiments (fresh weight). The figures in parentheses are 95% confidence intervals.

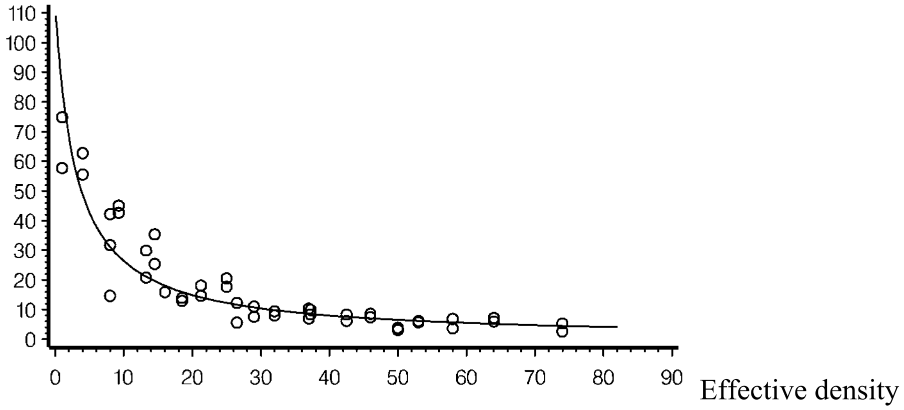
Estimerede parametre i konkurrenceforsøgene (friskvægt). Tallene i parentes er 95% konfidens intervaller.

Exp.	Plant species	Dose	*A* (g/box)	*B* (max. Prod)	C
1	*G. dissectum*	0	7.5 (6.6-8.4)	344.4 (205.5-483.4)	1.7 (0.8-2.6)
	G. dissectum	3	6.6 (5.8-7.5)	429.0 (225.3-632.5)	0.9 (0.3-1.5)
	C. bursa-pastoris	0	57.0 (47.3 – 66.6)	693.7 (538.3 – 849.1)	1.4 (0.8-1.9)
	C. bursa-pastoris	3	39.0 (31.6-46.3)	444.6 (337.6 –551.6)	1.0 (0.5-1.5)
2	*G. dissectum*	0	10.9 (9.8-11.9)	328.0 (199.6 –456.9)	1.9 (0.8-2.9)
	G. dissectum	0.5	10.5 (8.6-12.3)	299.3 (177.7 –420.9)	1.6 (0.7-2.5)
	G. dissectum	2.0	9.6 (8.0 –11.2)	362.1 (194.5- 529.7)	2.3 (0.9-3.6)
	C. bursa-pastoris	0	31.2 (25.7-36.8)	345.4 (256.2– 434.7)	1.2 (0.7-1.8)
	C. bursa-pastoris	0.5	31.0 (25.8-36.2)	342.1 (256.6-427.6)	1.3 (0.8-1.9)
	C bursa-pastoris	2.0	27.5 (22.5-32.5)	301.5 (222.4–380.6)	1.4 (0.8-2.0)

Fresh weight
g/plant Control a



Fresh weight
g/plant 0.5 g/ha mecoprop-P b



Fresh weight
g/plant 2.0 g/ha mecoprop-P c

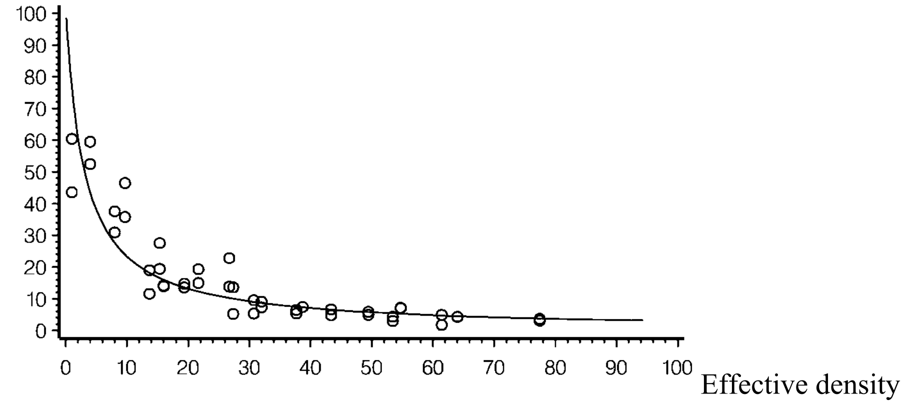
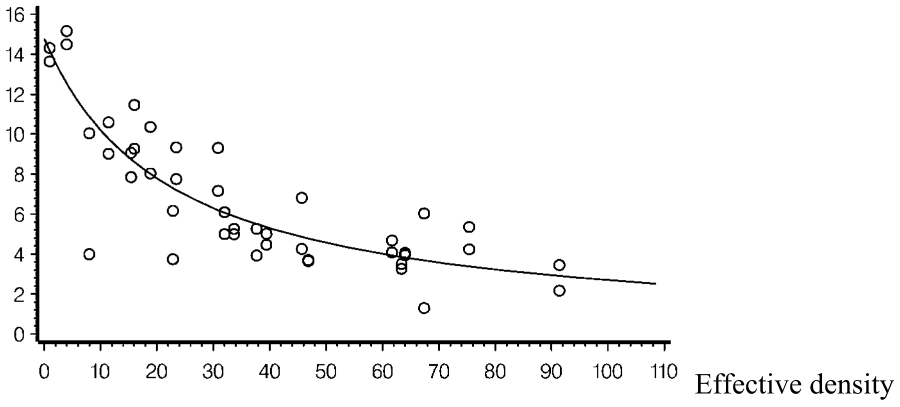


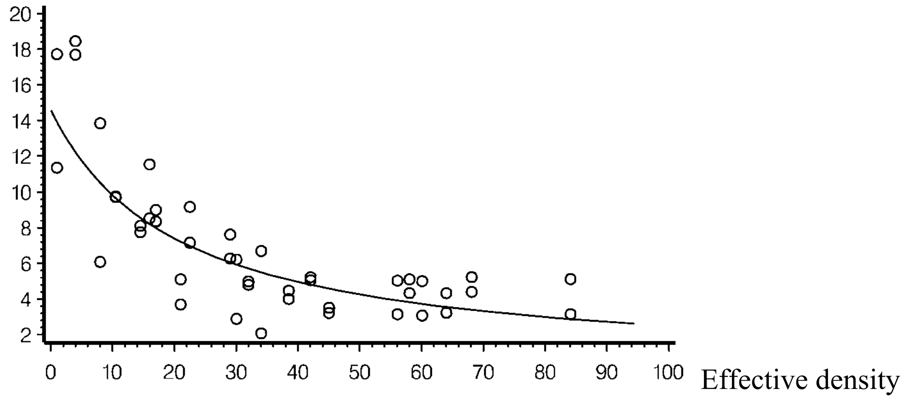
Figure 2
The influence of effective plant number on production of biomass per plant (A) of C. bursa-pastoris (a-c) and G. dissectum (d-f) without herbicide and after treatment with 0.5 or 2 g a.i. ha^{-1} of mecoprop. Experiment 2.

Indflydelse af effektivt plantetal på biomasseproduktionen pr. plante af C. bursa-pastoris (a-c) og G. dissectum (d-f) uden herbicid og efter behandling med 0.5 og 2 g ha-1 mechlorprop

Fresh weight
g/plant Control d



Fresh weight
g/plant 0.5 g/ha mecoprop-P e



Fresh weight
g/plant 2.0 g/ha mecoprop-P f

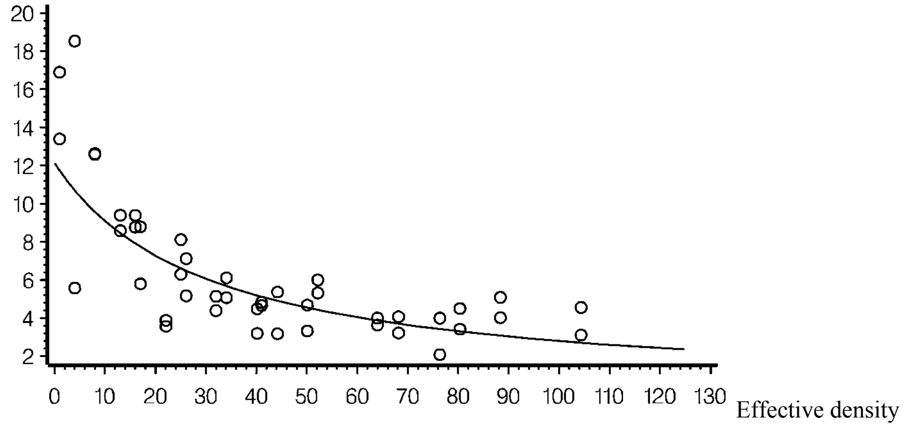


Figure 2 (continued)
The influence of effective plant number on production of biomass per plant (A) of C. bursa-pastoris (a-c) and G. dissectum (d-f) without herbicide and after treatment with 0.5 or 2 g a.i. ha^{-1} of mecoprop. Experiment 2.

Indflydelse af effektivt plantetal på biomasseproduktionen pr. plante af C. bursa-pastoris (a-c) og G. dissectum (d-f) uden herbicid og efter behandling med 0.5 og 2 g ha^{-1} mechlorprop.

4 Conclusions

The potential risk of adverse effects of mecoprop in precipitation has been assessed by applying different methods. The results have revealed that biomass is as susceptible a parameter as seed production. The substitution rate between species with similar competitive ability but different susceptibility to the herbicide was not significantly influenced by doses close to ED_{10} .

The results have shown that the No Observable Effect Level (in this study defined as the ED_{10} dose) of mecoprop-P on the most susceptible plant species included in this study was more than 3 times higher than the maximum yearly deposition of mecoprop in Danish rain water and 10 times higher than the maximum deposition within a two weeks period. Consequently, effects of mecoprop in precipitation is not very likely.

In this project we only studied the influence of a single herbicide, however the analyses of rain water have revealed the presence of several herbicides. A question to address in a future project is the possible effects of such 'pesticide cocktails' on terrestrial plants.

5 Acknowledgement

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Final conclusion

The report describes how volatility of pesticides can be determined by a laboratory model system; further models for pesticide diffusion and transport in the atmosphere as well as deposition are described and evaluated. Precipitation was collected and analysed for selected pesticides over a couple of years and further the effect of the herbicide mecoprop was determined on a number of sensitive test plants to see whether the found pesticide concentrations in rainwater possess a threat to plant communities.

The laboratory experiments have elucidated a great need for standardised laboratory systems to determine the volatility of pesticides. Especially the test conditions need to be described carefully.

Atmospheric transport and deposition models for pesticides have been developed, but information is lacking on some of the basis processes as emission, dry deposition, atmospheric reactions and conversion from the gaseous to the particulate phase. Information on transport, diffusion and wet deposition processes for pesticides is sufficiently known. The description of emission and dry deposition in such models can be improved if the processes that determine the concentration in the surface (soil, vegetation, water) are modelled at the same time.

The concentrations of pesticides found in rainwater seemed generally to be of the same order of magnitude as in other European countries. The pesticides appeared in the highest concentrations in the spraying season, and when the use of phenoxy-herbicides was limited in Denmark, they were only rarely found in the precipitation. This is known not to be true for the chlorinated hydrocarbon insecticides, which may be transported over long distances. The herbicide DNOC was found in the highest concentrations, but this compound seems to be formed in the atmosphere.

When the effects of pesticide concentrations found in rain water were determined on susceptible plant species, the experiments showed, that the NOEL (No Observable Effect Level) for mecoprop was more than three times higher than the maximum yearly deposition of mecoprop in Denmark. Tests have only been performed with single pesticides and need to be performed with the many combinations of pesticides that are normally found in rainwater.

Determination of volatilisation

Volatilisation of pesticides are influenced by many different factors under field conditions. It is difficult to study the influence of individual parameters (e.g. temperature, wind speed) on the emission with field experiments. Therefore standardised laboratory experiments can be a helpful tools. Since the German BBA-guidelines appeared in 1990 different methods have been developed.

In a test of the different methods with three pesticides, it was found, that chamber properties and size and experimental area and air exchange rates are the most important for the determination of volatilisation. Great variations between the different methods were found, which showed that it is very difficult to compare results from different test methods.

In this project is developed a laboratory system which makes it possible to determine evaporation from different surfaces and to compare different pesticides. Based on the findings from the experiments it is concluded, that:

- The BBA guideline should be improved and the description of the chamber and the conditions should be more specific
- Volatilisation chamber must be specified (a small chamber is recommended)
- Sampling after 1, 3, 6 and 24 hours seems reasonable
- It is important to measure the height over the surface and whether turbulent or laminar flow is used when air velocity is determined. A velocity of less than 1 m per sec. 1 to 5 mm above the surface might be sufficient.
- Approximately 50% relative humidity should be used and the surface to which the pesticide is applied should have the same humidity during the whole experiment
- Filter paper may be used to mimic leaf surface
- Standard soil with specified pH should be kept at 60% of maximum water holding capacity during the whole experiment
- It should be considered not to perform experiments with soil but only from artificial surface since volatility is always highest from the artificial surfaces. In this way a maximum emission rate can be determined.
- Several concentrations of a given pesticide should be tested and experiment must be carried out with both formulated product and active ingredient
- Preferably the test should be carried out at 10 and 30°C

Modelling atmospheric transport and deposition

The behaviour of pesticides in the atmosphere is very much dependent upon their solubility in water and their vapour pressure. Modelling of the fate of pesticides in the atmosphere is difficult, because information about important properties of pesticides is not available or is uncertain. Further it is very difficult to generalise their behaviour, because the properties of pesticides are so different, there is a large variety of surfaces with different properties. For the approval of pesticides general information is provided by the manufactures, but this is not sufficient to predict their behaviour in the atmosphere.

Emission and dry deposition depend on atmospheric turbulence, temperature and properties of the surface of soil and plants and the processes that take place in the surface (degradation and sorption). Temperature is especially important because the evaporation of water and the vapour pressure and water solubility of the pesticide depend on it.

It has been shown that for highly soluble gaseous pesticides a maximum of less than 25% of the emission can be deposited within 2 km from the source. For moderately soluble gaseous pesticides it in the order of 7% and for slightly soluble gases about 1% only. The dry deposition relatively close to the source has not been measured although models have shown that in extreme cases about 20% of the emission could be dry deposited within a few hundred metres from the source.

If the concentrations in air and in precipitation are measured simultaneously, the rate at which pesticides are removed from the atmosphere by wet deposition can be calculated, if the mixing height is known. For gaseous pesticides the removal rate by dry and wet deposition increases with their solubility in water. For pesticides in particulate form the removal rate by dry and wet deposition depends on the size distribution of the particles. In general particles are removed rather efficiently by wet removal processes where clouds are involved.

Photochemical atmospheric reactions of pesticides are not thought to be important within 2 km from a source but can play an important role during transport over longer distances. They will limit the distance over which gaseous pesticides can be transported if dry or wet deposition is not sufficient.

Conversion of pesticides from the gaseous to the particulate phase is thought not to be important within 2 km from the source, but is important during transport over longer distances. The reason is that dry and wet removal rates for gaseous and particulate pesticides are different. A phase change will therefore influence the removal rate.

Models can never replace measurements, but they can provide a best estimate, and especially in designing experiments models are useful, since experiments for pesticides should be planned with great care because chemical analysis are expensive. Laboratory experiments are useful, because they make it possible to study processes under controlled conditions, with only one factor varied at a time. A good research strategy should include both field and laboratory experiments and model development.

Compared to the air pollutants sulphur dioxide and nitrogen oxides, modelling of pesticides in the atmosphere is far from easy, they occur in much lower concentrations, and there are hundreds of different pesticides around in the atmosphere. On the other hand, it needs less knowledge to come to sound policy decisions than to get a quantitative scientific description of the whole system.

Pesticides in air and in precipitation

Rainwater has been collected on three locations on the island of Zealand.
The analysis of phenoxyalkanoic acids (mecoprop, dichlorprop and MCPA) and of isoproturon showed that there was an obvious connection between the findings of pesticides in rainwater and the time of spraying with the herbicides. Concentrations and deposition were of the same order of magnitude as found in other European countries.

Phenoxyalkanoic herbicides were detected during the first years of the experiment, but in 1998 no phenoxyalkanoic acid were detected on the three locations. This indicates that the limitations in the use of these herbicides have greatly reduced their appearance in precipitation.

The herbicide DNOC was found in high concentrations both during and outside the spraying season, even though this compound has not been allowed in Denmark for the last 10 years. The concentrations detected in the rain in Denmark are of the same order of magnitude as found in England, Germany and Switzerland. The finding of DNOC indicates that either the compound can be transported in the atmosphere over long distances or other sources of DNOC than pesticide use are important. Most likely, the finding of DNOC is caused by formation of the compound in the atmosphere, probably from reaction between toluene and nitrous oxides under influence of sunlight.

The pesticide concentrations found are regarded as minimum concentrations since the samples are not adequately stable especially in the summer season if the rain falls in the beginning of the collection period.

Effects on plants and plant communities

The herbicide mecoprop-P was used as model pesticide. The influence of low doses of this herbicide was determined on the following testplants, which are all very susceptible to phenoxyalkanoic acid herbicides (*Capsella bursa-pastoris*, *Thlaspi arvense*, *Sinapis alba*, *Cirsium arvense*, *Lapsana communis*, *Chenopodium album* and *Stellaria media*. Further the effects were determined on the competition between *Capsella bursa-pastoris* and *Geranium dissectum*.

The No observable Effect Level (NOEL) was defined as the ED_{10} value (the calculated dose that caused a 10% reduction in the growth of the test plant). The results show that the NOEL of mecoprop on the most susceptible plant species in the study was more than 3 times higher than the maximum yearly deposition of mecoprop in Denmark.

Plant biomass was found to be as susceptible as seed production to assess the pesticide influence. Further competitive ability between plant species was not found to be a more susceptible test method. Effects of the combinations of pesticides that have been found in rainwater still needs to be determined.