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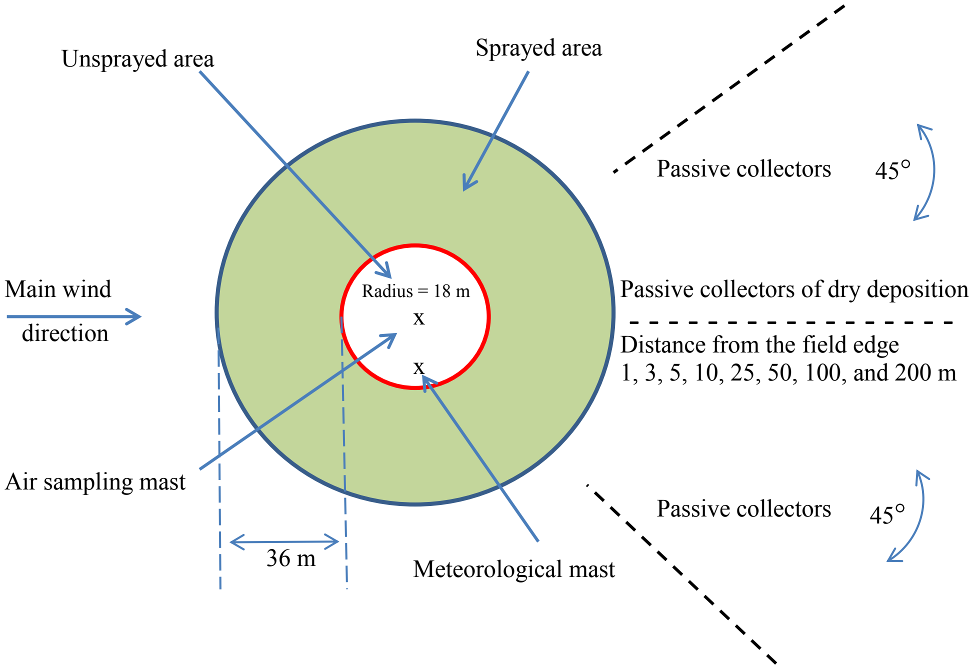

Volatilization and dry deposition of pesticides under Scandinavian climatic conditions – a three-year field study at Lövsta (central Sweden)

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Preface

Large amounts of pesticides are used yearly in the agricultural practice in Sweden, and at the same time rules and restrictions regulating this use has been strengthened during the last decades (Kemikalieinspektionen, 2006; Kreuger, 2001). In 2006 a centre for increased knowledge of environmental aspects of pesticides under Swedish conditions was established at SLU/Uppsala (*Centre for Chemical Pesticides*, CKB). Among the clearly expressed purposes of this Centre (Miljötrender, 2006) was the build-up of the knowledge in this field, and to promote development of the research about the properties and behaviour of pesticides in the environment. In line with this, also some of the statements in the survey "*Hållbar användning av växtskyddsmedel – förslag till handlingsprogram*" (Jordbruksverket, 2008) might be seen, particularly those in section 11.2.1 (*ibid.*), concerning the need for more basic research in this field. Considerable knowledge concerning environmental aspects of pesticides already exists at SLU, e.g. occurrence of pesticides in rain water, surface- and ground water, leaching into the soil and spray drift. According to our knowledge, however, no field studies of volatilization and dry deposition of pesticides have been performed (and published) in Sweden so far. In a study dealing with risk assessments in connection with pesticide use, Swedish farmers considered spray drift at application of herbicides (pesticides) to be a major risk factor in this context (Sjöberg et al., 2005). At the same time, there are some indications from both model and field studies that volatilization and subsequent dry deposition in the nearby area of the field may be of significantly larger proportions than deposition due to spray drift (Asman et al., 2003). Likewise, field studies of herbicide runoff and volatilization losses indicate that even for pesticides with comparatively low vapour pressures volatilization losses may be significantly greater than runoff losses (Gish *et al.* 2010). Contradictory statements like these mentioned points to an obvious need for research about the relative importance of the volatilization process and subsequent dry deposition of pesticides, especially under Swedish climate conditions.

In order to enhance our knowledge Tommy Arvidsson initiated this project in 2007. With Henrik Kylin as main applicant the project received funding from The Swedish Research Council Formas and a field experiment was set up in 2008. Results of volatilization and dry deposition of pesticides under field conditions during three consecutive years (2008-2010) were obtained. Due to staff turnover in 2011 the main responsibility for the project was transferred to Jenny Kreuger (previously co-applicant) and Stig Karlsson (PhD in meteorology and project collaborator since the start of the project) was given the task of data processing and reporting the results of the project. The present report marks the end of this project.

Summary

Volatilization of pesticides after application may be an important transport pathway for pesticides entering into the environment. To our knowledge very few field investigations on this subject have been performed within the Nordic countries and none before under Swedish climatic conditions.

In this report results from a field experiment on volatilization and dry deposition of pesticides are presented. During the years 2008-2010 three summer campaigns – in June 2008, and July 2009 and 2010, respectively – with growing crops (either winter wheat or barley, varying in height between 70 and 90 cm between the three years), and three with bare soil conditions (in September each year) were undertaken at the agricultural experimental site at Funbo-Lövsta; a rural site about 9 km east of Uppsala (Sweden), with large open fields and relatively homogeneous fetch in most directions.

Two masts of 16-m height each were erected about 10 m apart, one for meteorological measurements and the other, foldable, for air sampling. Wind speed was measured at 6 or 7 levels, and air samples for subsequent analysis at roughly the same levels. Also temperature, solar radiation and other meteorological parameters were recorded and stored using a data logger.

The air samples were taken by a high-volume pump system and PUF collectors, which were connected to the pump system via flow rate meters for each of them. The PUF samplers were shifted with varying time intervals, shorter (ca 3 hrs) close after a treatment and longer (up to several days) further into a campaign.

A tank mixture of several pesticides was applied with a tractor sprayer over a circular plot of 54 m radius with the air sampling mast at the centre. An inner circular area with radius of 18 m next to the measuring masts was left untreated. The pesticides were selected to represent both a variety of different usage types (herbicides, fungicides and insecticides) as well as different physico-chemical properties, in particular their vapour pressure. Thus, during 2008 the following pesticides were used (product name given within parenthesis): pirimicarb (*Pirimor*), prosulfocarb (*Boxer*), fenpropimorph (*Forbel*) and pendimethalin (*Stomp*). During 2009-2010 lindane and tolclofos-methyl (*Rizolex*) were added to the mixture.

The volatilization fluxes and source strengths of each pesticide under varying surface and weather conditions were determined according to the integrated horizontal flux (IHF) method. Also dry deposition was sampled downwind of the sprayed area with passive samplers, i.e. Petri dishes (10 by 10 cm in size) filled with dry soil, up to a maximum distance of 200 m downwind. This deposition sampling was performed during the campaigns in 2008 and 2009.

Under summer conditions, with volatilization from standing crops, the accumulated horizontal flux, expressed as percentages of the applied dose, varied considerably

between the investigated substances as well as between years. Thus, this flux was found to be least for fenpropimorph (scarcely 7% during the first 48 hrs in July 2009) and largest for lindane and prosulfocarb (about 58% for lindane in July 2009, and just above 60% for both lindane and prosulfocarb in July 2010, all of them after the first 48 hrs after the spraying). The variation between the years – still using the first 48 hrs as the time span, and the years 2009 and 2010 as the example (the experiment in 2008 being of shorter duration) – frequently amounted to a factor 2 (and almost a factor 4 in the case of fenpropimorph, and much less for lindane): e.g. pirimicarb: 12% in July 2009 and 26% in July 2010; pendimethalin: 25% (July-09) and 53% (July-10) but fenpropimorph: ~7% (July-09) and 26% (July-10). It was also apparent, that the very major part of the total volatilization often occurred during the first 3-6 hrs after treatment.

The volatilization fluxes from bare soil (the September campaigns) showed considerably less accumulated sums than during the summer conditions, but again with significant differences between substances and years. And like the summer cases, fenpropimorph and pirimicarb showed the least fluxes (with only 0.05% and 0.12% of the applied doses, respectively during the first 48 hrs in September 2009) compared with 10-11% for lindane the same year). The differences between the years varied markedly between the 6 substances. Thus, whereas the accumulated flux during the first 48 hrs was twice as large in September 2010 compared with Sept.-09 (21% vs. ~10%) for lindane, and a factor 3-4 greater in 2010 compared with 2009 for tolclfos-methyl, prosulfocarb and pendimethalin, it was more than 8 times greater in the case of pirimicarb (1.0% in 2010 vs. 0.12% in 2009). Differences between the two years may be explained by the markedly different soil moisture and rainfall conditions these years.

Contrary to the summer experiments, it was not the case during the autumn campaigns that the accumulated flux tended to level out already within the first 6 to 12 hrs after treatment. On the contrary, in many cases there was a clear increase in the flux rate towards the later parts of the sampling, assumed to be a consequence of changed (increased) soil moisture content.

Also dry deposition in the nearby area, mostly up to a downwind distance of 100 m from the treated circular area, but in September 2009 up to a distance of 200 m, was sampled. During the summer campaigns, the first sampling period, covered the first 26 hrs from treatment, both in 2008 and 2009. In 2009 also a second period, including the hours 27 to 48 from start, was sampled.

During the first 26 hr period in both years, the accumulated dry deposition, expressed as per mills of the applied dose per m^2, ranged from 0.1-0.5 (fenpropimorph) to 1.4 - 1.7 ‰ (pendimethalin) at 10 m downwind. At 100 m distance the corresponding deposition were about 1/10 of these values. The deposition during the second period (27-48 hrs) in July 2009 at the 10 m distance varied from 0.03 ‰ (fenpropimorph) to 1 ‰ (pendimethalin), and at 100 m about one tenth of these values (except for fenpropimorph and lindane, for which this quotient were higher).

The sampling during period 1 (0-27 hrs) in September 2008 showed very low deposition, at most 0.2 ‰ at 10 m. During the first period (0-24 hrs) in September 2009, the sampled deposition varied from 0.2 – 0.3 (prosulfocarb and fenpropimorph) to 5 ‰ (lindane) at the 10 m distance, and with detectable amounts also at 200 m, generally about 1/10 or less of those at 10m in magnitude (e.g. 0.02 for fenpropimorph and 0.2 ‰ for lindane). In the last sampling period, extending from 49 to 96 hrs after treatment, sizeable amounts of all substances except prosulfocarb were deposited at the 10 m distance: 1-2 ‰ for lindane and pendimethalin (and possibly slightly over that in the case of pirimicarb). At 200 m most substances were not detectable, but pendimethalin showed the same amount (1.4 ‰) as at 10 m distance.

It was emphasized, however, that deposition measurements like this are very site specific and highly dependent on the areal lay-out and its dimensions vis-à-vis the location of the sampling spots.

1 Introduction

Literature review

After field application, pesticides enter various environmental compartments: e.g. the ground- and surface waters, soil, plants, pristine areas and the atmosphere. Their occurrence in the atmosphere may mainly be the result of drift during application or, subsequently, volatilization from soil, plants or surface water and by wind erosion. Volatilization is the physico-chemical process by which a compound is transferred to the gas phase. It is the result of evaporation from a liquid phase or sublimation from a solid phase. In this context it represents the total outcome of all the processes leading to the transfer from soil or plant compartments into the atmosphere.

It has been shown by many authors that volatilization from plants may be significantly higher than from soil, especially because of the limited sorption sites and uptake rates of the leaves. Volatilization is governed by a combination of several factors who, in many cases, interacts with each other, such as:

1. Compound characteristics: Vapour pressure, water solubility, K_{ow} (the octanol/water partioning coefficient), Henry's constant, K_{oc} (coefficient for the adsorption readiness to organic carbon), molecular mass, chemical nature and reactivity are important parameters governing volatilization. Additionally, the degradation rate on plant surfaces (photolytic stability) and the possibility for uptake into leaves influence volatilization.
2. Meteorological conditions: Rainfall after application leads to wash off of applied substances from plant surfaces but increases the moist content of the topsoil. Volatilization is generally higher from a moist soil surface compared to a dry. Air temperature enhances volatilization as does wind speed and turbulence. Solar radiation influences photo degradation.
3. Soil properties: water content, soil temperature, soil density, content of organic matter, clay content, soil texture, pH.
4. Agricultural practices: Application rate and method, formulation of the pesticide mixture and soil management may influence volatilization (Bedos et al., 2002 a; FOCUS, 2006; Van den Berg et al., 1999).

Monitoring of pesticides in atmospheric wet deposition in Sweden was initiated in 2002 as a part of the national pesticide monitoring programme and is performed by the Swedish University of Agricultural Sciences. The overall aim of the on-going monitoring program is to get an overview of potentially harmful substances, such as pesticides, deposited in a pristine area in the south of Sweden (Vavihill), including long-range atmospheric transport of pesticides to Sweden. Summarising data from four years (2002 -2005) 28 substances were found in more than 20% of the samples. Twelve of these substances were not registered for use in Sweden at that time. The highest numbers of substances in rainfall were detected in May during all years (Kreuger et al., 2006).

In a study performed in Germany the volatilization of a large number of different pesticides (80) from soil and plants was evaluated. The study was performed under controlled conditions (laboratory and/or greenhouse) during 24 h. The volatile losses from soil and crop surfaces ranged widely from 0% to 87%. The majority of measurements showed less than 10% loss (85% of all soil measurements and 56% of all crop measurements). The data were, among other aspects, analysed to determine whether a correlation existed between volatilization and the physico-chemical characteristics of the substances. It was concluded that the vapour pressure of a substance (pesticide) is the best predictor of losses from soil and crops. They further concluded that there in general is no volatilization from bare soil if the vapour pressure is less than 1 mPa and not from vegetation if it is less than 0,1 mPa (Guth et al., 2004).

Most studies on volatilization and dry deposition of pesticides during the last decades have been performed in North America and Western Europe. These studies have been done under different conditions and using quite different methods, which make comparisons and generalisations of the varying results difficult (Bedos et al., 2002 a).

For investigation of volatilization of pesticides from arable land a number of different approaches and techniques may be used, among them laboratory studies, semi-field systems (e.g. wind tunnel and evaporation chamber studies), micrometeorological methods (e.g. the aerodynamic-profile method (APM) and the eddy accumulation method) and residue analysis. Several of these methods require relatively large and fairly homogeneous treated areas upwind the measuring site to give reliable results, e.g. the APM-method. Others, as the residue analysis, cannot distinguish between losses of a pesticide due to volatilization and degradation, respectively (Majewski, 1999; Bedos et al., 2002 a; Van den Berg et al., 1999). The method selected for the present study relies on the integrated horizontal flux method (IHF), (Majewski, 1999). The essential principle of IHF is to simultaneously measure the vertical profiles of concentration and wind speed, respectively, and then integrate the (time averaged) product of these two over a sufficient height interval, since this product express the average horizontal flux at each height of a substance – in this case a pesticide in the gas phase – which is carried (passively) by the wind. By subsequent integration of these fluxes from a level close to the surface up to a height in the vertical "window" where concentrations are negligible (or not deviates from a possible background concentration), the total flux of each volatilized pesticide during the given sampling period is given. This integral also gives an estimate of the rate of emission of a pesticide per unit area and unit time from the treated area, i.e. the average source strength per unit area (e.g. µg/s m^2) of a pesticide under prevailing conditions.

The necessary upper level for the air samplers is determined by the height to which the internal boundary layer (here in practice corresponding to the "plume" of gaseous pesticides) has reached during the wind transport from the outer border in the upwind direction (the "leading edge") to the measuring mast. The development of this internal boundary layer (IBL) is determined by the atmospheric stability, wind speed and the aerodynamic roughness of the underlying surface. The height of this layer at the mast position can be estimated as a function of the distance from the leading edge of the new surface (i.e. the surface treated with pesticides in this case) and knowledge of the surface roughness of the "new" surface and the atmospheric stability.

The growth of such an IBL (where steady state conditions concerning the vertical profiles of both meteorological parameters and concentration profiles of “passive” constituents in the air - such as a gas - with respect to the new upwind fetch conditions has been established), is considerably faster under unstable compared to stable atmospheric stability conditions. However, from the layout of our study, with a comparatively short fetch (54 m) from the upwind leading edge and based on experiences from other studies (e.g. Denmead, 1995, Andersen et al., 2006), we estimated that the very major part (~90-95 %) of the horizontal flux (per unit width) of the volatilized pesticides will pass through the vertical plane of unit width (the “measuring window”) below 16 m (i.e. the height of the mast supporting the air samplers). (In reality, as will be shown later, it became evident during the analysis, that in quite a number of all cases with unstable stratification, the horizontal flow was not negligible above the 16-m level). These circumstances thus imply that a relatively small area for application of pesticides may be used in the trials which, in turn, imply that the time between the application and the taking of the first air samples may be relatively short. This is of great importance since a study by Bedos et al. (2002 b) has shown that the largest evaporative flux occurs shortly after application and then decreases exponentially with time. This is a significant advantage of the IHF-method, compared with e.g. the aerodynamic profile method (APM); but still the IHF-method requires fairly homogeneous upwind fetch conditions and similar roughness structure over a larger area than the treated one. Another advantage of the IHF-method compared with the APM is, that it don’t require any questionable assumptions about the magnitude of the turbulent exchange (diffusivity) coefficients for pesticides under different stability conditions.

The accuracy of the final result by using the IHF method depends partly on the accuracy of the chemical analysis, and of the accuracy in the measurements of wind speed and concentration profiles, respectively, and on the fact that these profiles reach a sufficient height as to encompass the major part of the fluxes through the vertical ”window” of measurement.

Objective of the present study

- to understand the role of volatilization and subsequent dry deposition of pesticides in the contamination of the environment from Swedish agricultural practises
- to aid the development of recommendations to farmers on agricultural practises that minimize environmental problems
- to provide Swedish environmental authorities with knowledge and data for the development of policies, nationally and internationally, and in their establishing of new criteria for the approval of new pesticides on the Swedish market

2 Material and methods

2.1 Experimental design

In the first year of experiments a tank mixture of 5 selected pesticides and a fluorescent dye was applied with a conventional hydraulic field sprayer with low drift nozzles (*Hardy 03*). A 36 m wide circular area centred around the position of an air sampling mast was sprayed, but leaving an inner area with 18 m radius next to this mast untreated. With the purpose of achieving an as evenly spaced distribution as possible of the pesticides over the treated plot, the following strategy was used. The first four swaths (beginning at the inner rim) was sprayed using a 3- m wide section of the boom (thus covering an innermost 12 m wide circular section of the treated area). For the next two swaths a 6-m section of the spray boom was used, thus adding a further 12 m of treated circular area outside the first, and finally, for the outermost 12 m wide section, the full boom width of 12 m was used, thus ending up with a 36 m wide treated circular area around an inner, 36 m in diameter, untreated area next to the measuring masts (thus, the total distance from the leading edge of treated area to the air-sampling mast was 54 m, see figure 2.1). The individual pesticides included in the tank mix were added according to the recommended dosages. In the centre of the inner, untreated circular area were two measuring masts, 16 m in height, mounted; one for the air sampling equipment and one for the meteorological measurements. Determination of the applied dosages was intended to be done by sampling of the applied spray liquid on filter papers; witch included a fluorescent dye, for further analysis on a photofluorometer. The filter papers were placed in a sufficient number in the sprayed area and in a pattern as to properly represent the treated area, at 10 cm height above soil surface or 10 cm above the top of the crop, respectively. However the recovery of the fluorescent dye deposited on the filter papers was fairly low, about 60-70% of the intended field dose, and not regarded as reliable.

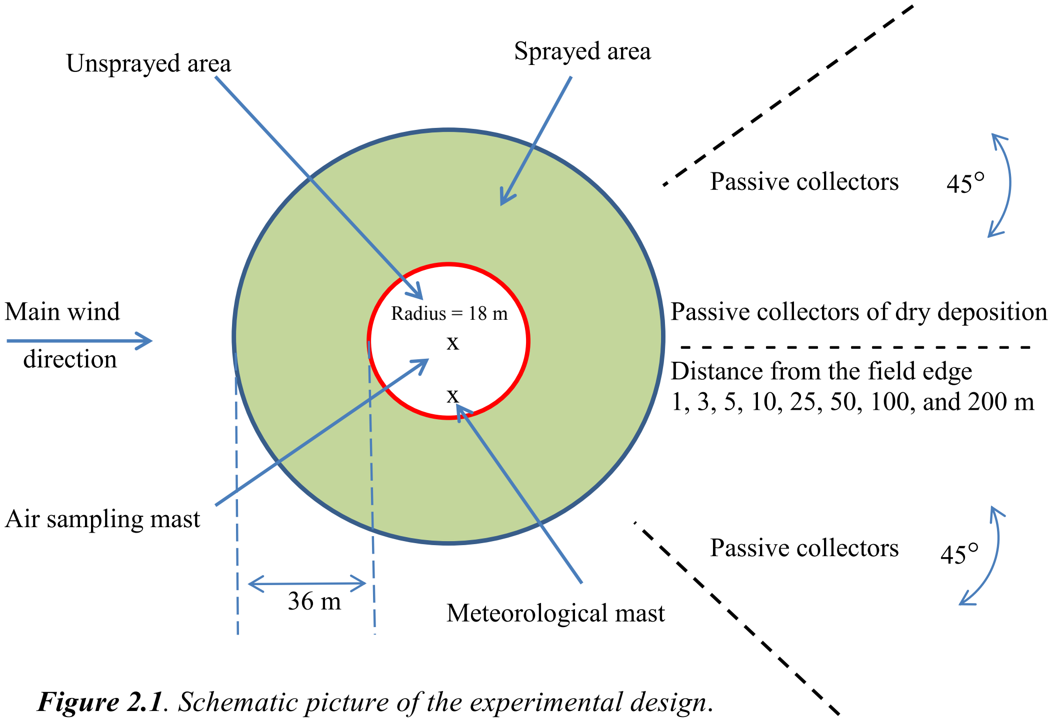

Figure 2.1. *Schematic picture of the experimental design.*

2.2 Meteorological instruments

Wind speed sensors: A100LM / PC3 Vector low power cup anemometers, with pulse output, were used. Starting speed about 0.2 ms^{-1}, stopping speed 0.1 ms^{-1} and with an accuracy stated to be 1% of reading. Measurement heights: 0.35, 0.65, 1, 2, 4, 8 and 16 m (0.35m not used during the summer campaigns).
Wind direction vane: W200P Vector potentiometer wind vane. Threshold value was 0.6 ms^{-1} and the accuracy 3% of reading. Measurement height: ~2 m
Solar radiation: Li-Cor 200SZ pyranometer for global (solar) radiation (at 2m height).
Rotronic MP100A sensor, with radiation shield, was used for measurement of the *relative humidity* (also giving a "secondary" 2-m temperature reading). Measurement height: 2 m
Thermo couples (Cu-constantan-Cu) with ventilated radiation shields, located at the differential heights of 0.15-2 m and 2-16 m above the ground, were used to measure the *air temperature* differences between these heights. A thermo couple was also used for measurement of the soil temperature at a depth of about 5 cm.
An IRTS-P *infrared sensor* was used for measurement of the *surface temperature* (i.e. at the upper parts of the vegetation or at the bare soil surface, respectively, depending on season). Measurement height: ~2 m.
A *pluviometer* of tipping-bucket type, of the model "Mjk professional", with a threshold value of 0.2 mm, was used for precipitation measurement. Measurement height: 2 m

2.3 Samplers of pesticides

During the first year of experiments the evaporated pesticides were sampled by sucking air through a cylindrical sandwich of PUF (polyurethane foam), XAD-4 (polymer resin), and a second PUF. The diameter of the PUF was 7 cm and each 4 cm in length. Cleaned PUF and XAD-4 were placed in a plastic bottle (HDPE) with the bottom cut off. The air flow rate through the air samples was approximately 200 L min^{-1}. During experimental year two and three the air samplers consisted only of two PUF´s arranged in series (this latter arrangement was decided since the chemical analyses of the first year air samples showed more or less negligible amounts of the pesticides in the XAD-resin).
Air was drawn through the different air samplers (PUF- sandwiches) by two electrical pumps via a large cylinder (ca 1.6 m in length and 0.3 m in diameter) as to, as far as possible, equalize the strength of the airflow between the eight "outlets" to which the different air hoses were mounted. A background air sampler was located 100 m upwind the first year. The last two years the background sampler was located about 1000 m away from the treated area, with a separate pump.
Passive soil samplers were used to measure dry deposition of pesticides. The samplers consisted of square-shaped petri dishes made of rigid plastic, about 10 cm * 10 cm * 1 cm in size. About 2 mm of the top soil in these dishes was later removed for chemical analysis.

The dry deposition on soil, downwind of the treated area, was measured at different distances from the outer edge (1, 5, 10, 25, 50, 100 and 200 m) and in three directions from the centre of the treated area (see figure 2.1.). With this configuration where two of the sampling paths deviate with 45° angle from the estimated main wind directions, determination of the dry deposition will be possible also in cases of moderate fluctuations of wind direction during the course of a trial. Passive samplers were also located inside the unsprayed inner circle. (The air sampling, on the contrary, was independent of the wind direction due to the experimental lay-out, with the treated circular area uniformly surrounding the measuring mast.

Table 1. The intended samplings intervals for measurements of volatilization and dry deposition are described below

Hours after application	Air samples: time intervals	Dry deposition: time intervals
3	0-3 h	
6	3-6 h	0-6 h
24	6-24 h	6-24 h (only 0-24 h the first year)
48	24-48 h*)	24-48 h
96	48-96 h*)	48-96 h
192	96-192 h*)	

*) = were not performed during experimental year 1 (2008). In 2010, the last sampling interval was extended to 203 hrs in July and to 232 hrs in September, respectively.

When collecting the passive deposition samplers at the specified times these samplers were replaced in new directions according to the prevailing wind direction at these times.

The pesticides selected for the study the first year were: fenpropimorph (F), fluazinam (F), pendimethalin (H), pirimicarb (I) and prosulfocarb (H), (H = herbicide, F = fungicide, I = insecticide). The selected pesticides were selected as to represent active substances with different physico-chemical characteristics with respect to vapour pressure, Henrys constant, lipophility (K_{ow}-value) and adsorption potential to soil organic carbon (K_{oc}), and at the same time representing some of the most common types of pesticides used in Swedish agriculture practise (Kemikalieinspektionen, 2006). Three of them are among those pesticides frequently found in rainwater samples in southern Sweden (Kreuger et al., 2006). The pesticides selected for year two and three were: fenpropimorph (F), tolclofos-methyl (F), pendimethalin (H), pirimicarb (I) prosulfocarb (H) and lindane (I). (Fluazinam was excluded after the first year due to difficulties connected to the chemical analysis.)

2.4 Measurement and control system

The airflow through the air samplers was measured by a thermic mass flow meter, FCI ST75-AB1DH00, FCI Fluid Components International LCC. Eight such mass flow meters were used, seven of them corresponding to the seven air-sampling heights in the sampling mast and one for the background sampler (the first year). Two light-weight aluminium masts, 16 m in height, one for the meteorological measurements and one of a folding type, for the air sampling equipment, were raised about 10 m apart.
A Campbell CR1000 data logger, Campbell Scientific Inc., equipped with an AM 16/32B relay analogue multiplexer and a SDM-INT8, 8-channel interval timer (pulse counter) was used for the data collection

2.5 Chemical analysis

Air and soil samples were transferred to the lab the same day, followed by storage at either 4 °C (air samples year 1) or at -18 °C (soil samples and air samples year 2 and 3). Chemical analytes included fenpropimorph, fluazinam (year 1), lindane (year 2 and 3), pendimethalin, pirimicarb, prosulfocarb and tolclofos-methyl (year 2 and 3). However, analysis of fluazinam did not give results with the required precision and was therefore omitted from the report.

Soil samples

About 2 mm of the topsoil in the petri dishes was gently collected, of which a sub-sample (4 g) was mixed with a drying agent (2 g). The mixture was placed in a pre-cleaned (400 °C) glass fibre cartridge and extracted together with the internal standards ethion and terbuthylazin-D5 by a Soxtec Avanti 2050 Auto System using dichloromethane and acetone (1:1) for ca 3 hours. The extract was evaporated and diluted in cyclohexane and acetone (9:1), where after they were injected on a GC-MS System (Agilent Technologies GC 7890, MS 5975C) quantifying against an external standard calibration. The standards used were obtained from Dr Ehrenstorfer GmbH.

Air samples

Each PUF was cut into smaller pieces to fit into 3 separate glass fibre cartridges pre-cleaned at 400 °C and with the internal standards ethion and terbuthylazin-D5 added. Extraction was performed using a Soxtec Avanti 2050 System with dichloromethane and acetone (1:1) during the first year and only dichloromethane during the following years. Subsequent treatment of the extracts (merged into one extract per sample) and analysis was performed in the same way as for the soil samples.

2.6 Calculation procedures for determining vaporization fluxes

The concentration of an evaporating substance is generally found to decrease exponentially with height in the air according to the functional form ln(c) = az + b where c is concentration in air and z is the vertical height (with z = 0 at the surface), i.e. ln(c) is supposed to be a linear function of height z. Thus, through linear regression of ln(c) on height z, concentration equations are fitted to measured concentrations for each substance and measuring period. Two examples are shown in Figs. 2.2a-b below.

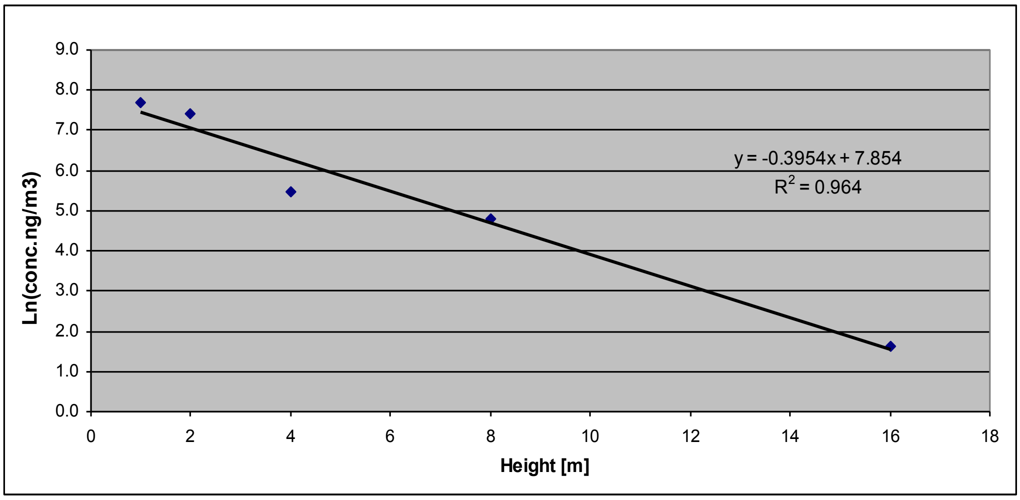

***Fig. 2.2 a.** Regression determined concentration equation for **prosulfocarb** for sampling period 2 (21:30 24/6 – 9:30 25/6), June 2008 (dots indicate the measured, time averaged concentrations).*

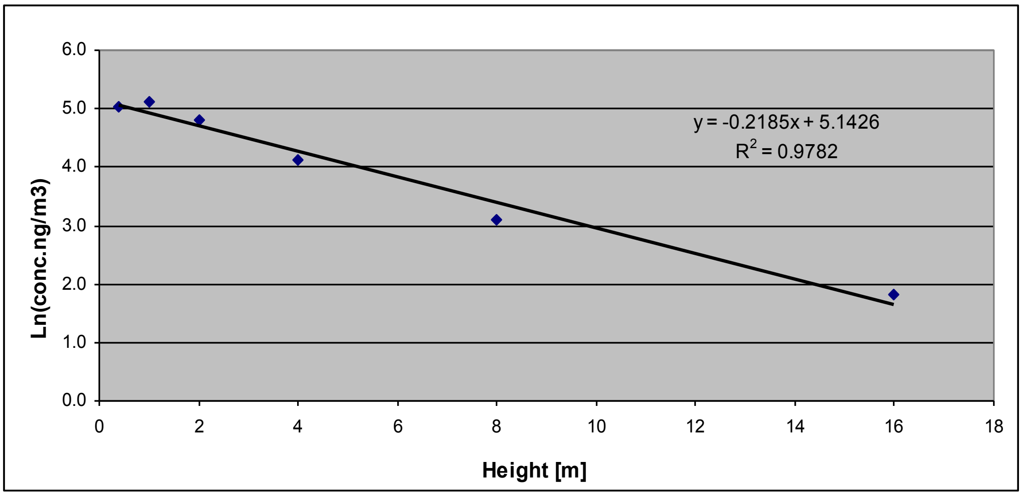

***Fig. 2.2 b**. Regression determined concentration equation for **pirimicarb** for sampling period 1 (8/9 12:20 – 15:16), Sept. 2010 (dots indicate the measured, time averaged concentrations).*

In many cases, however, the linear fit to the determined concentrations are less good than in the examples shown above. Either one ore more of the concentrations

at the lower levels (mostly values from within the height interval 0.25-1 m) deviate towards lower than expected values. This might well have been caused by a disturbance (at least for some "unfavourable" wind directions during the campaigns in 2008 and 2009) on the wind field in lower levels by a nearby located trailer, which hosted parts of the air suction system, and reached about 0.8-0.9 m above ground surface. (This trailer was moved away from the immediate vicinity of the mast supporting the air sampling probes, and partially also buried into the ground, before the campaigns during 2010.)
Another type of deviation from the expected log-linear course of the concentration line, which appeared quite frequently, is when concentrations at the upper levels not decrease as rapid as expected, chiefly at the 16-m level but sometimes appearing also at 8 m and then perhaps starting at even lower levels. Some examples of this behaviour can be seen in Figs. 2.3 below.

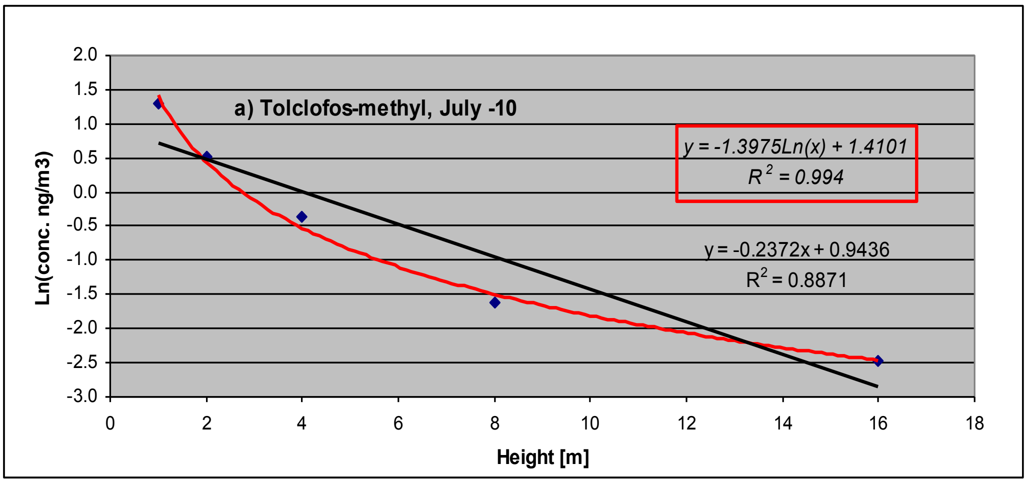

Fig. 2.3a. *One examples of concentration profiles where an equation of the type Ln(c) = f(ln(z)) gives a better representation of the profile shape (filled dots are measured conc.). Tolclofos-methyl (1-16m); period 7 (144-203hr after treatment), July 2010*

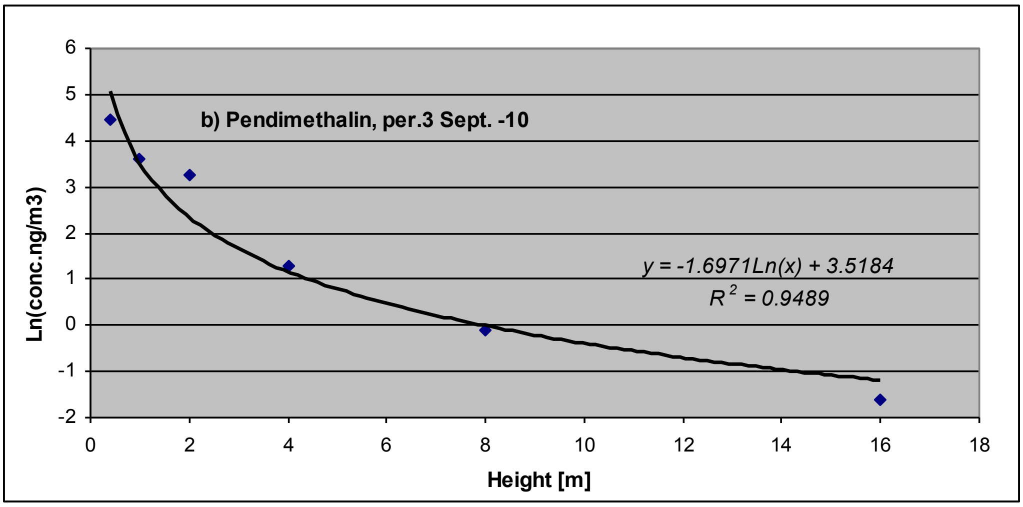

Fig. 2.3b. *A second example of concentration profiles where an equation of the type Ln(c) = f(ln(z)) gives a better representation of the profile shape (filled dots are measured conc.). Pendimethalin (0.4-16m); period 3 (8/9 18:16- 9/9 12:06), Sept. 2010.*

In those cases, an equation of the type ***Ln(c) = aln(z)+b*** evidently gives a better apparent fit in general to the measured concentrations than the anticipated, exponential, form: ***Ln(c) =az+b*** otherwise regularly used (c is the period mean of concentration and z is height above the soil surface as before). And, finally, there are a number of cases where one ore more of the data points in a concentration profile behaves even more irregularly, with e.g. C(16m) > C(8m) or C(4m) ≥ C(2m) etc. (where C(z m) is the measured concentration at height z m). Here, one may suspect, for example, a mix-up between height levels at the labelling of the sample probes or confusion of actual heights during the chemical analysis.
Such circumstances, briefly outlined above, have made it more or less tempting to try alternative equations describing the concentration profile in many cases, for one and the same substance and sampling period. This will thus lead to more than one possible estimate on the total vaporization flux and coupled source strength, respectively. This way of analysis may appear indecisive, but will at the same time give some apprehension of the uncertainties involved in the calculation procedure used.

The total, average horizontal flux Q of a substance across a vertical plane of unit width on the downwind side of the treated area is, according to the i*ntegrated horizontal flux* (IHF) method, given by integrating the product the time averaged product of the instantaneous concentration c(z) – given by the profile equations determined as discussed above – and the instantaneous horizontal wind speed u(z) at the same height:

$$Q = \int_0^z \overline{uc}\,\mathrm{dz} \qquad [\mu\mathrm{g\ s^{-1}m^{-1}}] \qquad (1a)$$

Here, and in the following, the overbar denotes a time average, and height dependent variables such as u(z), c(z) and u′(z) etc are written without the z for convenience.
The corresponding average surface flux density ($\overline{F}$) – the source strength of the emitting surface per unit area – is determined by:

$$\overline{F} = \frac{1}{X}\int_0^z \overline{uc}\,\mathrm{dz} \quad [\mu\mathrm{g\ s^{-1}m^{-2}}] \qquad (1b)$$

where X is the distance from the leading edge of the emitting area to its downwind end along the direction of the wind (in the present case = 36 m).

If we regard the instantaneous wind speeds u(z) and concentrations c(z) as sums of their respective time averages ($\overline{u}$ and $\overline{c}$) and an instantaneous departure, denoted by a prime, from the average: u = $\overline{u} + u'$ and c = $\overline{c} + c'$, this expression may be expanded to:

$$\overline{F} = \frac{1}{X}\int_0^z \left(\overline{u}\,\overline{c} + \overline{u'c'}\right)\mathrm{dz} \qquad (1c)$$

The first term on the right ($\overline{u}\,\overline{c}$) is the advective horizontal flux due to the mean wind, and the second term ($\overline{u'c'}$) denotes the turbulent horizontal diffusion which in the present case is a backward flow in the *upstream* direction. This latter term is often considered very small in comparison with the mean advective flow, and is therefore frequently neglected, especially since this term is difficult (if even possible) to actually measure (e.g. Majewski, M.S.,1999; Wilson, J.D. et al, 1983). However, several comparative field tests and also theoretical considerations suggest that neglecting the turbulent diffusive flux may lead to an overestimation of the true flux. Thus, for example Desjardins et al.(2004) found an overestimation by 5% by the IHF method when substituting $\overline{uc}$ with $\overline{u}\,\overline{c}$ (and neglecting $\overline{u'c'}$), Leuning et al.(1985) claimed that this overestimation was probably less than 15%, and Wilson and Shum (1992) calculates this overestimation, using a Lagrangian stochastic model, for different plot radii (R) and roughness lengths (z_0). At a plot radius R= 50m and a z_0 = 0.01m (i.e. roughly similar to our September campaign conditions) they estimate the overestimation (which is stability dependent) to vary from near zero in very stable stratification to about 4% in very unstable conditions. At the same radius but with z_0 = 0.1m (fairly similar to our summer conditions) the corresponding estimates goes from 9 % under very stable conditions, to about 16 % under very unstable.
In all flux calculations in the present report we have *not* applied any corrections for this possible overestimation of the "true" flux, which should be kept in mind when comparing our results, "internally" or with other studies.

Further, the integration is in practice accomplished by a summation over a number of sufficiently small height intervals Δz_i :

$$\overline{F} = \frac{1}{X}\int_0^z (\overline{u}\,\overline{c} + \overline{u'c'})\, \mathrm{dz} \approx \frac{1}{X}\int_o^z \overline{u}\,\overline{c}\ \mathrm{dz} \approx \frac{1}{X}\sum_{i=1}^{N} \overline{u}\,\overline{c}\,\Delta \mathrm{z_i} \tag{1d}$$

where the summation should be carried out from the surface, z =0, (or the lowest practical height for taking measurements) and up to a sufficient height where the concentration has dropped to zero (or to background levels if any). In the present study we have used the summation form of the equation with summation steps Δz =10 cm, regularly up to z =16 m (the height of the sampling mast) but with extensions to considerably higher levels (occasionally to 32 m) when necessary, as it turned out to be in many cases where the horizontal flux at the height of 16 m was far from negligible (sometimes of the order 5-10 % of the flux at the peak flux-level).
The proper upper limit for the integration is determined by the assumed height of the new internal boundary layer (IBL) that grows in the downwind direction from the upwind (leading) edge of the treated area. This issue is discussed further in Chap. 5.

For describing the vertical wind profile – thereby giving the necessary wind speed along the vertical integration in Eq. (1c) – we use the logarithmic wind law in its simple form, that is, without any stability dependent terms. This form of the equation is evolved for neutral atmospheric stratification, but as was evident both from this study and elsewhere (e.g. *Karlsson, S., 1986*) – and for the present purpose – it obviously works fairly well also under other stability conditions if not strongly deviating from the neutral case):

$$\bar{U} = u_*/k \cdot \ln[(z-d)/z_o] \quad [\mathrm{m/s}] \qquad (2)$$

Here, ū is the mean wind speed at height z, u_* is the *friction velocity* [m/s], a "scaling" parameter which depends on the turbulence intensity in the atmospheric surface layer, k is von Kármán´s constant (≈ 0.40), z_o is the *roughness length* [m], expressing the aerodynamic friction at the particular surface, and d is *the displacement height* (m). The latter takes care of the "zero plane" displacement when the logarithmic wind expression is used over a rough surface, where the roughness elements of the surface, e.g. tall grass, crops or trees, are sufficiently high as to displace the z-plane (where the wind approaches zero) away from the ground surface (z =0) to some higher level. There are numerous ways described in the literature, more or less elaborated how to determine the magnitude of both z_o and d in each actual case. The most simple among these are some rule of thumbs relating z_o and d to the average height of the roughness elements (h). Thus, values for z_o in the range 0.1h – 0.13h and for d in the range 0.6h -0.75h are commonly suggested (based on numerous measurements of wind speed over surfaces with very varying roughness). For our purposes, different values of d in the vicinity of d= 0.6h to 0.7h were tested with linear regression of $\bar{u}$ (z_i) against ln(z_i - d) where $\bar{u}$ (z_i) is the mean wind speed at level z_i for each measuring(sampling) period, thereby searching the best linear fit. Values of u_* and z_o will thereby be given by the resulting equation of the type $\bar{u}$ (z_i) =a· ln(z-d) + b, where a (= the slope of the line) gives u_*/k and b stands for – $(u_*/k)\cdot\ln(z_o)$ and thereby giving z_o. (This is evident from the following extension of Eq. (3): $\bar{u}(z) = u_*/k \ln(z-d) - u_*/k\cdot \ln z_o$.) Thereby it was found that a d-value = 0.45 m mostly gave a good fit for the summer wind profiles in 2009 and 2010, whereas d= 0.25 m gave a better fit to the summer profiles of 2008. These d-values may seem slightly low, according to the mentioned rules of thumb, since the average crop height in our case varied between 0.70 and 0.90 m during the experimental years, with the higher value (h= 0.9m) in July 2010. However, also other factors such as vegetation density (e.g."leaf area density") are of importance in this respect. For the autumn experiments, with bare ground, d was taken as 0.

Below, two examples of wind profile equations determined in the way described above are shown, one from a summer period (period 3, June 2008, which is a daytime period with a Ri_B(16-0.15m) = -0.087, i.e. fairly unstable stratification; d=0.25 m, z_o =0.107 m) and one from an autumn period (period 4, Sept. 2010, which is a ~24-hr period with an over all Ri_B(16-0.15m) = 0.80 and daytime Ri_B = -0.02, thus going from slightly unstable conditions during daytime hours to very stable during the night time part; d=0, z_o =0.0079 m). The in this way implied z_o values are also in fair agreement with common rules of thumb and reported values in the literature.

However, the logarithmic wind law is not valid below the top of the roughness elements. Therefore, for the summer periods, with a standing crop of wheat of average height 70 to 90 cm, a constant wind speed equal to the calculated (average) friction velocity (u_*) for the respective period was assigned to height levels below this height.

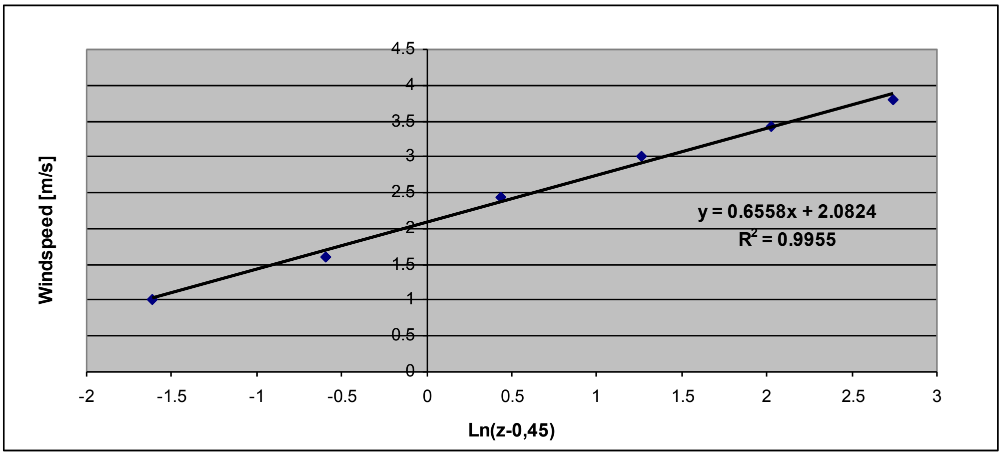

Fig. 2.4a. *The logarithmic wind profile equation (u(z) =0.6558ln(z-0.45)+2.0824) determined for sampling period 1, July 2009 (4/7 10:30-14:30); d=0.45 m (zo=0.042 m);* Ri_B *= -0.16. (Filled dots represent measured wind speeds.)*

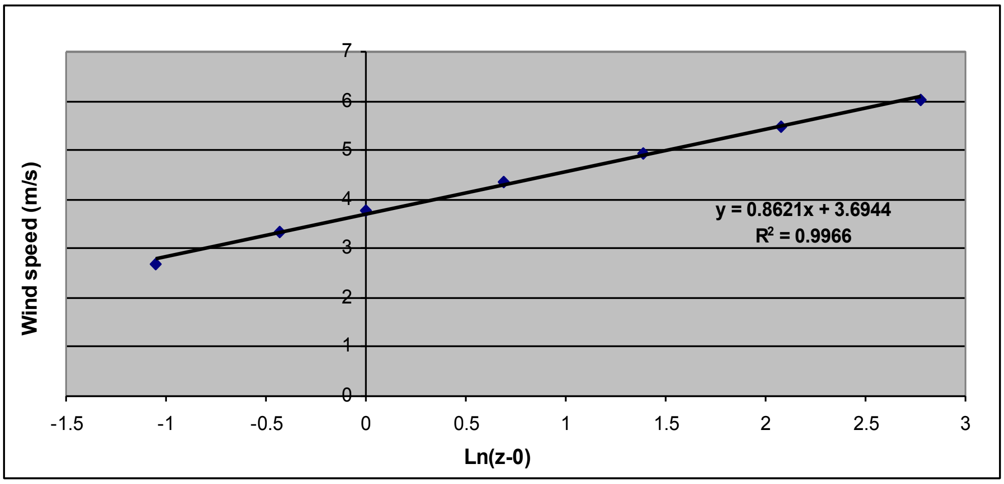

Fig. 2.4b. *The logarithmic wind profile equation (u(z) =0.862ln(z)+3.694) determined for sampling period 6, Sept. 2009 (22/9 12:30-26/9 12:20); d=0 m,* Ri_B *(whole per.) =0.087,* Ri_B *(night: 55 hrs)= 0.15,* Ri_B *(daytime: ~38 hrs)= -0.008.*

Though occasionally there were periods with slightly less good linear fit of the determined wind equation to measured wind speeds, even in periods with either pronounced unstable stratification, $Ri<0$ (as in the case of Fig. 2.4a) or an overall stable stratification, $Ri >0$ (as in Fig.2.4b), and also periods with fairly long averaging times – encompassing both unstable daytime and stable nocturnal periods (as in the case of Fig. 2.4b) – the goodness of fit was generally quite good and therefore it seemed superfluous, for the present purpose, to use some of the more sophisticated forms of the logarithmic wind law, also incorporating stability dependent correction terms when the atmospheric stability deviates from neutral conditions. (This issue has been examined and discussed in more detail in the concluding discussion, Chapter 5.)

For comparison, an example from a near neutral stability situation (Ri ≈ 0) is shown in Fig. 2.4c.

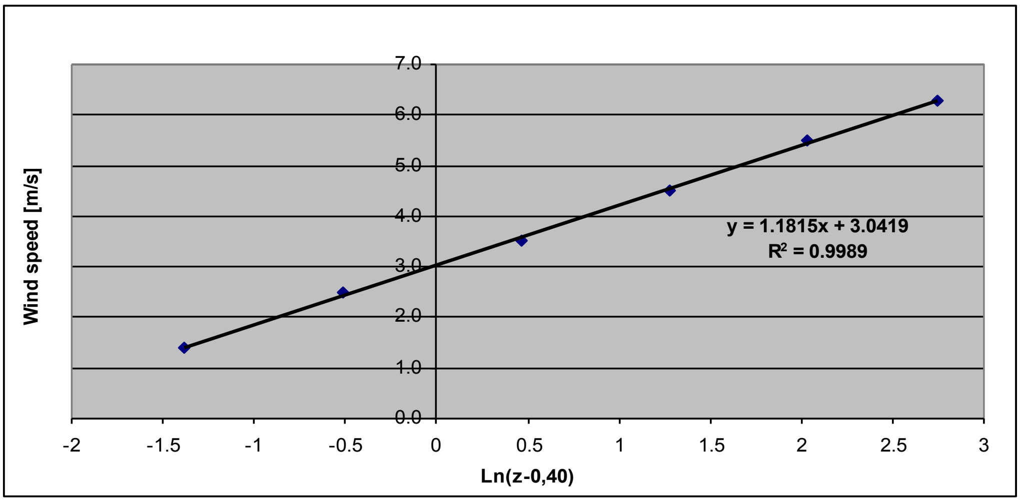

Fig. 2.4c. *The logarithmic wind profile equation (u(z) =1.182ln(z-0.40)+3.042) determined for sampling period 2, July 2010 (3/7 14:30-17:00); d=0.40 m (z_0=0.076 m); Ri_B = -0.012.*

3 Prevailing weather conditions

The values presented in *Table 3.1a-c* (and the corresponding *Table 3.2a-c* for the autumn campaigns) are *mean* values over the different measuring (sampling) periods (where one period is the time between two consecutive changes of air sampling probes in the sampling mast). Also the maximum temperature (at 2m above ground) and precipitation sum for each period are given. (Data on wind directions have not been included in these tables since they are considered not to be of prime importance here, due to the experimental lay-out for the air sampling, and with radial alignment of the dry deposition samplers in several directions as to match the prevailing wind direction in each case, but are included in the extended presentation of weather variables in Appendix 1).

The summer campaign in *June 2008* was comparatively short and covered the period 24/6 17:20 – 25/6 16:50, divided into three separate sampling periods. It was characterized by moderate wind speeds and comparatively low temperature for the season. No precipitation occurred, and the relative humidity of the air (RH) was quite normal for the season (due to initial technical problems with some of the instruments, there are no measured data on either RH or incoming solar radiation (R_{sol}) available from the experimental site from this first measuring event; data on RH in *Table 1* are from the climate station at Ultuna campus ca 9km west from the Lövsta site. The daily (24hr) averages of R_{sol} from that station for the two days involved were 199 (24/6) and 319 Wm^{-2} (25/6), respectively (source for the Ultuna climate station data: http://grodden.evp.slu.se/slu_klimat/slu_files/dygn_man_dat.html).

The measuring period in *July 2009* covered the period 4/7 10:45 – 7/7 09:30, separated into 5 sampling periods. During this campaign winds were weaker (typically around 2 ms^{-1}) and temperatures slightly higher than in June 2008. Also the relative humidity was slightly higher than during the previous summer. The solar radiation (R_{sol}), was fairly normal for this time of the year during the first 4 sampling periods, taken on an average daily basis, whereas it was lower than ´normal´ during the fifth period (even when taking the slightly biased distribution of daytime and dark hours in this period into account) – the 10-year daily average 2003-2012 for the period 1/7-11/7 at the Ultuna station being ~230 Wm^{-2}, and the average daily maximum for the same period being 900 Wm^{-2} (maximum 30-min values of R_{sol} for the different sampling periods can be found in Appendix 1, but when comparing with the average maximum from Ultuna station given above, it should be recognized that this value is based on maximum 1-min values whereas ours (mostly) on 30-minute means (2-min. means in Sept.-09). No rain was recorded during the experiment.

The summer campaign in *July 2010* covered the period 3/7 11:20 – 11/7 22:30, comprising 7 sampling periods. During this period wind speeds during the first two periods were similar to those in June -08 (i.e. about 3-3.5 ms^{-1}) but noticeably weaker during the following five periods (chiefly around 1.5-2 ms^{-1}), but with temperatures significantly higher than during any of the two foregoing summer periods, the maximum values exceeding 28 ˚C in five of the periods. The radiative temperature of the surface (i.e. the effective radiation temperature of the crop surface, here winter wheat averaging about 70 cm in height) was in general about 1-2 ˚C higher than the average air temperature at the height of 2 m (which was the case also in July 2009). Solar radiation during the first 24 hrs (comprising sampling periods 1-3), with an average $R_{sol} \approx 307\ Wm^{-2}$, was well above the ´normal´ daily average, and the same is valid for the last two periods, whereas the periods 4 and 5 were fairly close to average. Also the 30-min maximum radiation values were on the whole on a par with the ´normal´ average for the beginning of July at the Ultuna station (900 Wm^{-2}), accounting for the different time resolution at the two sites. And like the two previous summer campaigns, the whole period passed without precipitation.

The first autumn campaign in *September 2008* included the period 21/9 14:30 – 22/9 18:00, divided into two sampling periods. The wind speeds were low (typically around 1 ms^{-1}) and so were the temperature with maximum values during daytime around 14-15 ˚C. Also the incoming solar radiation (R_{sol}) was fairly low for this time of the year, with a total average over the two periods just below 50 Wm^{-2} (the 10-year (2003-2012) daily average for the second part (16/9-30/9) of September at the Ultuna station is just above 90 Wm^{-2}, and with an *average daily maximum* value for the same period about 535 Wm^{-2}). (Needless to say, that averages of R_{sol} taken over longer periods, including night time hours, are lowered due to the zero solar radiation during the dark parts of the day).

In *September 2009* the field measurements lasted from 18/9 11:40 – 26/9 12:20, including six separate sampling periods. The wind speed conditions varied markedly between those periods as is evident in Table 2b. That was also the case regarding the temperatures, which generally were markedly higher compared with the previous year, maximum values now reaching ~18-20 ˚C in the last four periods. The average surface temperatures were chiefly very similar to the corresponding air temperatures. Solar radiation was comparatively high during the first and fourth periods, otherwise fairly normal for the season. The fifth period (20/9 13:00 – 22/9 11:50) received some rain with a total of about 8 mm at a nearby station.

In *September 2010* the measuring campaign extended from 8/9 12:20 to 18/9 04:50, comprising seven sampling periods in all. Wind speeds were rather weak during the first 6 periods (with averages around 2 ms^{-1} at the 2m height), but slightly higher during the long last period. The average temperatures were similar in magnitude to the year before except for the first period (8/9 12:20 – 15:15) which was slightly warmer than any of the 2009 periods. The incoming solar radiation, taken on a daily (24 hr) basis, was below the 10-year (2003-2012) average for the period 8-18th of September at the Ultuna station, 112 Wm^{-2}, during most of the periods, excepting period 4 which had an average slightly above the 10-year ′normal′ (the long and last period 7 was mainly normal regarding the overall period average).
This campaign was dry until the morning of September 13 in the later part of sampling period 6, when a small amount of rain (1.4 mm) was received (on the other hand, the possibility of occurrence of fog or dew during the night periods cannot be excluded since no registration of dew was performed). And this was the starting point of a longer period with intermittent rain mostly every day of sampling period 7 (lasting from 12:20hr 13/09 until 4:50hr 18/09), typically with daily amounts around 2-3 mm but with a bigger share on the 16th (9.0 mm), and with a total sum during the period of 19 mm.

Table 3.1. Overview of prevailing weather conditions during the three summer campaigns at the experimental site at Funbo-Lövsta, Uppsala

a) Average weather conditions during the three June 2008 - campaign sampling periods

Period/ date:hour	*U(2m) mean (ms^{-1})*	*Temp (2m) mean (°C)*	*T_{max}(2m) (°C)*	*$T_{surface}$ mean (°C)*	*RH (%)*	*$R_{sol\ mean}$ (Wm^{-2})*	*Precip. (mm)*
1: *24/6: 17:20 – 21:00*	**4.4**	**16.5**	**17.1**	**16.0**	**(58)***	**-**	**0**
2: *24/6 21:35 – 25/6 9:35*	**2.6**	**9.8**	**14.9**	**9.4**	**(58)***	**-**	**0**
3: *25/6: 10:20 – 16:50*	**3.9**	**18.2**	**19.5**	**23.7**	**(48)***	**-**	**0**

*) Values are 24-hour averages of RH from the climate station at Ultuna (ca 9km from the Lövsta site) for the 24/6 and 25/6

b) Average weather conditions during the five July 2009 - campaign sampling periods

Period/ date:hour	*U(2m)mean (ms^{-1})*	*Temp(2m) mean (°C)*	*T_{max} (2m) (°C)*	*$T_{surface}$ mean (°C)*	*RH (%)*	*$R_{sol\ mean}$ (Wm^{-2})*	*Precip. (mm)*
1: *4/7: 10:45 – 14:15*	**2.2**	**21.1**	**22.0**	**25.6**	**61**	**641**	**0**
2: *4/7: 14:30 – 17:25*	**1.9**	**20.4**	**21.8**	**22.6**	**67**	**280**	**0**
3: *4/7 17:45 – 5/7 11:30*	**2.0**	**13.0**	**20.8**	**14.4**	**77**	**148**	**0**
4: *5/7 12:15 – 6/7 11:10*	**1.5***	**13.0**	**18.0**	**14.2**	**72**	**198**	**0**
5: *6/7 12:25 – 7/7 09:30*	**2.3**	**13.9**	**17.0**	**14.2**	**78**	**64**	**0**

*) estimated value

c) Average weather conditions during the seven July 2010 - campaign sampling periods

Period/ date:hour	*U(2m) mean (ms^{-1})*	*Temp (2m) mean (°C)*	*T_{max}(2m) (°C)*	*$T_{surface}$ mean (°C)*	*RH (%)*	*$R_{sol\ mean}$ (Wm^{-2})*	*Precip. (mm)*
1: *3/7: 11:21 – 14:12*	**2.9**	**28.0**	**28.8**	**30.5**	**48**	**691**	**0**
2: *3/7 14:28 – 17:08*	**3.6**	**28.4**	**28.7**	**31.2**	**49**	**609**	**0**
3: *3/7 17:24 – 4/7 11:43*	**1.7**	**20.7**	**28.1**	**22.4**	**63**	**201**	**0**
4: *4/7 12:03 –5/7 11:26*	**2.1**	**20.7**	**29.2**	**22.0**	**63**	**247**	**0**
5: *5/7 11:42 – 7/7 11:12*	**1.1**	**17.9**	**25.9**	**19.3**	**74**	**194**	**0.2**
6: *7/7 11:35 – 9/7 11:24*	**1.8**	**20.1**	**26.7**	**21.8**	**64**	**282**	**0**
7: *9/7 11:39 – 11/7 22:32*	**2.0**	**22.5**	**32.4**	**24.3**	**60**	**307**	**0**

Table 3.2. Overview of prevailing weather conditions during the three autumn campaigns at the experimental site at Funbo-Lövsta, Uppsala

a) Average weather conditions during the two September 2008- campaign periods

Period/ date-hour	*$U(2m)_{mean}$ (ms^{-1})*	*Temp (2m) mean (°C)*	*$T_{max}(2m)$ (°C)*	*$T_{surface}$ (°C)*	*RH (%)*	*$R_{sol\ mean}$ (Wm^{-2})*	*Precip. (mm)*
1: *21/9 14:30 – 22/9 7:30*	**0.74**	**6.1**	**15.2**	**5.2**	**90**	**19**	**0**
2: *22/9: 08:30 – 18:00*	**1.2**	**11.8**	**14.4**	**12.6**	**83**	**100**	**0**

b) Average weather conditions during the six September 2009- campaign periods

Period/ date-hour	*$U(2m)_{mean}$ (ms^{-1})*	*Temp (2m) mean (°C)*	*$T_{max}(2m)$ (°C)*	*$T_{surface}$ (°C)*	*RH (%)*	*$R_{sol\ mean}$ (Wm^{-2})*	*Precip. (mm)*
1: *18/9: 11:40 – 15:12*	**3.6**	**16.2**	**17.2**	**17.8**	**55**	**298**	**0**
2: *18/9: 15:40 – 18:35*	**1.8**	**16.4**	**17.1**	**17.0**	**60**	**106**	**0**
3: *18/9 19:00 – 19/9 12:05*	**0.9**	**8.0**	**17.9**	**8.5**	**90**	**84**	**0**
4: *19/9 12:40 – 20/9 12:05*	**2.8**	**12.6**	**20.4**	**12.9**	**77**	**133**	**0**
5: *20/9 13:00 – 22/9 11:50*	**3.4**	**13.8**	**19.9**	**13.9**	**81**	**83**	**8**
6: *22/9 12:30 - 26/9 12:20*	**4.3**	**11.9**	**18.6**	**11.9**	**78**	**95**	**0***

***)** Four single `ticks` (each of 0.2mm) on four separate days disregarded (judged as false signals)

c) Average weather conditions during the seven September 2010- campaign periods

Period/ date-hour	*$U(2m)_{mean}$ (ms^{-1})*	*Temp (2m) mean (°C)*	*$T_{max}(2m)$ (°C)*	*$T_{surface}$ (°C)*	*RH (%)*	*R_{sol} mean (Wm^{-2})*	*Precip. (mm)*
1: *8/9: 12:22 – 15:16*	**2.0**	**18.6**	**19.9**	**18.8**	**63**	**219**	**0**
2: *8/9 15:25 – 17:53*	**1.7**	**17.8**	**18.7**	**17.4**	**68**	**103**	**0**
3: *8/9 18:16 – 9/9 12:06*	**1.7**	**11.9**	**18.1**	**12.2**	**89**	**80**	**0**
4: *9/9 12:24 – 10/9 12:36*	**2.2**	**12.5**	**18.2**	**12.7**	**82**	**131**	**0**
5: *10/9 12:57 – 11/9 11:34*	**1.9**	**13.7**	**18.0**	**13.8**	**87**	**63**	**0.2**
6: *11/9 11:53 – 13/9 12:00*	**2.2**	**15.4**	**20.7**	**15.6**	**91**	**54**	**1.4**
7: *13/9 12:22 – 18/9 04:48*	**3.0**	**11.8**	**17.0**	**12.1**	**88**	**90**	**19**

A more comprehensive summary of the meteorological conditions, giving both the average, maximum and minimum values for each sampling period during the three years, together with calculated bulk Richardson numbers for two height intervals: 16 - 0.15m (*Ri_B (16-0.15m)*) and 2m -"the surface" (*Ri_B (2m-surf.)*) are presented in ***Appendix 1 a-e.***

The bulk Richardson number used here is defined by:

$$Ri_B = (g/\theta_o) \cdot [(\theta_2 - \theta_1)(z_2 - z_1)/(\bar{u}_2 - \bar{u}_1)^2] \qquad (3a)$$

which is the finite-difference form of the gradient Richardson number**:**

$$Ri = (g/\theta_o) \cdot \partial\theta/\partial z)/(\partial\bar{u}/\partial z)^2. \qquad (3b)$$

Here, g is the gravitational acceleration, θ_o is the absolute temperature at a reference height (here the surface), θ_2 and θ_1 are the mean potential temperature at two heights z_2 and z_1, respectively, and $\bar{u}_2$ and $\bar{u}_1$ are the mean wind speeds at the same heights.

Ri (and Ri_B) is a dimensionless number expressing the ratio of buoyant ("thermal") suppression (or the opposite) of turbulence to the generation of dynamic turbulence by the wind shear in the atmosphere or, in other words, a measure of *the thermal atmospheric stability* and the atmosphere's disposition to dispersion (of momentum, heat, water vapour or other passive contaminants) through turbulent diffusion. Thus, the sign and magnitude of Ri (or Ri_B) is of significant importance in determining the rate of vaporization and subsequent vertical dispersion/diffusion of the pesticides. Values of $Ri > 0$ implies a stable stratification that tend to suppress turbulent mixing in the vertical direction. At some critical value of Ri, usually taken as $Ri_c = 0.25$, air becomes so dynamically stable that the air flow ceases to be turbulent, but due to hysteresis effects, there are indications that turbulence may exist up to $Ri = 1$. The opposite holds for Ri-values < 0. The stratification is then unstable and vertical motions are promoted. Values of Ri near zero indicate a neutral stratification which is more or less indifferent with respect to (vertical) turbulent diffusion. (In the present context values roughly in the interval $-0.02 < Ri_B < 0.02$ may be regarded as indicating near-neutral stratification).

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4 Results

4.1 The horizontal volatilization fluxes and source strengths of the pesticides

4.1.1 Measurement of possible background loads

For the purpose of measuring a possible background load of any of the active substances used in our field trials, a separate air sampler of the same construction as described in the section on “Material and methods” above was used. The background air sampler was mounted ~2m above ground and located 100 m upwind the first year. The last two years the background sampler was located about 1000 m away from the treated area, with a separate pump. The sampling times for these measurements were the same as for the corresponding air sampling periods in the mast.

These background concentrations (which for June and September 2008, and July 2010 are shown together with the other concentration values in Appendix 2) show in a few cases values above the respective detection limits, but in the majority of cases they are below this limit or indicate just traces of the substance. In most of the cases when they are measurable, these values are higher than the measured values on the 16-m level (this holds for pendimethalin and fenpropimorph in measuring period 1 in June 2008, and for pendimethalin and prosulfocarb both in period 1 and 2 in September 2008). In just two cases these values were of about the same magnitude or less than the corresponding 16-m concentrations (prosulfocarb in period 1 and period 2, June 2008). However, since a real background load of any of the substances are considered (primarily) as due to long-range transport, this “background” should also be manifested in the 16-m level measurements since this height, at least in neutral and stable atmospheric conditions, most certainly lies above the internal boundary layer affected by the nearby treated area, and this is mostly not the case. Furthermore, in the cases of pendimethalin and prosulfocarb in September 2008, these high “background” values in both periods (0.8-3.3µg/PUF, corresponding to air concentrations in the range 10-63 ng/m^3) are much higher (with a factor 10 to 50) than those found as most in the background air at an air quality monitoring site in the south of Sweden (Söderåsen, Skåne; *Graaf, Adielsson and Kreuger, 2010, 2011*) in the late summer and autumn , despite the fact that this site is located quite close to e.g. Denmark where these two substances are used in the farming practice in much higher quantities than in Sweden. These circumstances, therefore, make us believe that our quantifiable “background” values are due to local contamination from our treated area, either during the spraying operation itself, or later due to light and meandering winds (during both sampling periods in September 2008 e.g., winds were mostly fairly weak with period averages even at the 16-m level of 1.2 and 1.6 ms^{-1}. Due to these considerations, and the otherwise either very low values, we have disregarded any possible background loadings in our measurements.

4.1.2 Summer conditions – vaporization from standing crop

Primarily, the total horizontal flux of each of the pesticides through a vertical "window" of unit width (1 m) for each of the separate sampling periods during the three years (three periods in June 2008, five in July 2009 and seven in July 2010) was determined in the way outlined in Section 2.6. From these total fluxes also the corresponding average source strength (ng/s.m^2) for each period was calculated. As mentioned in Sec. 2.6, due to the not always obvious course of the concentration profile for a given period (whether using the ln(c) =f(z) or the ln(c) = f(ln(z)) type of relation), this frequently left open for different interpretations of the possible concentration profile shape and the pertaining equation (and thereby also for the determined fluxes). Therefore, two different (although sometimes quite similar) versions of calculated accumulated fluxes, average source strengths etc. have generally been included in the tables and graphs below. Hereby, "version 1" has generally been considered as the first hand choice, but with "version 2" being a fully plausible alternative.

Below, some examples of vertical profiles of concentration, wind speed and horizontal flux are shown.

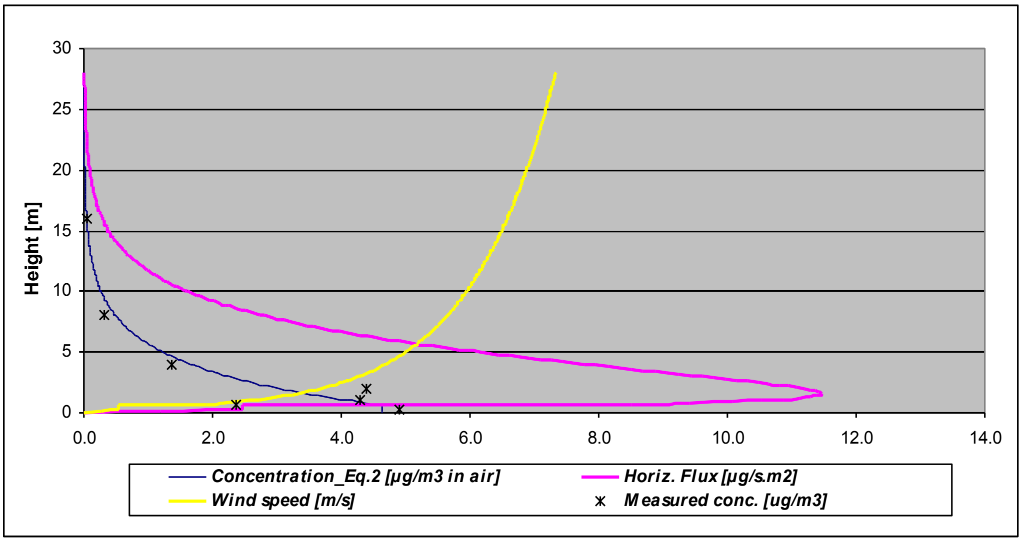

Figure 4.1*. Concentration, wind speed and flux profiles of prosulfocarb from period 3(17.5-24 hrs after spraying) in June 2008. Height interval used for determination of the conc. equation here is 1to16- m levels (giving an* R^2*=0.971).*

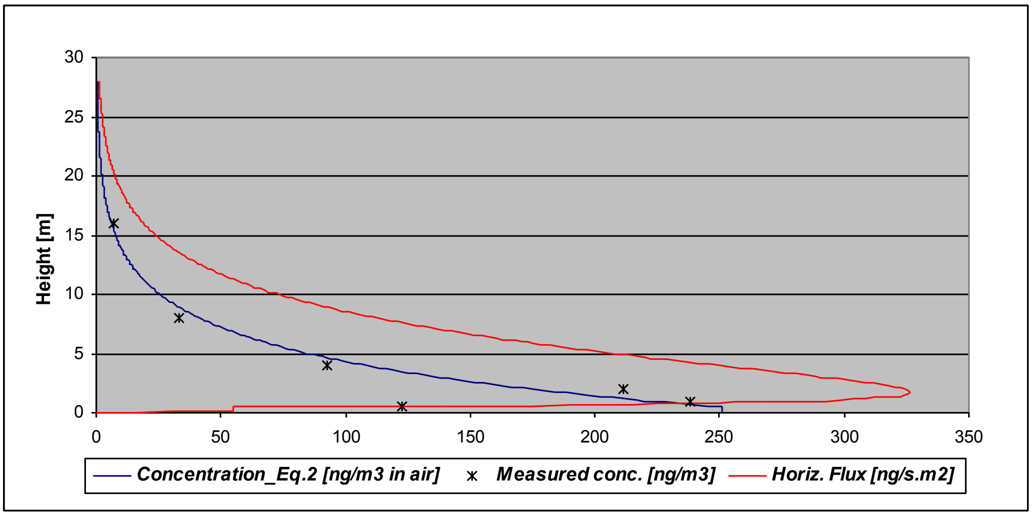

Figure 4.2. *Concentration and flux profiles of* ***lindane*** *from the second period (4-7hrs after spraying) in July 2009. Height interval used for concentration equation is 1 to 16 m (giving an* R^2*=0.985).*

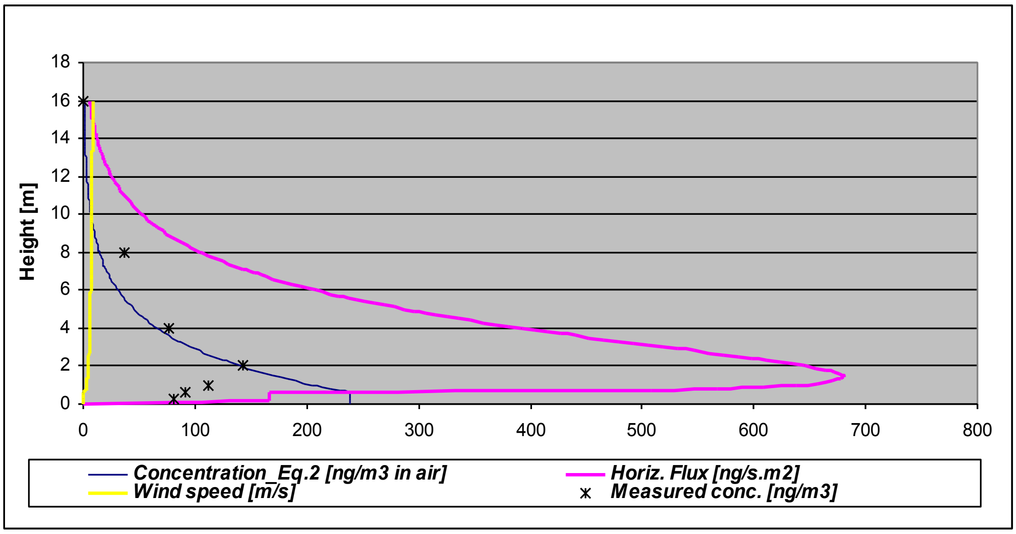

Figure 4.3. *Concentration, wind speed and horizontal flux profiles of* ***fenpropimorph*** *from period 1(0-4hrs), June 2008. Height levels used for the concentration equation is 1to16 m as above (giving an* R^2*=0.937). Notice the deviating conc. values at lower levels.*

In the summer periods, concentration was held constant below z = 0.50 m at the integration, i.e. through the major, lower, part of the crop. In fact, there may well be a gradual decrease of the concentration in the crop canopy downwards from a maximum concentration level inside the vegetation canopy, but we do not know how rapid in that case, and since the wind speeds certainly are very low in this region, it should not make a significant difference for the total flux computations whichever of these two possibilities you choose.

From the first two figures (4.1 and 4.2) it is also clear, that the vertical integration of the flux should be extended to higher levels than 16 m in some (as a matter of fact, in rather many of all cases) since the horizontal flux (according to the flux equation) is not approaching zero at the 16-m level.

Figure 4.3 gives an example of the problem with disturbed concentration values at lower heights, chiefly from 1m height and downwards. These cases were probably caused by a disturbed flow field caused by the trailer supporting the air-pump equipment, at least in certain wind directions.
Figures 4.4 and 4.5 illustrates, first and foremost, that two different versions of the concentration equation, both with very good fit, may cause noticeable differences in the flux profiles, naturally resulting in corresponding differences in the estimated total flux and in the calculated source strengths. Both equations are here of the conventional, exponentially decreasing, type ($\ln(c) = -a z + b$ where c is concentration and z is the height (m)), viz. in the first case (*Fig. 4.4*): $\ln(c) = -0.380z + 8.556$, and in the second (*Fig. 4.5*): $\ln(c) = -0.394z + 8.717$. Thus fairly similar, but implying an average source strength that is ~11 % higher in the latter case compared with the first (1100 ng/s.m^2 versus ~988 ng/s.m^2).

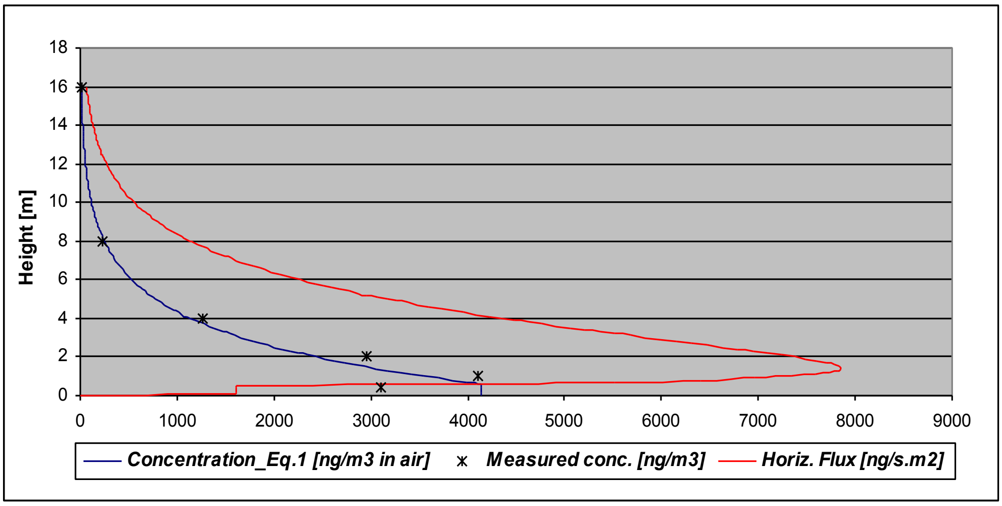

Figure 4.4. *Concentration and horizontal flux profiles of* ***tolclofos-methyl*** *from the first sampling period (0-3hrs) in July 2010 according to conc. equation vers.1.* ***Height interval used for conc. equation 0.4 to 16m*** *(R^2 = 0.992).*

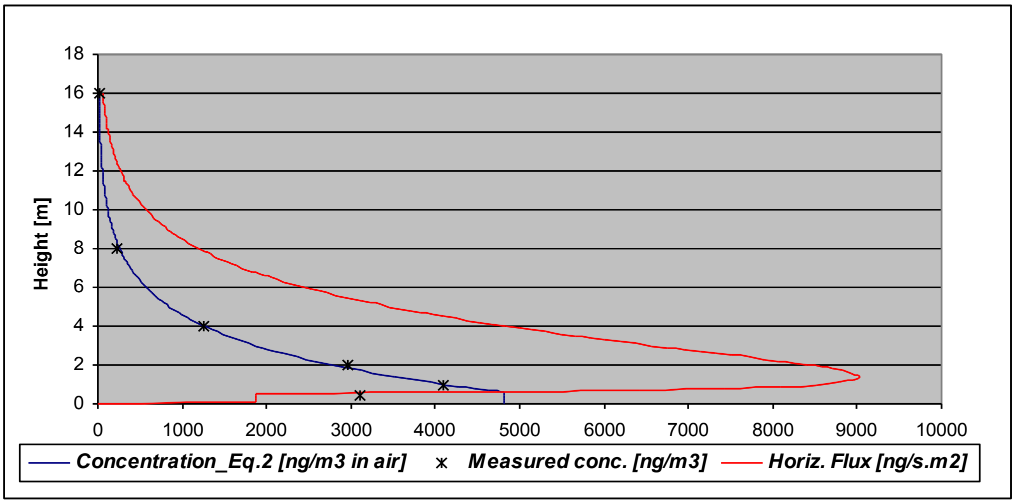

Figure 4.5. *Concentration and horizontal flux profiles of* ***tolclofos-methyl*** *from the first sampling period (0-3hrs) in July 2010 according to conc. equation vers.2.* ***Height interval used for conc. equation is 1 to 16m*** *(R^2 = 0.999).*

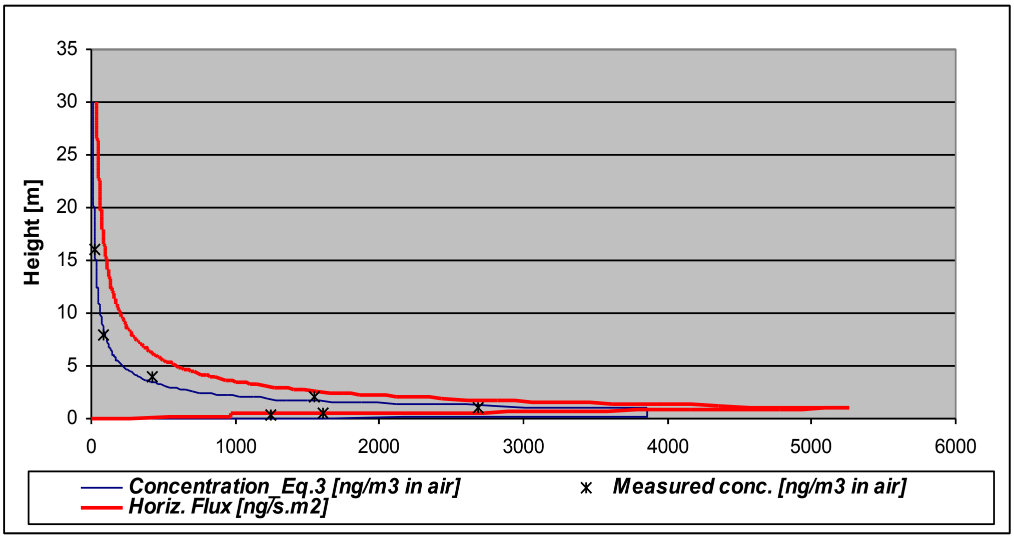

Figure 4.6. *Concentration and horizontal flux profiles of* ***pendimethalin*** *from period 3(7-24hrs after spraying) in July 2009, according to conc. equation vers.2. Height interval used for the conc. equation: 1-16 m ($R^2 = 0.978$).*

Figure 4.6, finally, gives an example where the second type of concentration equation has been used, i.e. ln(c) = f(ln(z)) (in this case: $\ln(c) = -1.787 \cdot \ln(z) + 8.259$). With this type of equation it was frequently necessary to extend the integration (summation) up to heights considerably above 16 m. In the present case, terminating the summation at z =16m implies a calculated source strength just under 94 % of that resulting from extending it to 30 m, but this difference was sometimes even greater.

In June 2008, a growing crop of winter wheat, not particularly dense, and of an average height around 75 cm was sprayed with a tank mixture of pirimicarb, prosulfocarb, fenpropimorph, pendimethalin and fluazinam (the same mixture was also used during the autumn campaign in 2008). All field doses used during this and the other two years are summarized in Table 4.1 below. The applied dose in each case was calculated from careful measuring of the filled up water (and pesticide) quantities in the tank before the spraying and then a likewise careful determination of the residue liquid after each treatment. In June and September 2008 a slightly simpler procedure was used (cf. the note in Table 4.1). (Note that quite appreciable changes in the applied field doses were made between the different years; especially so in the cases of prosulfocarb and pendimethalin.)

In July 2009, the average height of the sprayed crop (barley this year) was ~65 cm (~75 cm including the bristles). This year (and the next) fluazinam was excluded, but lindane and tolclofos-methyl were added to the pesticide mixture.
In July 2010, the crop (winter wheat) averaged about 90 cm in height and was fairly dense.

Table 4.1 *Field doses (**mg/m^2** of active substance) of pesticides during the field campaigns at Lövsta (Uppsala) during the summer and autumn seasons of 2008 – 2010* [1)]

	2008		***2009***		***2010***	
	June	*Sept.*	*July*	*Sept.*	*July*	*Sept.*
Lindane	-	-	10.0	9.5	7.8	8.4
Pirimicarb	15	15	18.7	89.2	14.7	78.4
Tolclofos-methyl	-	-	31.1	29.8	24.5	26.1
Prosulfocarb	320	320	398	19.0	15.7	16.7
Fenpropimorph	75	75	93.4	89.2	73.5	78.4
Pendimethalin	160	160	199	19.0	15.7	16.7

1) For the two latter years calculated values are based on filled quantities in tank, tank residual volume after spraying and sprayed area in m2. For 2008 doses were estimated from filled quantities of respective pesticides and the assumption that the intended sprayed volume (200 l/ha) of tank mixture was achieved.

From June (and September) 2008 only four of the substances will be considered in the presentation hereafter due to analysis problems with fluazinam as mentioned before. The summer 2008 experiment comprised three sampling periods: 24/6 17:20-21:00 (~3.5 hrs), 24/6 21:30-25/6 09:30 (12 hrs) and 25/6 10:20-16:50 (6.5 hrs) with a total sampling time of barely ~24 hrs (the intermediate time between two sampling periods, used for the change of sampling probes, are included in the calculation of the accumulated fluxes by letting the first half of this period belong to the first period, with this period´s source strength, and the second half of the probe-shifting period to the next measuring period). The average temperature at 2m height during these three periods was 16.5, 9.8 and 18.2 ˚C, respectively, average wind speeds at 2m were 4.4, 2.6 and 3.9 ms^{-1} and average bulk Richardson number (Ri(16-0.2m)) 0.004 (almost neutral stability), 0.11 (stable) and -0.10 (unstable stratification), respectively.

The relative accumulated horizontal fluxes expressed as percentages of the respective applied field doses over different time spans are shown in Tables 4.2a and 4.2b. In these tables each substance is represented by two columns (Vers.1 and Vers.2). The first column (Vers.1) presents the values which are the result of the selection of those concentration equations that seemed to give the "best" fit to measured concentrations, thereby also taking into account, among other things, that some of the lower measuring levels, especially during the summer campaigns in the first two years, seems to have been disturbed.
The concentration profile equations in the second alternative (Vers.2) often include more measuring heights than Vers.1, thus with the possibility of sometimes including one or more of the presumed disturbed lower measuring heights. Therefore, the goodness of fit (in terms of R^2 - value) of these equations often are less good than in the first alternative, although sometimes almost as good as or even slightly better than in version 1.
In general, the concentration equations – whether grouped in Vers.1 or Vers.2 – are of the expected, exponential type: i.e. $\ln(c) = -az + b$ (where c=concentration and z= height), but for some periods (5 of the 15 summer sampling periods and 6 of the 15 autumn periods) the equation best fitting the concentration data is of the type: $\ln(c) = -a_2 \cdot \ln(z) + b_2$, indicating an (apparently) more slow decrease of concentration with height. However, the strategy in selecting the equations for the

two alternatives has been to use the same type of equation, both regarding the functional type of equation and the height interval utilized, as far as possible, for all substances within one and the same period. The latter requirement has not always been possible to achieve because sometimes one or more of the substances did not reached detectable concentration levels at the 16-m or even 8-m heights whereas the others did. This feature (when it occurred) was primarily confined to lindane and pirimicarb and, but less frequent, also pendimethalin.
Thus, in summary, the second alternative of concentration equations ("Vers.2") could be considered as a somewhat more uncertain, but still a quite plausible, alternative to the first (in fact, in many cases it was actually not obvious which of the two that gives the most realistic representation of the concentration profile in question). Besides this, this procedure also gives some indication of the sensitivity of the determined quantities (i.e. the accumulated fluxes and corresponding source strengths) to the uncertainty in the fitted concentration equations.

In Tables 4.2a and 4.2b on the following pages the accumulated horizontal flux during the summer campaigns, as a percentage of the respective applied doses, for the different pesticides used are shown for different time intervals elapsed after the treatment was completed.

During the barely 24 hours of sampling in June 2008 the total accumulated flux ranged from just about 2-3 % for fenpropimorph to almost 25 % for prosulfocarb. Pirimicarb comes next to fenpropimorph with about 7-9 % , and pendimethalin reached just above 18 %.

When examining the time course of the cumulative fluxes it may be noted that in the case of pirimicarb and fenpropimorph, the absolutely major part of the flux occurred during the first twelve hours, with about 62 % of the total 24-hr flux for pirimicarb and about 86 % of the total for fenpropimorph. By contrast, the corresponding figure for pendimethalin was just about 14 % and for prosulfocarb 33 %. These first 12 hours encompassed a 4- hour late afternoon and evening period with moderately high temperatures (16-17 ˚C) both at the height of 2 m and at the ´surface´ (i.e. the upper part of the wheat canopy), but also 8 hours of night conditions with average temperatures below 10 ˚C and minimum temperatures, especially at the crop surface, down to ~ 4-5 ˚C. The following 12 hours, however, encompass to a major part the whole of sampling period 3 (~6.5 hrs) with an average temperature at 2m of 18.2 ˚C and surface temperatures between 20 and 25 ˚C with an average of 23.7 ˚C (cf. ***Table 1*** or ***Appendix 1a***).
The observed difference in vaporization behaviour between the pesticides might be interpreted as if the latter pesticides need a markedly higher temperature to keep evaporating at a more marked rate (average wind speeds were slightly lower during the latter 12-hr period but fairly similar).

The measuring campaign in the summer of 2009 encompassed a total of almost 71 hours during 5 consecutive sampling periods between the 4th and 7th of July. Now, the average surface temperature (at the top of the canopy) during the first two sampling periods (both together 7 hours) were about as high as during the warmest period in June 2008 (25.6 and 22.6 ˚C, resp.) with a maximum of 27.9 ˚C, but with markedly higher temperatures at a height of 2 m compared to 2008, (the averages being around 20-21 ˚C). The following 18 hours (sampling period 3) include a whole night but both the surface and 2-m temperatures were significantly higher than during the night period (sampling period 2) in June 2008 (cf. ***Appendix 1b***).

Table 4.2a Relative accumulated horizontal flux of a substance for different time intervals after spraying, expressed as a ***percentage of the applied field dose*** – the summer campaigns.(Vers.1 and Vers.2 corresponds to the two alternative choices of the concentration equation; see p.29).

Pesticide: *Lindane*		**June 24-25 2008**			**July 4-7 2009**			**July 03-11 2010**		
Elapsed Time [hrs]		Conc. Equat. Altern	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs						*29.9*	*26.2*		*51.8*	*47.5*
0-6 hrs						*42.0*	*37.2*		*54.4*	*50.1*
0-12						*47.2*	*41.8*		*55.7*	*51.3*
0-24						*54.5*	*47.9*		*58.4*	*53.7*
0-48						*58.4*	*51.6*		*60.7*	*55.9*
0-96									*63.5*	*58.2*
0-168									*65.4*	*60.8*
Whole period						*60.8* **(70.8h)**	*54.0* **(70.8h)**		*66.4* **(203h)**	*61.3* **(203h)**

Pesticide*:* *Pirimicarb*		**June 24-25 2008**			**July 4-7 2009**			**July 03-11 2010**		
Elapsed Time [hrs]		Conc. Equat. Alternat	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs			*3.01*	*2.36*		*5.45*	*4.76*		*24.7*	*23.2*
0-6 hrs			*4.42*	*3.56*		*8.03*	*7.15*		*26.3*	*24.6*
0-12			*5.87*	*4.98*		*9.32*	*8.38*		*26.7*	*25.0*
0-24			*9.4**	*7.4**		*11.0*	*10.0*		*27.5*	*25.7*
0-48						*12.8*	*11.3*		*28.1*	*26.2*
0-96									*28.5*	*26.5*
0-168									*28.7*	*26.8*
Whole period			*9.30* **(23.5h)**	*7.32* **(23.5h)**		*13.60* **(70.8h)**	*12.20* **(70.8h)**		*28.8* **(203h)**	*26.8* **(203h)**

Pesticide: *Tolclofos-methyl*		**June 24-25 2008**			**July 4-7 2009**			**July 03-11 2010**		
Elapsed Time [hrs]		Conc. Equat. Alternat	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs						*11.1*	*9.54*		*48.7*	*43.7*
0-6 hrs						*17.8*	*15.6*		*54.2*	*48.8*
0-12						*22.3*	*19.9*		*55.5*	*50.1*
0-24						*28.9*	*26.1*		*58.2*	*52.6*
0-48						*33.4*	*30.8*		*60.3*	*54.6*
0-96									*61.7*	*56.0*
0-168									*62.8*	*57.1*
Whole period						*35.3* **(70.8h)**	*33.0* **(70.8h)**		*63.1* **(203h)**	*57.4* **(203h)**

*) Extrapolated value from the 23.5-hrs measuring period

Table 4.2b Relative accumulated horizontal flux of a substance for different time intervals after spraying, expressed as a ***percentage of the applied field dose*** – the summer campaigns.

Pesticide: ***Prosulfocarb***		**June 24-25 2008**			**July 4-7 2009**			**July 03-11 2010**		
Elapsed Time [hrs]		Conc. Equat. Altern:	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs			*3.40*	*2.71*		*11.2*	*9.27*		*51.3*	*47.4*
0-6 hrs			*5.45*	*4.54*		*18.0*	*15.3*		*56.5*	*52.3*
0-12			*8.42*	*7.41*		*23.1*	*20.2*		*57.8*	*53.6*
0-24			*25.6**	*24.5**		*31.1*	*27.9*		*60.4*	*56.1*
0-48						*36.4*	*33.6*		*63.2*	*58.8*
0-96									*64.4*	*60.0*
0-168									*65.9*	*61.5*
Whole period			*24.7* **(23.5h)**	*23.5* **(23.5h)**		*38.7* **(70.8h)**	*36.4* **(70.8h)**		*66.2* **(203h)**	*61.7* **(203h)**

Pesticide*:* ***Fenpropimorph***		**June 24-25 2008**			**July 4-7 2009**			**July 03-11 2010**		
Elapsed Time [hrs]		Conc. Equat. Alternat.:	***Vers. 1***	***Vers. 2***		***Vers. 1***	***Vers. 2***		***Vers. 1***	***Vers. 2***
0-3 hrs			*1.68*	*1.27*		*4.13*	*3.63*		*24.7*	*22.8*
0-6 hrs			*2.25*	*1.71*		*5.61*	*4.91*		*26.4*	*24.3*
0-12			*2.44*	*1.90*		*6.06*	*5.30*		*26.6*	*24.6*
0-24			*2.84**	*2.30**		*6.61*	*5.79*		*27.1*	*25.0*
0-48						*6.84*	*6.01*		*27.8*	*25.6*
0-96									*28.3*	*26.2*
0-168									*28.8*	*26.6*
Whole period			*2.82* **(23.5h)**	*2.27* **(23.5h)**		*6.96* **(70.8h)**	*6.12* **(70.8h)**		*29.0* **(203h)**	*26.8* **(203h)**

Pesticide: Pendimethalin		**June 24-25 2008**			**July 4-7 2009**			**July 03-11 2010**		
Elapsed Time [hrs]		Conc. Equat. Alternat.:	***Vers. 1***	***Vers. 2***		***Vers. 1***	***Vers. 2***		***Vers. 1***	***Vers. 2***
0-3 hrs			*0.93*	*0.72*		*3.62*	*3.05*		*37.3*	*33.7*
0-6 hrs			*1.60*	*1.31*		*6.62*	*5.77*		*46.5*	*42.2*
0-12			*2.72*	*2.41*		*10.7*	*9.74*		*47.9*	*43.4*
0-24			*19.0**	*19.3**		*18.1*	*17.2*		*50.7*	*46.0*
0-48						*25.5*	*25.3*		*53.1*	*48.0*
0-96									*54.8*	*49.5*
0-168									*56.4*	*50.9*
Whole period			*18.1* **(23.5h)**	*18.3* **(23.5h)**		*29.2* **(70.8h)**	*29.3* **(70.8h)**		*56.8* **(203h)**	*51.2* **(203h)**

*) Extrapolated value from the 23.5 hrs measuring period

During the last two sampling periods (encompassing the hours 26 to 71 after treatment) temperatures were comparatively low with maximum surface values of ~21 and 19.8 ˚C and average 2-m temperatures of 13.0 and 14.0 ˚C for the two periods, respectively. Wind speeds were markedly lower during all 5 sampling periods compared with the periods in June 24-25 2008.

This year, 6 pesticides were used in the mixture, but like the case in June 2008 the one which showed the least total horizontal flux during the almost three days (70.8 hrs) was fenpropimorph with a total relative flux of just 6 to 7 %. The highest total relative flux pertained to lindane with almost 61 % according to Vers.1 (54 % in Vers.2). Next to lindane, in descending order were prosulfocarb (38.7%), tolclofos-methyl (35.3%), pendimethalin (29.2%) and pirimicarb (13.6%) (all figures here refer to Vers.1). It may be pointed out, that the difference in the total, relative flux between the two alternatives (viz. Vers.1 and 2, respectively) is at most around 13 to 14 % (in the case of lindane and fenpropimorph), and in one case (pendimethalin) almost negligible.

As regards the course over time of the fluxes it is again evident that a very appreciable part of the total occurred during the first few hours after the treatment. In fact, almost 50% or even more (~69% for lindane and ~80% for fenpropimorph) occurred during the first 6 hours. An exception to this seems to be pendimethalin for which the accumulated flux after 6 hours is about 20-23 % of the total during the 71 hrs followed. Examples of these two types of behaviour regarding the time course of the volatilization are shown in Figs. 4.7 to 4.9.

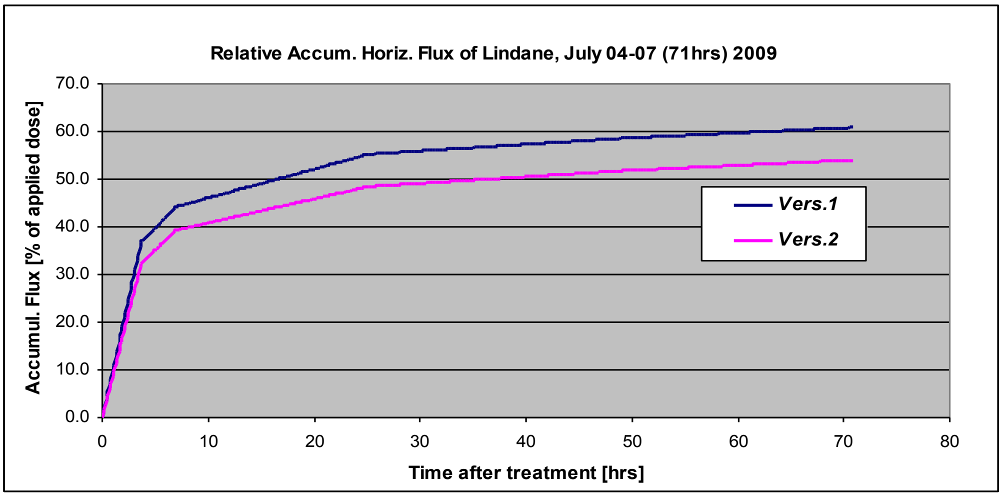

Fig. 4.7 *The accumulated horizontal flux of* ***lindane*** *(as a percentage of the applied dose) as a function of time after spraying in July 04-07, 2009.*

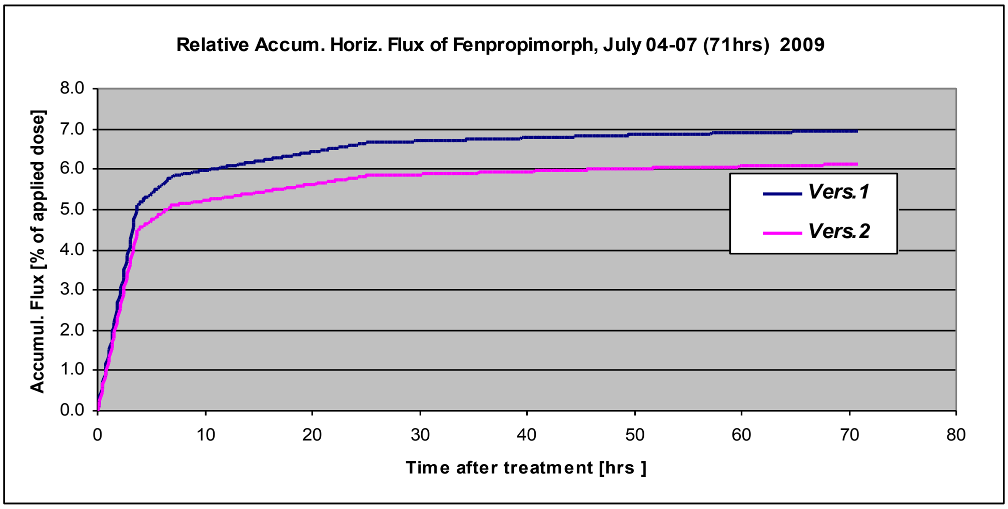

Fig. 4.8 *The accumulated horizontal flux of* ***fenpropimorph*** *(as a percentage of the applied dose) as a function of time after spraying in July 2009.*

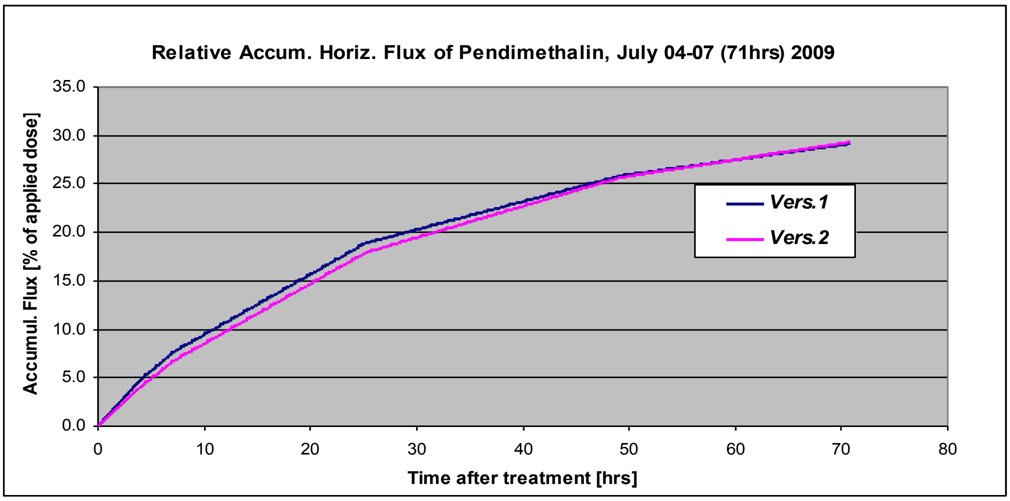

Fig. 4.9 *The accumulated horizontal flux of* ***pendimethalin*** *(as a percentage of the applied dose) as a function of time after spraying in July 2009. Note the slower increase with time in this case.*

These differences in the accumulated flux rates are of course the direct manifestation of the corresponding changes over time in the underlying source strengths. Figs. 4.10 a-c show the respective time course of the average source strengths, normalized with respect to the respective applied doses, for the consecutive sampling periods of the same cases as shown in Figs. 4.7-4.9 above.

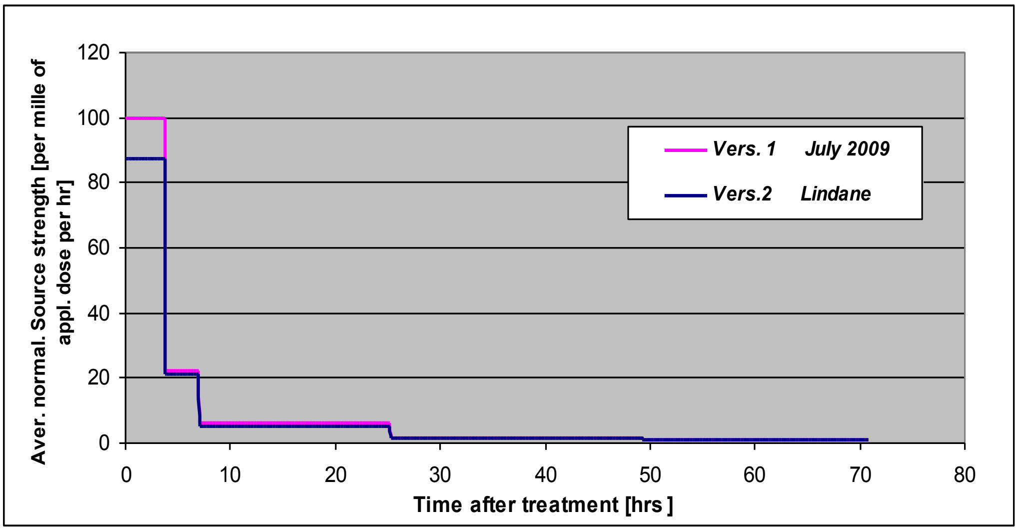

Figure 4.10 a. *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***lindane*** *during the five consecutive sampling periods (~71 hrs in all) following treatment in July 2009.*

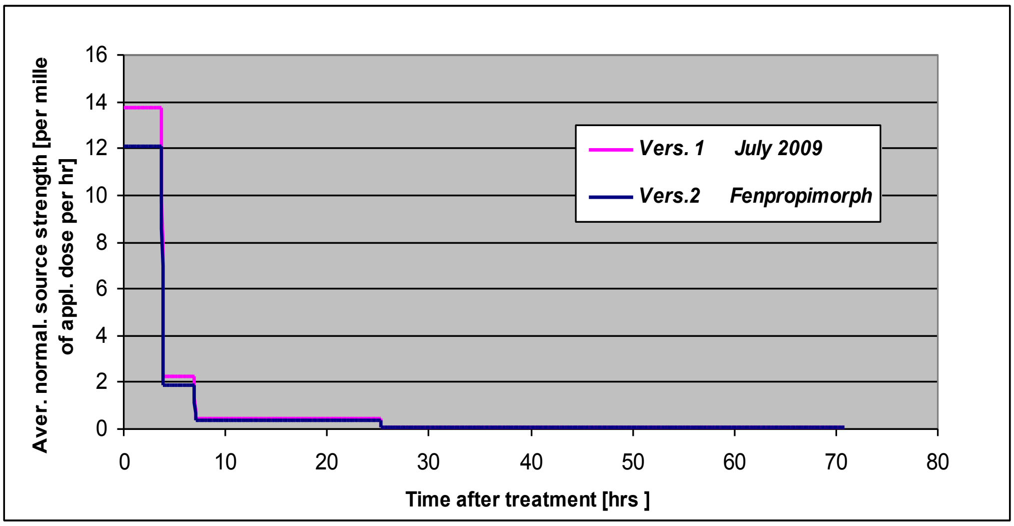

Figure 4.10 b. *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***fenpropimorph*** *during the five consecutive sampling periods (~71 hrs in all) following treatment in July 2009.*

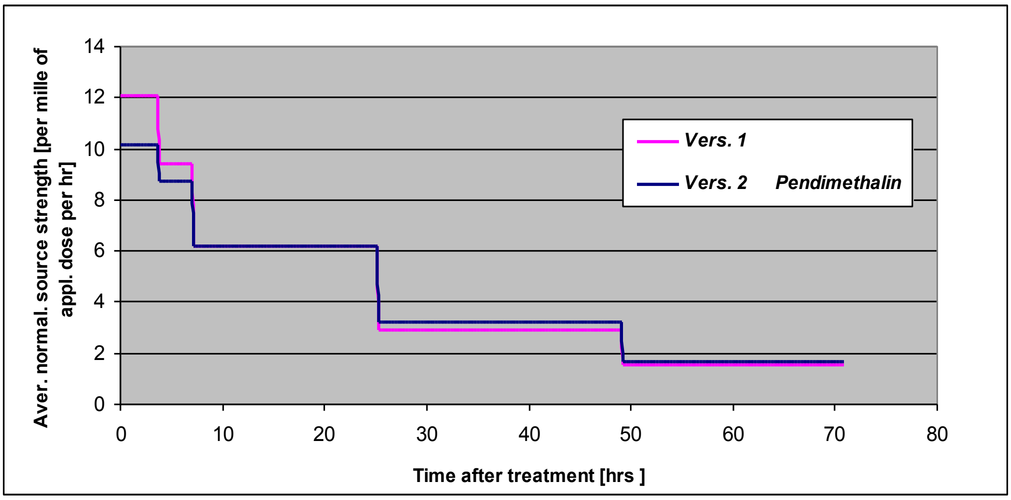

Figure 4.10 c. *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***pendimethalin*** *during the five consecutive sampling periods (~71 hrs in all) following treatment in July 2009.*

It is evident that in the case of the first two substances, lindane and fenpropimorph, the source strength has fallen off very markedly already after the first seven hours (period 1+2), whereas the decrease in the case of pendimethalin (Fig. 4.10c) are much more gradual.

In the summer 2010 the field campaign lasted from midday the 3rd of July to the late evening of the 11th, 203 hours in all, partitioned on seven consecutive sampling periods. This was the warmest of the experimental years, with an average air temperature at the 2 m height exceeding 20 ˚C during 6 of the sampling periods and exceeding 28 ˚C during the two first. The surface temperatures were still higher with average values above 30˚C during the first two periods, and maximum values above (or very close to) 30˚C in all periods (cf. App.1d). Winds were mostly fairly weak with averages in the range 1 to 2 ms^{-1} at the 2-m level during periods 3-6, but slightly higher in periods 1 and 2 (Table 3.1). This summer campaign, like the previous two, was also dry as a whole, with chiefly no precipitation (except for a possible 0.2mm in the second half of per.5 (in the evening of the 6th of July)).

During the whole sampling period this summer (203 hours) the total relative fluxes were, in ascending order, 28.8% (pirimicarb), 29.0% (fenpropimorph), 56.8% (pendimethalin), 63.1% (tolclofos-methyl), 66.2% (prosulfocarb) and 66.4% (lindane) (again referring to the first concentration alternative). This is in practise the same order among the pesticides as in the summer 2009 (let it be, that pirimicarb and fenpropimorph now roughly are of the same magnitude, which in the upper end of the scale also holds for prosulfocarb and lindane). Of the two pesticides in the upper end of the scale, lindane also has the highest vapour pressure (4.4 mPa at 25 ˚C) among the six, whereas prosulfocarb has the second lowest (0.79 mPa; PPDB, Table 4.3). Among the substances in the lower end, pirimicarb also has the lowest vapour pressure (0.43 mPa; 25 ˚C) whereas fenpropimorph has the second highest (3.9 mPa).

(However, regarding the above cited vapour pressure figures, confer the discussion in Sect. 4.2 and also Table 4.9 in that section.)

Table 4.3 *Selected physico-chemical properties of the pesticides used (Pesticide Properties DataBase (PPDB); Agric. And Environmental Unit; University of Hertfordshire, 2012)*

	Lindane	***Pirimicarb***	***Tolclofos - methyl***	***Prosulfocarb***	***Fenpropi - morph***	***Pendimethalin***
Mol. Weight [g mol^{-1}]	*290.8*	*238.4*	*301.1*	*251.4*	*303.5*	*281.3*
Solub. in water [mg/l]	*8.52*	*3100*	*0.71*	*13.2*	*4.32*	*0.33*
Vapour pr. at 25 °C [mPa]	*4.4*	*0.43*	*0.877*	*0.79*	*3.9*	*1.94*
Henry´s const. at 20 °C [dim.less]	$6.10x10^{-5}$	$1.40x10^{-7}$	$1.40x10^{-2}$	$5.38x10^{-5}$	$5.50x10^{-5}$	$1.50x10^{-3}$
Henry´s const. at **25°C** [Pa m^3 mol^{-1}]	$1.48x10^{-6}$	$3.30x10^{-5}$	$3.70x10^{-1}$	$1.52x10^{-2}$	$2.74x10^{-4}$	$2.73x10^{-3}$
K_{foc} $^{1)}$ [mL/g]	*477* (46 – 866) $^{2)}$	*388* (45.0 – 730)	*3620* (1649 – 6139)	*1693* (1367 – 2339)	*4382* (2772 – 5943)	*15744* (6700 – 29400)

1) The Freundlich soil adsorption coefficient 2) Range given by PPDB

And, like the previous year, but even more accentuated, the very major part of the flux apparently occurred during the first few hours after treatment. In fact, for four of the pesticides ~82-86 % of the total flux (during 203 hrs) toke place during the first 6 hours, and in the cases of pirimicarb and fenpropimorph this figure is above 90 %.

Examples of the time courses of the horizontal fluxes from the summer 2010 are shown in *Figs. 4.11-4.13* below.

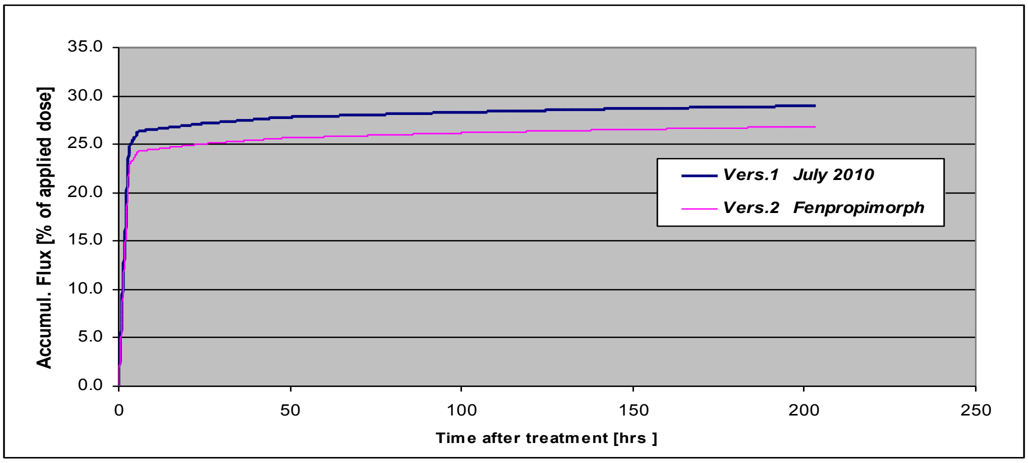

Fig.4.11 *The accumulated horizontal flux of* ***fenpropimorph*** *(as a percentage of the applied dose) as a function of time after spraying in July 2010. In this case, ~91 % of the total flux during the whole experimental period (203 hrs) has occurred after the first 6 hours.*

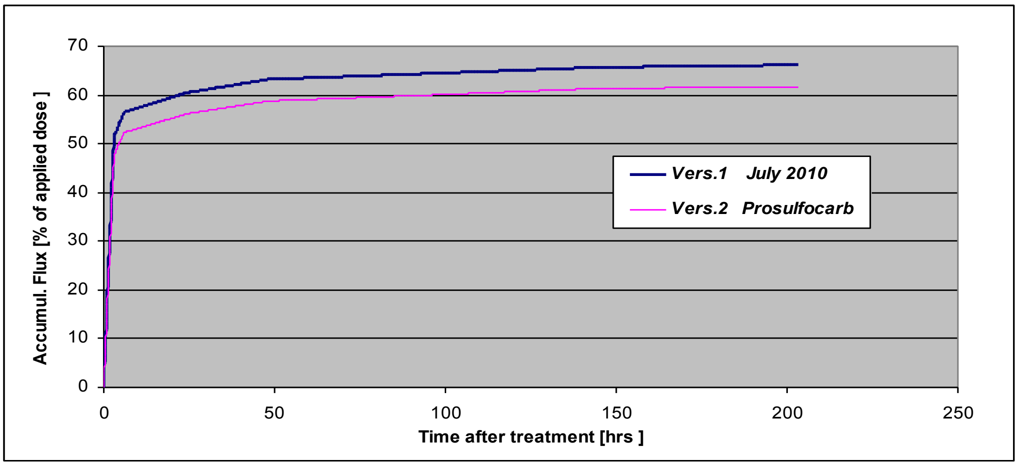

Fig.4.12 *The accumulated horizontal flux of* ***prosulfocarb*** *(as a percentage of the applied dose) as a function of time after spraying in July 2010. About 85 % of the total flux during the whole period (203 hrs) was reached after 6 hours.*

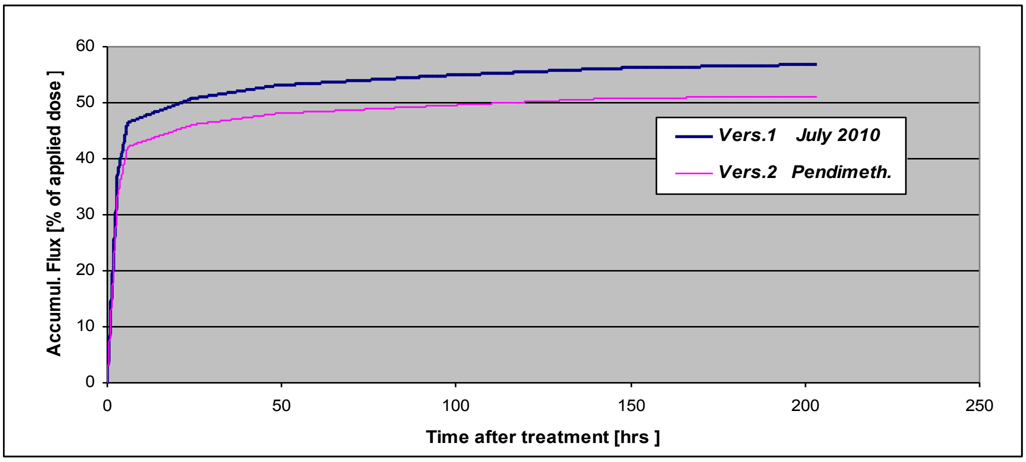

Fig.4.13 *The accumulated horizontal flux of* ***pendimethalin*** *(as a percentage of the applied dose) as a function of time after spraying in July 2010. More than 80 % of the total flux during the whole sampling period is accomplished after 6 hours.*

The corresponding time courses of the source strengths during this summer are shown in Figs. 4.14 - 4.15, illustrating the cases for fenpropimorph and pendimethalin.

A complete account of the normalized source strengths (q-values), both for the summer and autumn campaigns, with the resulting estimates from the two alternative versions of the respective concentration equation is given in *Appendix 3.* (Although these q-values are normalized with respect to the different applied doses, they are, naturally, still dependent on variations in other external factors such as prevailing weather conditions, type and state of surface/crop cover etc.)

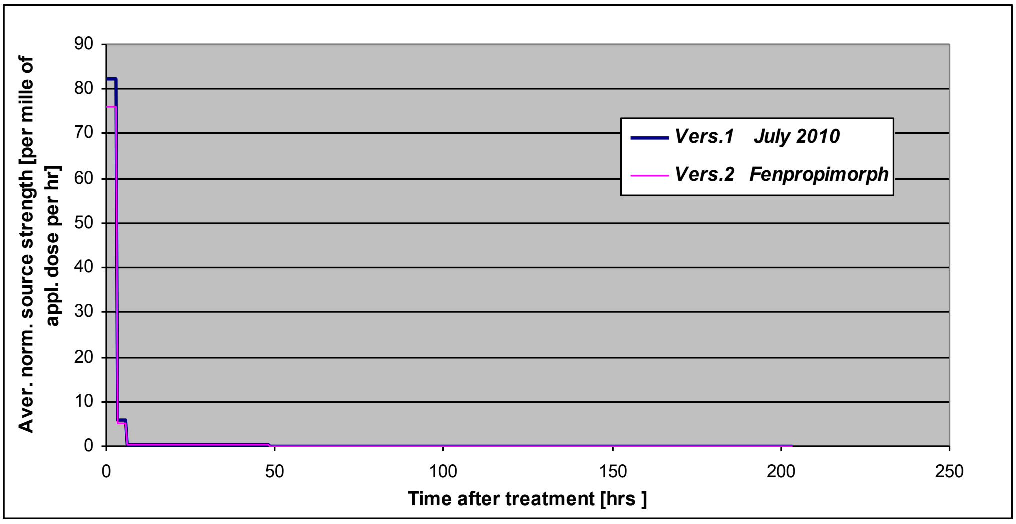

Figure 4.14 *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***fenpropimorph*** *during the seven consecutive sampling periods (~203 hrs in all) following treatment in July 2010.*

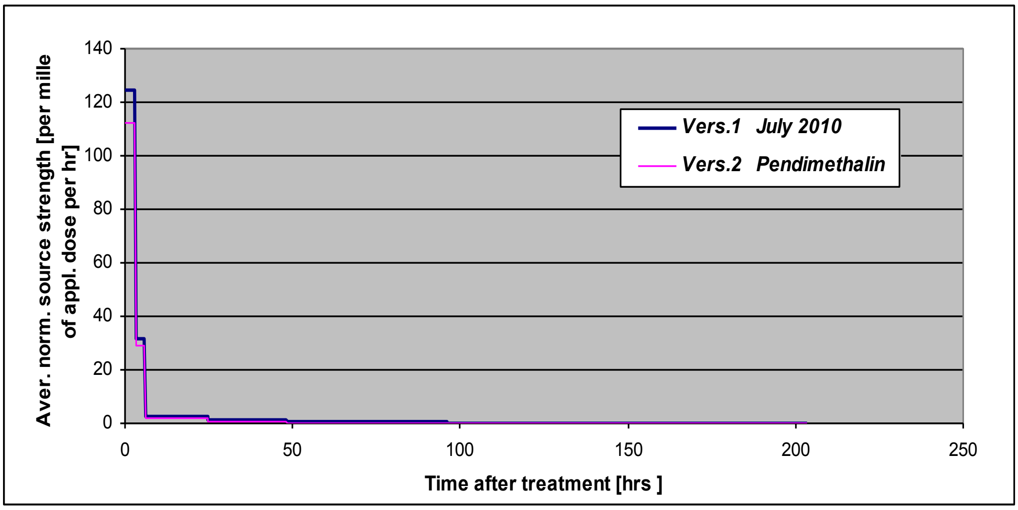

Figure 4.15 *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***pendimethalin*** *during the seven consecutive sampling periods (~203 hrs in all) following treatment in July 2010.*

When comparing the accumulated fluxes between the three years after a common elapsed time, say 24 hours, the influence of the varying, weather conditions may be illustrated. (The influence of the varying field doses between the years is already eliminated in Table 4.2 through the normalization of the accumulated fluxes to a unit dose for each substance and case.)
Thus, the accumulated flux after 24 hours increased moderately from the values in June 2008 to those in July 2009 for two of the pesticides (pirimicarb by ~17% and prosulfocarb by ~21%), and by ~130% for fenpropimorph (although from a very low value in this case). Pendimethalin showed no increase at all - possibly even a small decrease.
When comparing the fluxes between the campaigns in July 2009 and July 2010, respectively, the accumulated fluxes during the first 24 hrs after spraying an increase by a factor between ~2 (prosulfocarb) and almost 3 (pendimethalin) can be seen for four of the substances, and with a factor 4 in one case (fenpropimorph), but by merely 7 % in the case of lindane (although from an already high level in July 2009).

The most marked difference in the weather conditions during this 24-hr period between the three years is slightly higher mean air and surface temperatures in 2009 compared to 2008. In 2010 they were markedly higher than during both of the preceding years, in particular the surface temperature during most of the sampling periods, with average values above 30 ˚C during both period 1 and period 2. Wind speeds, on the other hand, were slightly higher in 2008 compared with both 2009 and 2010 – these latter years being quite similar in this respect. As already mentioned, all three summer campaigns passed without rain.

The number of hours with unstable stratification ($Ri_b(16\text{-}0.15m) < 0$) during the 24-hr periods considered was comparable in 2009 and 2010 (about 12 hrs each year) but with a lower average value (thus indicating more unstable conditions) during these hours in 2009 ($Ri = -0.091$) than in 2010 ($Ri = -0.039$). In June 2008 only ~6.5 hours of the 24 were unstable with an average $Ri_b = -0.10$ (thus comparable with the value in July 2009). As stated earlier, unstable stratification ($Ri < 0$) supports vertical turbulence and diffusion and thereby it should contribute to strengthen the volatilization flux. The situation in July 2009 should therefore, judging from the atmospheric stability only, be most favourable for a high evaporative flux. However, as it turned out, it appears more likely that the high temperatures in July 2010 were the dominating factor in determining the total fluxes.

The total accumulated flux after 7 days (168 hours) in July 2010 (the only of the summer campaigns with this duration) could be compared with the corresponding cumulative flux data given by Smit *et al.* (1998), based on an empirical relation between various published volatilization data and the vapour pressure of a great number of pesticides. These authors give the following estimates (in Annex 4, *ibid.)* for the cumulative volatilization flux from crops (in % of dosage) after 7 days:

Lindane 75% (the present study: 65%), pirimicarb 35% (present study: ~29%), tolclofos-methyl 100% (present study: 62.8%), prosulfocarb 7% (ours: ~66% (!)), fenpropimorph 50% (ours: ~29%) and pendimethalin 47% (our value: ~51-56%).

4.1.3 Autumnal conditions – volatilization from bare soil

During three autumn periods: 21-22/9 2008 (27.5 hrs), 18 - 26/9 2009 (~193 hrs) and 8 - 18/9 2010 (~232 hrs), the horizontal vapour fluxes from a sprayed bare soil, through the vertical "window" of unit width, were determined according to the same procedure described in *Sec. 4.1.2* for the summer campaigns.
The soil – a silty clay soil (see the table below) – was dressed with a disc cultivator, leaving an even but yet noticeably rough surface. The soil moisture conditions were markedly different between the three years. These varying moisture conditions will be discussed further in connection with the presentation of the results below.

Clay	***Fine silt***	***Coarse silt***	***Very fine sand***	***Sand***	***Sand***	***Coarse sand***	***Glowing loss***
d<0.002 [mm]	0.002-0.006	0.006-0.02	0.02-0.06	0.06-0.2	0.2-0.6	0.6-2	
49%	*12%*	*13%*	*15%*	*11%*	*0%*	*0%*	*8%*

The weather conditions during the three September-campaigns are summarized in Table 3.2 and in more detail in Appendix 1. The comparatively short experiment in 2008 was characterized by fairly low temperatures: the total average air temperature taken over both sampling periods (i.e. 27.5 hrs) at the height of 2m was just above 8˚C and the corresponding surface temperature almost the same (7.9˚C). Also the wind speeds were chiefly lower than during any of the following two years (average over both periods 0.9 ms^{-1}). The average solar radiation (R_{sol}) taken over the two periods was only about 50 Wm^{-2} which is well below normal averages for the second half of September at the latitude of Uppsala (the 10-year average for the period 2003-2012 over the days 16-30 in September at the nearby climate station at Ultuna campus is 93 Wm^{-2} for comparison).

The campaigns in September 2009 and 2010 were fairly similar regarding the temperatures with averages over the total sampling periods at the 2-m height of 12.3 (Sept. 2009) and 13.0 ˚C (Sept. 2010), respectively, and with similar average surface temperatures: 12.5 (2009) and 13.2 ˚C (2010), respectively. The average global radiation (taken over the total sampling time each year) was slightly higher in Sept. 2009 (105 Wm^{-2}) compared with that in 2010 (85 Wm^{-2}). (Note that the average radiation values encompass at least 50 % of dark night-time hours.) Wind speeds were mostly higher in Sept. 2009 compared to 2010, particularly during the two last, comparatively long periods 5 and 6. Regarding the relative humidity, Sept. 2008 and Sept. 2010 were very similar with overall averages around 87 % both years, whereas Sept. 2009 was less humid with an overall average humidity around of 70 %.

When it comes to precipitation, however, there were more significant differences between the years. The campaign in Sept. 2008 passed without any rain. In Sept. 2009 about 8 mm was recorded at a nearby site (< 1 km from the experimental site) towards the middle of sampling period 5 (~74 hrs from start). (A number of single 0.2-mm ´ticks´ from the tipping-bucket device at the experimental site in the last sampling period this year have been judged as spurious signals.) During the campaign in September 2010, the three last sampling periods achieved a total amount of rain of 20.6 mm, distributed over these three periods as follows: 0.2 mm (at the end of period 5, ~69 hrs after spraying), 1.4 mm (towards the end of period 6, ~117 hrs after spraying) and finally 19.0 mm distributed on several days in the last sampling period.

4.1.3.1 Concentration and flux profiles

Figures 4.16 – 4.17 below show some examples of the vertical profiles of concentration, wind speed and horizontal vapour flux from different sampling periods in September 2009 and 2010, respectively.
Fig. 4.16 shows the average profile for prosulfocarb from sampling period 3 in Sept. 2009, covering the period 7-24 hrs after the pesticide spraying.

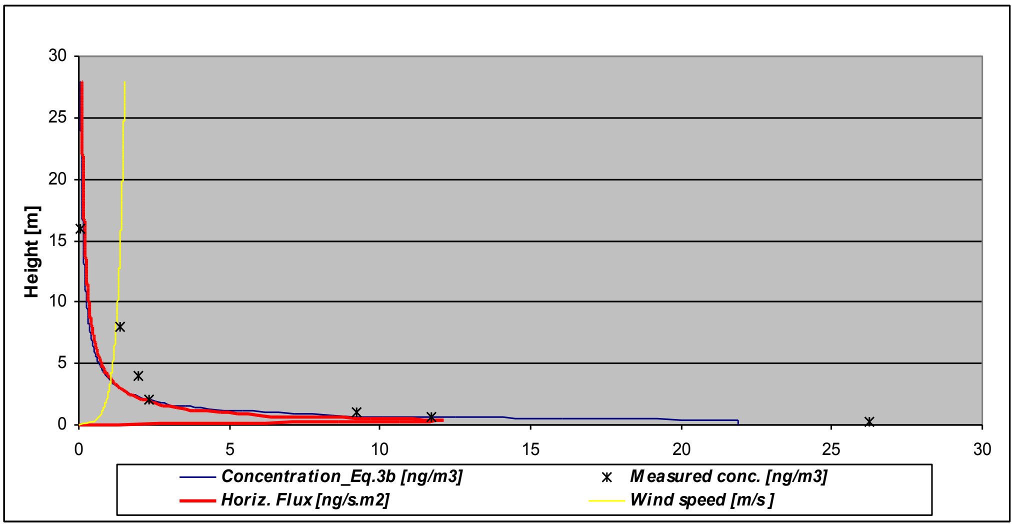

Fig.4.16 *Concentration, wind speed and flux profiles of* ***prosulfocarb*** *from period 3(7-24hrs after treatment) in September 2009. Height interval used for determination of the conc. equation is 0.25 to16 m (the deviating value at 8 m excluded), giving an* R^2*=0.938.*

The situation shown here may be compared with that shown in Fig. 4.1, also for prosulfocarb, but from a summer period, viz. period 3 (in that case 17-24hrs after treatment)
in June 2008. At this comparison it should be taken into account, that the scales for concentration and horizontal flux in Fig. 4.1 are in µg/m^3 and µg/s m^2, respectively, but in ng/ m^3 and ng/s m^2 in Fig. 4.16, and also that the applied dose of the substance was almost 17 times lower in Sept. 2009 (19 mg/m^2 versus 320 mg/m^2 in June 2008).

Keeping these differences in mind, it is clear that the maximum flux was more than a factor 50 greater in sampling period 3 in June 2008 than in the corresponding period in September 2009. Having accounted for the higher dose – by a factor 17 in the June -08 case – it still remains to explain the major part of the factor 50 between the summer and the September cases. Partly, this difference may most certainly be attributed to the much higher temperature during the summer episode, but probably also to a higher general readiness to evaporation from plant surfaces than from bare soil. Concerning the differences in weather conditions between the two cases, it can be noticed that the average surface temperatures during the respective periods differ markedly from each other: 23.7 ˚C in June-08 compared to 8.5˚C in Sept.-09. Also the average wind speed was significantly higher in June-08 (3.9 ms^{-1}) compared to Sept.-09 (just below 1 ms^{-1} at the 2-m level).

Fig. 4.17 below shows the average profiles for lindane from period 2 (4-7 hrs after treatment) in September 2009.

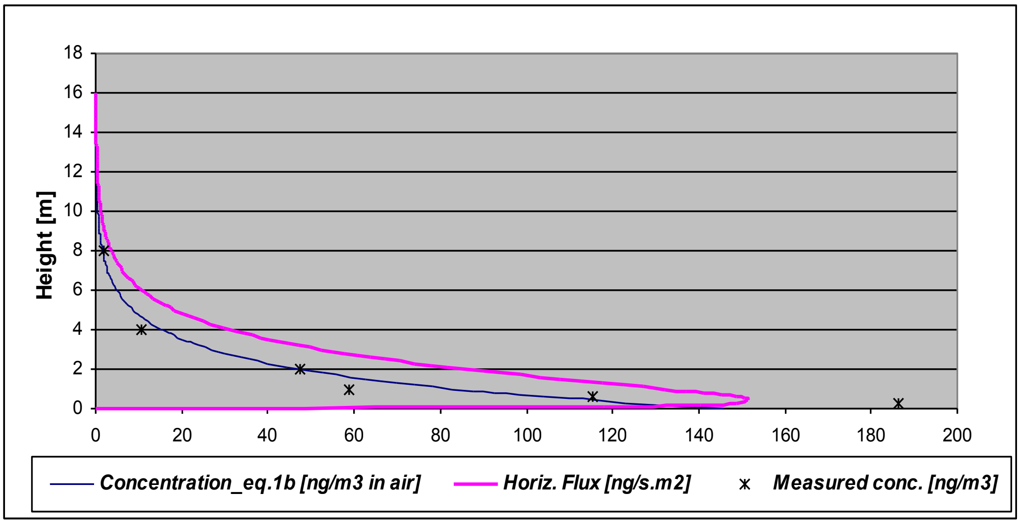

Figure 4.17 *Concentration and flux profiles of* ***lindane*** *from the second period in Sept. 2009. Height interval used for concentration equation is 0.25 to 8 m (giving an $R^2=0.969$).*

This case may be compared with that shown in Fig. 4.2 from sampling period 2 (4-7hrs after treatment) in July 2009. (In this case scales are equal and the applied dose in Sept. 2009 is 95% of that in July.) Also here the maximum flux is significantly lower in September compared to July but now with a factor about 0.5. The total accumulated flux, however, differ considerably more than the peak flux between the two seasons. Thus, the total flux during the first 12 hours after spraying was somewhere between 42 and 47 % of the applied dose in July 2009 but only 6.8 % in the September case.

Fig. 4.18 for fenpropimorph is taken from period 1 (0-3.5 hrs after treatment) in September 2009. Compared to the case shown in Fig. 4.3 for the same substance but for period 1 in June 2008 (which was the least “favourable” year as regards volatilization of the three summer campaigns) the two situations represent quite different volatilization behaviours Thus, the peak horizontal flux (at a height of about 1.5 m in the first case, Fig.4.3, and below 1m in the latter, Fig. 4.18), seems to be almost 50 times larger in the summer case, which also holds for the accumulated flux during 3 hours after the spraying (about 1.6 % of the applied dose in June 2008 versus 0.03% in Sept. 2009). (The field dose is almost 20% higher in Sept. -09 than that in June 2008.) It may be noticed, however, that the accumulated flux of fenpropimorh appears to have been exceptionally small, at least during the first 48 hours in Sept. -09, even when compared with the other two autumn campaigns (cf. Table 4.4).

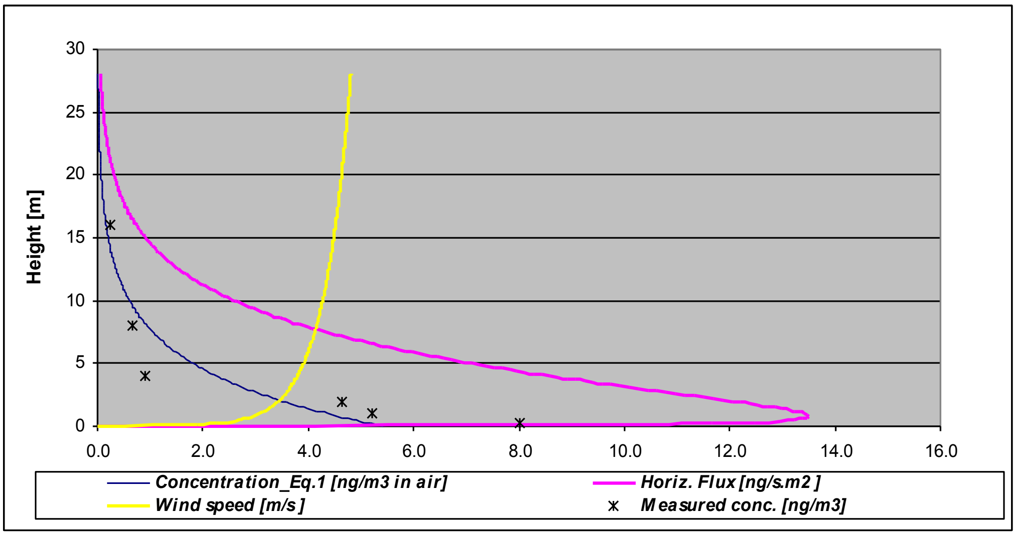

Figure 4.18. *Concentration, wind speed and horizontal flux profiles of* ***fenpropimorph*** *from period 1, September 2009. Height levels used for the concentration equation is 0.25 to16 m (giving an* R^2*=0.860). Note the need for extension of the integration range well above the 16-m level.*

Figure 4.19 shows the average concentration and horizontal flux profiles for pirimicarb from the first sampling period (0-3 hrs) in September 2010. The fit of the concentration equation (of the expected exponential form) to measured values is quite good (R^2 =0.98), even including the 16-m level. However, to acquire a comparably good fit in many of the subsequent periods, the second type of equation: ln (c) = a+b· ln(z) was preferred – unless the16-m level value was rejected.

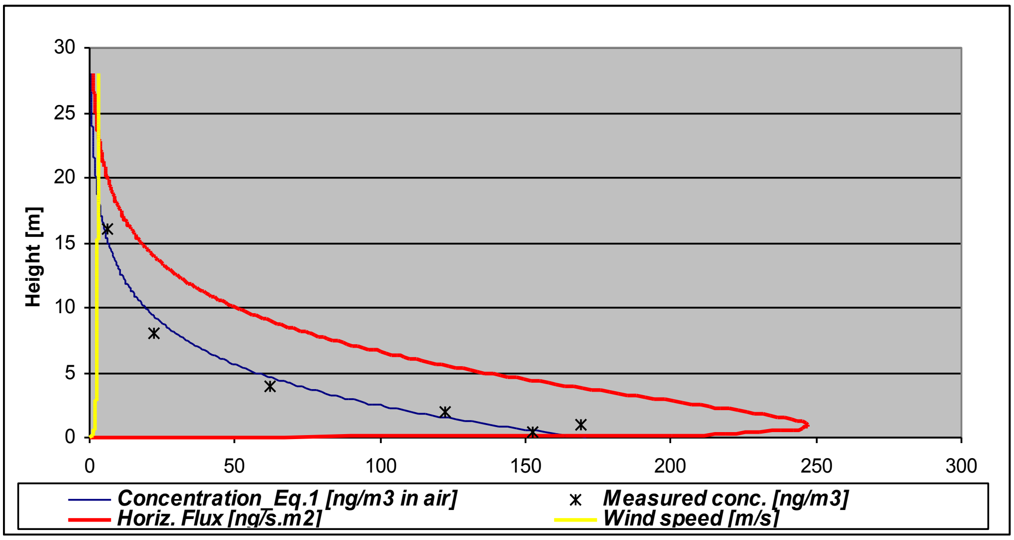

Figure 4.19. Concentration, wind speed and horizontal flux profiles of ***pirimicarb*** *from period 1, September 2010. Height levels used for the concentration equation is 0.4 to16 m (giving an* R^2*=0.978). Note the need for extension of the integration range well above the 16-m level.*

Figures 4.20 - 4.21, finally, give a pair of examples for pendimethalin from the first (0-3 hrs) and last (7th) period (120-233 hrs after spraying), respectively, in September 2010.

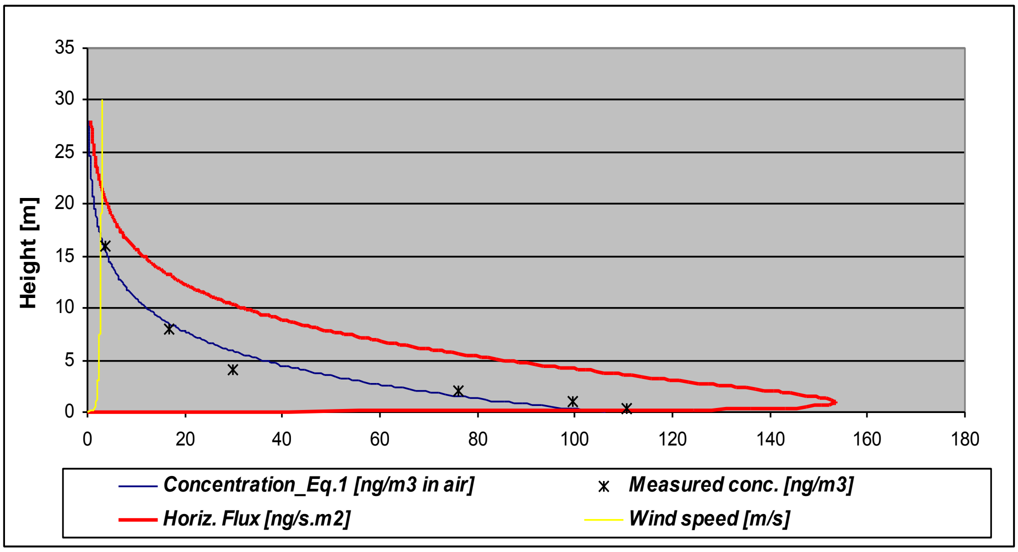

Figure 4.20. Concentration, wind speed and horizontal flux profiles of ***pendimethalin*** *from period 1 (0-3hrs), September 2010. Height levels used for the concentration equation is 0.4 to16 m (giving an* R^2*=0.972). Note the need for extension of the integration range well above the 16-m level.*

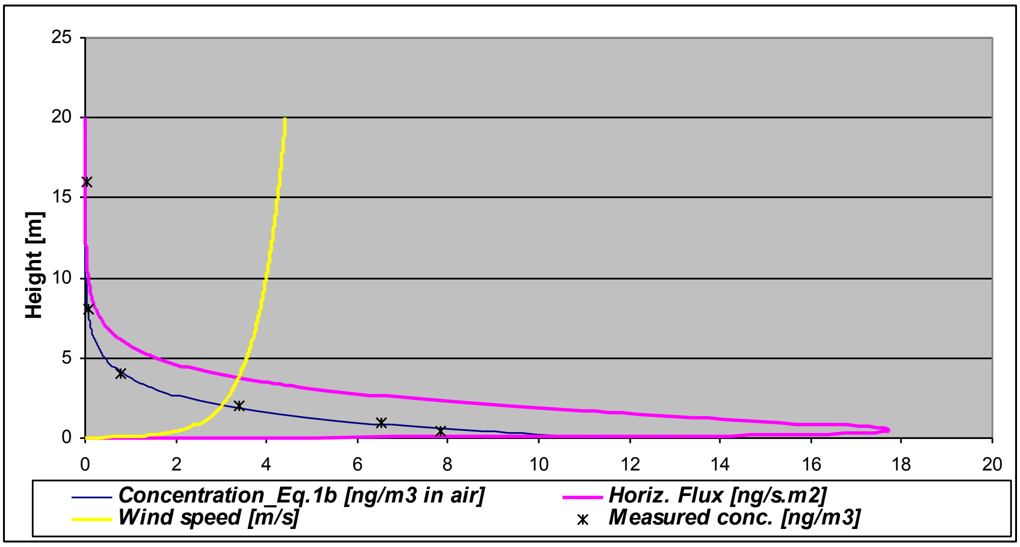

Figure 4.21. *Concentration, wind speed and horizontal flux profiles of* ***pendimethalin*** *for period 7 (120-232hrs), September 2010. Height levels used for the concentration equation is 0.4 to 8 m (giving an R^2=0.998).*

The fit of the concentration equation to measured values is quite good in the first case (including the 16-m level) and very good in the second ($R^2=0.998$) when omitting the 16-m level value. The goodness of fit decreased markedly, however, if the 16-m level concentration was included. This very good fit in the latter case may appear astonishing and remarkable having both the very long sampling time in mind, and also the advanced stage after the treatment (this period begins 5 days after the spraying was finished, and lasted for almost a further 5 days).
As can also be seen, although there is a very pronounced decrease of the horizontal flux between the two periods (the peak flux has decreased with almost a factor 10), there is still a quite substantial average flow going on also during this late period and in fact about as much as 33 % of the total accumulated flux during all of the seven sampling periods (i.e. ~232 hours) occurred during this last sampling period.

The evolution over time of the vaporization fluxes will be discussed in more detail in the following section.

4.1.3.2 Accumulated horizontal flux over time

Table 4.4a-b shows the calculated, accumulated horizontal fluxes during different elapsed time intervals during the three autumn campaigns, and as before, according to two alternative determinations – Vers.1 and Vers.2 – of the underlying concentration equations.
According to these results, the relative order of magnitude of the accumulated fluxes of the 6 pesticides (whether after the first 24 hrs or during the whole measuring period) was as follows: Lindane > tolclofos-methyl > prosulfocarb >pendimethalin >fenpropimorph >pirimicarb (with a possible exception for fenpropimorph). The extremely low flux values for fenpropimorph in

September 2009 – particularly until 48 hrs from start – may appear somewhat puzzling and might be questionable for some, not identified reason, but also pirimicarb showed a very small flux during these first 48 hrs. A possible reason for this behaviour could possibly be find in the soil moisture conditions during this campaign, with some rain falling about 60 hrs (in sampling period 5) after the treatment, as will be discussed further below.

Table 4.4a Relative accumulated horizontal flux of a substance for different time intervals after spraying, expressed as a *percentage of the applied field dose* – **the autumn campaigns**.(Vers.1 and Vers.2 corresponds to the two alternative choices of conc. equation; see p.29).

Pesticide: ***Lindane***		**Sept. 21-22 2008**			**Sept. 18-26 2009**			**Sept. 08-18 2010**		
Elapsed Time [hrs]		Conc. Equat. Altern:	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs						*3.79*	*3.42*		*7.99*	*6.73*
0-6 hrs						*5.75*	*5.21*		*10.3*	*9.00*
0-12						*6.76*	*6.48*		*12.6*	*11.0*
0-24						*8.16*	*8.56*		*17.2*	*15.0*
0-48						*10.7*	*10.4*		*21.4*	*19.5*
0-96						*27.2*	*26.9*		*28.7*	*26.1*
0-168						*31.8*	*31.3*		*34.9*	*32.8*
Whole period						*33.3* **(192.7hrs)**	*32.8*		*38.9* **(232.4hrs)**	*38.2*

Pesticide*:* ***Pirimicarb***		**Sept. 21-22 2008**			**Sept. 18-26 2009**			**Sept. 08-18 2010**		
Elapsed Time [hrs]		Conc. Equat. Alternat:	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs			*0.055*	*0.047*		*0.074*	*0.040*		*0.64*	*0.56*
0-6 hrs			*0.110*	*0.093*		*0.101*	*0.057*		*0.77*	*0.72*
0-12			*0.219*	*0.186*		*0.107*	*0.063*		*0.84*	*0.78*
0-24			*0.380*	*0.331*		*0.112*	*0.069*		*0.97*	*0.88*
0-48						*0.118*	*0.076*		*1.02*	*0.94*
0-96						*0.161*	*0.122*		*1.14*	*1.06*
0-168						*0.177*	*0.133*		*1.21*	*1.12*
Whole period			*0.41* **(27.5hrs)**	*0.36*		*0.18* **(192.7hrs)**	*0.14*		*1.24* **(232.4hrs)**	*1.15*

Pesticide: ***Tolclofos-methyl***		**Sept. 21-22 2008**			**Sept. 18-26 2009**			**Sept. 08-18 2010**		
Elapsed Time [hrs]		Conc. Equat. Alternat:	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs						*1.10*	*0.73*		*3.05*	*2.65*
0-6 hrs						*1.62*	*1.12*		*3.95*	*3.57*
0-12						*1.85*	*1.38*		*5.19*	*4.53*
0-24						*2.12*	*1.79*		*7.65*	*6.43*
0-48						*2.75*	*2.26*		*9.59*	*8.63*
0-96						*11.9*	*12.8*		*13.2*	*12.2*
0-168						*14.5*	*15.4*		*16.4*	*14.9*
Whole period						*15.4* **(192.7hrs)**	*16.3*			*16.9*

Table 4.4b Relative accumulated horizontal flux of a substance for different time intervals after spraying, expressed as a *percentage of the applied field dose* – **the autumn campaigns**. (Vers.1 and Vers.2 corresponds to the two alternative choices of conc. equation; see p.29).

Pesticide: ***Prosulfocarb***		**Sept. 21-22 2008**			**Sept. 18-26 2009**			**Sept. 08-18 2010**		
Elapsed Time [hrs]		Conc. Equat. Altern:	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs			*0.65*	*0.60*		*0.92*	*0.74*		*2.90*	*1.97*
0-6 hrs			*1.30*	*1.20*		*1.49*	*1.35*		*2.97*	*2.62*
0-12			*2.60*	*2.41*		*1.68*	*1.62*		*3.87*	*3.41*
0-24			*6.10*	*5.65*		*1.80*	*1.83*		*5.65*	*5.00*
0-48						*2.02*	*2.02*		*7.12*	*6.60*
0-96						*7.66*	*8.00*		*9.34*	*8.97*
0-168						*11.8*	*12.1*		*11.2*	*11.1*
Whole period			*7.35* **(27.5h)**	*6.79*		*13.2* **(192.7h)**	*13.5*		*12.6* **(232.4h)**	*12.8*

Pesticide: ***Fenpropimorph***		**Sept. 21-22 2008**			**Sept. 18-26 2009**			**Sept. 08-18 2010**		
Elapsed Time [hrs]		Conc. Equat. Alternat:	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs			*0.16*	*0.11*		*0.030*	*0.028*		*1.04*	*0.85*
0-6 hrs			*0.32*	*0.23*		*0.039*	*0.037*		*1.30*	*1.09*
0-12			*0.63*	*0.45*		*0.041*	*0.039*		*1.48*	*1.24*
0-24			*1.16*	*0.82*		*0.043*	*0.042*		*1.85*	*1.53*
0-48						*0.053*	*0.052*		*2.05*	*1.76*
0-96						*0.380*	*0.372*		*2.35*	*2.05*
0-168						*0.421*	*0.411*		*2.52*	*2.21*
Whole period			*1.29* **(27.5h)**	*0.90*		*0.43* **(192.7h)**	*0.42*		*2.64* **(232.4h)**	*2.33*

Pesticide: **Pendimethalin**		**Sept. 21-22 2008**			**Sept. 18-26 2009**			**Sept. 08-18 2010**		
Elapsed Time [hrs]		Conc. Equat. Alternat:	***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***		***Vers.1***	***Vers.2***
0-3 hrs			*0.24*	*0.22*		*0.83*	*0.54*		*1.87*	*1.68*
0-6 hrs			*0.48*	*0.44*		*1.15*	*0.79*		*2.42*	*2.21*
0-12			*0.96*	*0.88*		*1.21*	*0.86*		*3.08*	*2.77*
0-24			*2.51*	*2.36*		*1.24*	*0.92*		*4.40*	*3.89*
0-48						*1.33*	*0.99*		*5.51*	*5.12*
0-96						*6.68*	*7.25*		*7.80*	*7.34*
0-168						*8.57*	*8.89*		*10.0*	*9.40*
Whole period			*3.11* **(27.5h)**	*2.94*		*9.20* **(192.7h)**	*9.44*		*11.7* **(232.4h)**	*11.1*

This is roughly the same order as for the summer experiments with two exceptions: during the summer conditions (with volatilization from a standing crop) pirimicarb seems generally to have a higher accumulated flux than fenpropimorph, and prosulfocarb tended to slightly exceed tolclofos-methyl in this respect.
This ordering of the pesticides regarding apparent disposition for volatilization may be compared with their respective physical-chemical properties. Taking the vapour pressure (at 25 ˚C) first, it is found that Lindane, which according to the findings above showed the highest vapour flux during both summer and autumn conditions, also has the highest vapour pressure (cf. Table 4.3) whereras pirimicarb, which showed the least accumulated flux within a given time period during the autumn experiments, and the second least during the summer conditions, also has the lowest vapour pressure. On the other hand, prosulfocarb, which according to our findings is among the more volatile of the 6 pesticides, especially during summer conditions, has the second lowest vapour pressure, whereas fenpropimorph with a vapour pressure not far from that of lindane (3.9 mPa versus 4.4 mPa for lindane) exhibited the lowest (during summer conditions) or second lowest (autumn conditions) flux among the six substances investigated.
Regarding the magnitudes of Henry´s constant (at 20 ˚C) according to data from PPDB (Table 4.3) two of the pesticides have values at least two (pendimethalin) or three (tolclofos-methyl) order of magnitude greater than the rest of them; three have fairly similar values (lindane, fenpropimorph and prosulfocarb) whereas pirimicarb has a value, two orders of magnitude lower than the group just mentioned (and thus five orders of magnitude lower than tolclofos-methyl).
It may be noticed, that pirimicarb, with a very low Henry's constant (referring e.g. to the form given for 20 ˚C in Table 4.3), also showed very low fluxes, whereas tolclofos-methyl, with a very high Henry´s constant, showed a comparatively high flux during the Sept. -09 and Sept.-10 experiments. On the other hand, lindane with a much lower Henry´s constant than tolclofos-methyl, showed at least twice as high flux in a given time than tolclofos-methyl as well in Sept.-09 as in Sept.-10.

When comparing the accumulated fluxes after given time intervals between the three September campaigns, some striking features will be evident. Thus, when comparing the accumulated fluxes after 24 hrs from spraying, it seems obvious that for all of them (possibly with the exception for prosulfocarb) the highest fluxes occurred during the September 2010 campaign when these 24-hr values mostly are about 1.5 to 2.5 times as high as during September 2008 and with the September 2009 values even lower (cf. Table 4.4). Thus, the September 2010 24-hr values are typically around 2 to almost 4 times larger than the corresponding fluxes from 2009 with significant exceptions for pirimicarb, for which the 24-hr flux is almost 9 times higher in 2010 than in 2009, and fenpropimorph, whose extremely low value (0.043 %) in 2009 is about 35 times lower than that determined for 2010 (taking the lowest alternative, 1.53%, for 2010). (However, the extremely low flux values for fenpropimorph during at least the first 48 hrs in September 2009 might possibly be questionable, as mentioned before.)

These patterns regarding the differences in magnitude of the accumulated fluxes during 24 hrs between the three years seems only partly in concordance with the corresponding differences in the general weather conditions during the respective

24-hr periods. Thus, it seems quite reasonable that the largest fluxes are found in September 2010 which had the highest first 24-hr average values for both the 2-m air temperature and the surface temperature ($T(2)$ =13.5 ˚C and T_{surf}= 13.7 ˚C) as well as for wind speed at 2-m height ($\bar{u}(2)$ =1.7 m/s) among these years. However, the second highest values regarding these variables occurred in September 2009: $T(2)$ =10.4 ˚C, T_{surf}= 11.0 ˚C and $\bar{u}(2)$ =1.4 m/s, respectively, and the markedly lowest averages during this 24-hr period in September 2008: $T(2)$ =7.2 ˚C, T_{surf}= 6.9 ˚C and $\bar{u}(2)$ =0.78 m/s. Average solar insolation (R_{sol}) and relative humidity (RH) were fairly equal during these 24 hours in 2009 and 2010 (around 100-110 Wm^{-2} and just above 80%, respectively), whereas in September 2008, the average insolation was about half of that (47 Wm^{-2}). The average relative humidity was slightly higher (RH=90%) in September 2008.

Thus, September 2008 might seem to be the least ´favourable´ for a high volatilization, only considering the general weather variables mentioned above (no precipitation occurred during the first 24 hours in any of the years). There are, however, two other factors that most probably are important for the volatilization and vertical diffusion process in this case, viz. the atmospheric stability and the soil moisture conditions.
To quantify the atmospheric stability a bulk Richardson-number, determined for to different height layers, has been used in this study: 0.15 to 16 m, ($Ri_B(16\text{-}0.15)$) and a more shallow layer, reaching from the "surface" (either the top of the crop canopy or the ground surface, depending on the season) to the height of 2 m (Ri_B(2-surf.)). In the table 4.5 below these Ri-numbers are given for the first 24 hrs after spraying during the three September occasions discussed.

Table 4.5 *Selected data on the atmospheric stability, expressed as Ri-number calculated as averages for the first 24 hrs after spraying during the campaigns in 2008, 2009 and 2010 and for two different height intervals.*

	Sept. 2008	***Sept. 2009***	***Sept. 2010***
Ri_B (16-0.15); 24 hrs	0.98	1.6	0.53
Ri_B (16-0.15); ***daytime hrs***	-0.15	-0.08	-0.027
Ri_B (2-surf.); 24 hrs	0.12	0.020	0.009
Ri_B (2-surf.); ***daytime hrs***	-0.070	-0.032	-0.0022

As is obvious from the table, the Ri-number is height dependent but let us confine the comparison to the lower layer (0-2 m). When comparing the full 24-h periods it is evident that Sept. 2008 had the largest positive value (0.12), which implies the most stable stratification (and therefore presumably most unfavourable for turbulent diffusion) and 2010 the least positive, indicating near neutral stability. However, comparing the averages taken over the daytime periods only, it is obvious that September 2008 also has the largest negative Ri-value (-0.070) implying the most *unstable* daytime period of the three, thus implying the most favourable conditions (in this respect) for turbulence and vertical diffusion.

The other and possibly even more important factor is the soil moisture conditions. It has been claimed by many authors (e.g. *Glotfelty et al., 1984,* Ferrari *et al., 2003, Prueger et al., 2005, Yates, 2006, Schneider et al., 2013*) that a moist soil surface,

seems to enhance volatilization of pesticides from a bare soil. In the present study, we have soil moisture determinations from Sept. 2009 and Sept. 2010 only. These indicate that the topsoil in Sept. -09 was comparatively dry at the beginning and at the end of the experiment with average moisture content in the upper few centimetres at these times around 17-18 %, but with a marked increase a few days into the experiment as will be discussed further below. In Sept. 2010, on the other hand, the moisture content of the topsoil layer increased gradually during the experiment, from about 27 % on the 8th of September, to about 34 % on the 15th, roughly in the middle of the last sampling period this year. (Note that the soil moisture values given here and further on are the *gravimetric* water contents, expressed as percent of the mass *of the dry soil*).
Regarding the situation in September 2008, with no precipitation during the two days of measurements, we can only speculate. One assumption could be that the soil moisture might have been rather high also this year, based on the fact that the previous month (August) this year was rainy, with a total amount of ~127 mm at the regular climate station at Ultuna some 9 km W of our experimental site. However, a fact that points in the opposite direction is that the major part (~ 97 mm) of this amount fell during the first half of August, and in fact, during the ten day period preceding the onset of the measurements on September 21st practically no rain was recorded at that station. Therefore, the soil surface – even after a good share of rain the month before – would probably have dried up before the onset of our measurements.

The pronounced difference in the observed flux during 24 hrs between the years 2009 and 2010 decrease markedly, however, when the accumulated flux after 168 hrs (7 days) are compared (in 2008 the total sampling time was only 27.5 hrs). The cumulative values are then almost equal between these two years for four of the pesticides (though still with a tendency to slightly higher values in 2010, except for prosulfocarb). Only in the case of the two weakly evaporating pesticides pirimicarb and fenpropimorph a striking difference remains between 2009 and 2010, with total accumulated, relative fluxes after 168 hours that are at least a factor 6 to 7 times larger in 2010 compared to 2009 (cf. Tables 4.4a-b).
The general weather conditions during the additional six days of this longer period (i.e. the period after the first 24 hrs discussed above) are summarized in Table 4.6 below.

Table 4.6 *Average and maximum values of selected weather variables for the six day period following after the first 24 hrs after spraying during the campaigns in 2009 and 2010*

	$T(2m)$ [˚C]	***T_{surf}*** [˚C]	***R_{sol}*** [W/m^2]	***$\bar{U}(2m)$*** [m/s]	***RH*** [%]	***P*** [mm]
Mean 144 hrs 19/9-25/9 2009	12.2	12.3	97	3.8	79	(~8)[1]
Maximum over same period	20.4	21.5	654	10.2	99	
Mean 144 hrs 9/9-15/9 2010	13.8	14.0	76	2.4	89	8.8
Maximum over same period	20.7	21.3	483	6.8	99.5	

[1] At a nearby station, < 1km from the experimental site (see further commentary in the text)

Selected data regarding the atmospheric stability are given in Table 4.7. The information of the Ri-number averaged over long periods (especially over several days as here) is certainly of rather limited value as unstable periods during daytime hours will be outweighed by stable periods during the nights, tending to give over all averages close to zero, as the example for ***Ri_B* (2-surf.)** over the whole 144-hr period shows. The average taken over all daylight hours during the period, however, may possibly be of more guidance, partly because it is assumed that a major part of the volatilization flux occurs during these, mostly unstable, parts of the day (even though the problem of smoothing out the finer details of the time course of the stability conditions by averaging over (still) quite long periods remains).

Table 4.7 *Selected data on the atmospheric stability: average bulk Ri-number calculated for the six day period following after the first 24 hrs from spraying during the campaigns in 2009 and 2010 and for two different height intervals.*

	Sept. 19-25 2009	***Sept. 09-15 2010***
Ri_B* (16-0.15)**; *mean* - ***daytime hrs	-0.018	-0.032
Ri_B* (2-surf.)**; *mean* - ***144 hrs	0.003	0.001
Ri_B* (2-surf.)**; *mean* - ***daytime hrs	-0.0062	-0.0075

Thus, it is seen (Table 4.6) that mean temperatures, at a height of 2m as well as at the surface, were somewhat higher in 2010 compared to 2009 during this 144-hr period, even if the differences are smaller than during the first 24-hr period after spraying, while the average solar radiation (R_{sol}) were slightly higher in Sept. 2009. The wind speed at 2m was also higher in 2009 during this longer period.

Regarding precipitation, unfortunately the precipitation gauge (a tipping - bucket device) was malfunctioning at the time of the 2009 experiment, giving probably spurious signals to the logger, but at a nearby agricultural research station (about 1 km from our experimental site) a total amount of 8 mm rain was received during the night between the 20th and 21st of September (i.e. during the early stage of our sampling period 5, about 60 hrs after spraying). The very marked increase in the moisture content of the soil surface layer in the samples taken in the morning of the 21st – to an average above 33 % compared to just below 18 % at the onset of the sampling in period 1 – also confirms that the experimental site has got a good share of rain at this time.

During the September 2010 campaign 0.2 mm of rain was recorded during sampling period 5 (48-71 hrs from start), 1.4 mm during period 6 (~71-120 hrs) and 19 mm during period 7 (~120-243 hrs after spraying), of which 8.8 mm came within the first 168 hours and 11.8 mm during the last ~75 hrs of period 7. This is concordant with the gradual increase in soil moisture content determined during the course of the Sept. 2010 experiment mentioned earlier – but from a value that was higher than those found during 2009 already before the onset of the precipitation on the morning of the 11th of September.

Also when considering the differences in stability conditions (expressed as Ri-numbers, Table 4.7) data seem to indicate slightly more favourable conditions for volatilization in Sept. 2010. Thus the average Ri-numbers, when taken as means over daytime hours – irrespective of which of the two height intervals that is considered – show more negative values in 2010 indicating somewhat more unstable conditions this year. However, the differences are quite small and particularly the Ri-numbers for the lower layer (Ri_B (2-surf.)), are both of them close to zero, which implies a rather weak instability (i.e. close to neutral) on the average.

4.1.3.3 Time course of the source strengths and the accumulated volatilization fluxes

The graphs 4.22-4.24 show the average source strengths for some of the pesticides for the six separate sampling periods in September 2009.

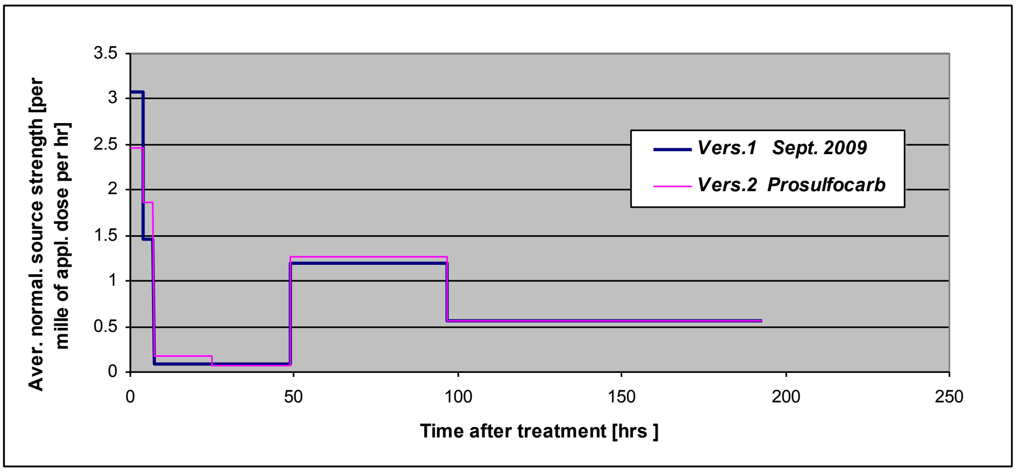

Figure 4.22 *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***prosulfocarb*** *during the six consecutive sampling periods (~193 hrs in all) following treatment in September 2009.*

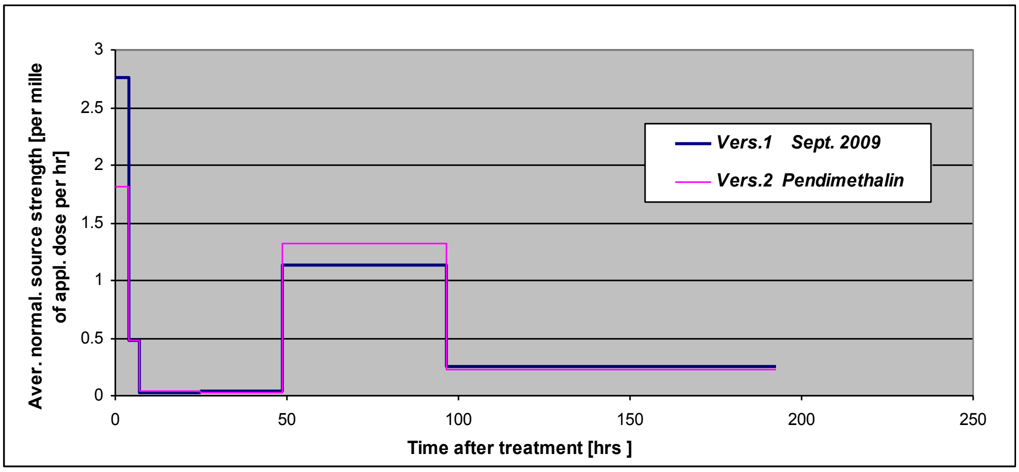

Figure 4.23 *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***pendimethalin*** *during the six consecutive sampling periods (~193 hrs in all) following treatment in September 2009.*

In the last period but one (period 5, lasting between 49 and 96 hrs from start) there is a striking increase of the source strength in the first two figures. This marked rise is also present in the corresponding graphs (though not shown here) for lindane, tolclofos-methyl and fenpropimorph. Also in the case of pirimicarb (Fig. 4.24) there is an increase but very less pronounced. In fact, the calculated source strength in period 5 for pirimicarb is about 3.7 times higher than in the previous period, whereas this relation in the case of prosulfocarb (Fig. 4.22) is somewhere between 13 and 16 times greater (depending on which of the two alternatives of concentration equation is used), and for pendimethalin – which showed the largest relative increase of all – this increase was at least a factor 30 according to vers.1 (and even larger in vers.2). This latter fact may suggest that pendimethalin is particularly strongly adsorbed to the soil when the surface is dry. The least relative increase from period 4 to period 5 showed lindane and pirimicarb (cf. Appendix 3d, which also shows the quotients for the source strengths between per.5 and per.4 in Sept. 2009).

As mentioned above, the soil surface was fairly dry at the beginning of the experiment in Sept. -09 with an average moisture content in the upper few centimetres around 17.5 % (by weight) in the morning of the 18th which then increased markedly to about 34 % in the morning (9:00 a.m.) of the 21st, and thereafter decreased again to 18 % in the morning of the 26th (a few hours before the end of the last sampling period).

It should be noted, that several of the pesticides used in the present study both under summer and autumn conditions, are not normally applied on bare soil. One of them is pirimicarb, but this substance has been included in the present comparison because of its very high water solubility compared with any of the other substances (conf. Table 4.3). This high water solubility combined with a rainfall might have resulted in increased “washout” of pirimicarb followed by percolation into deeper soil layers and thus counteracting a strong increase of the evaporative flux compared to the other, less soluble, substances.

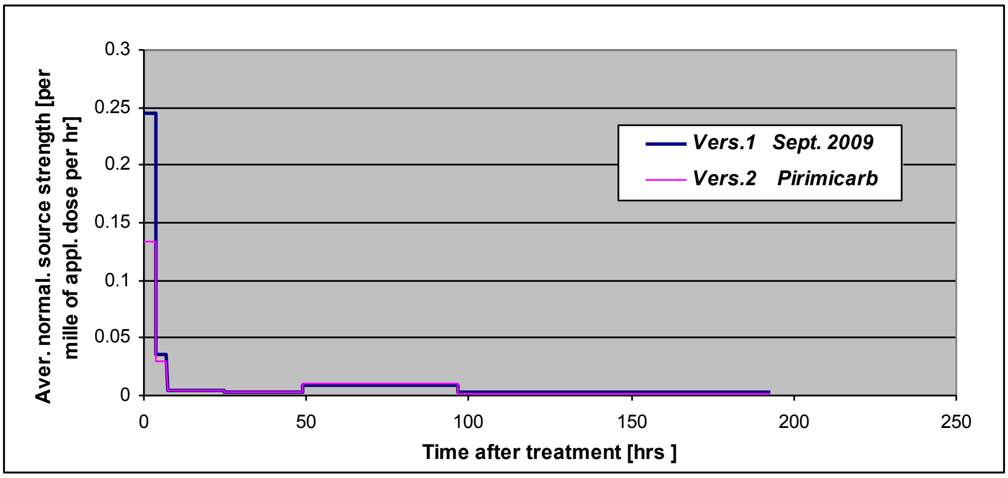

Figure 4.24 *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***pirimicarb*** *during the six consecutive sampling periods (~193 hrs in all) following treatment in September 2009.*

When it comes to September 2010, the course of volatilization appears somewhat different.

The corresponding graphs showing the seven sampling periods in September 2010 do not show any such striking rise in the source strength (q) during any of these

periods, as is illustrated by the examples below, Fig.4.25 - 4.27. Certainly, there is a tendency to an increase from period 4 to period 5, after ~50 hrs from start, in the case of four of the substances: pendimethalin, pirimicarb, tolclofos-methyl and fenpropimorph (the latter two not shown here), whereas prosulfocarb and lindane show a small decrease. This increase is mostly rather small – in relative terms between 9 and 19 % in three of the cases. Only pirimicarb showed a a larger increase (about 55 %) but then from a very low value of 0.02 ‰ of applied dose/hr in period 4. The rather small increase which is observed in the case of four of the substances this year may either be the result of a slightly higher temperature, a greater atmospheric instability in period 5 (the daytime average for the lower layer, Ri_B(2- surf), was -0.016 in per.5 vs. -0.004 in per.4), the very small amount of rain (~ 0.2 mm) recorded towards the end of period 5 may, or merely variations within the margins of error. The small amount of rain (~ 0.2 mm) might thus have had a similar, though much less pronounced, effect on the volatilization as that assumed to be responsible for the very marked increase observed in Sept. -09. The much smaller effect in 2010 should then be due to the higher soil moisture content already before this rain, compared to case in Sept. 2009.
Regarding the precipitation and soil moisture conditions during the Sept. 2010 campaign, it has already been mentioned that the moisture content of the surface soil were markedly higher during the entire experimental period this year: starting with a moisture content in the upper ~2- 4 cm layer of the soil around 27 % in the afternoon of the 8th, increasing to ~29.5 % (at 14:00 p.m. the 14th, i.e. about 24 hours into the last period 7) and even higher (~34 %) on the 15th of September, roughly in the middle of the long last period (112 hrs in total). On the 11th 9:00-9:30 a.m., 2 hours before the end of period 5, 0.2 mm of rain was recorded at the experimental site. At this time, the soil surface might possibly have dried up to some extent from the value of 27% determined about 2.5 days earlier at the onset of the sampling. Therefore, even this small amount of rain might have led to a certain rewettening of the topsoil layer. (As before, soil moisture values are the mass wetness in percent of the dry soil.)

(In reality, of course, the transitions of the source strength between subsequent periods is *not stepwise* as shown in the graphs above, but continuous and with gradual variations within each period - particularly in the cases with long sampling periods. The source strengths presented are just the *time averages* over each sampling period.)

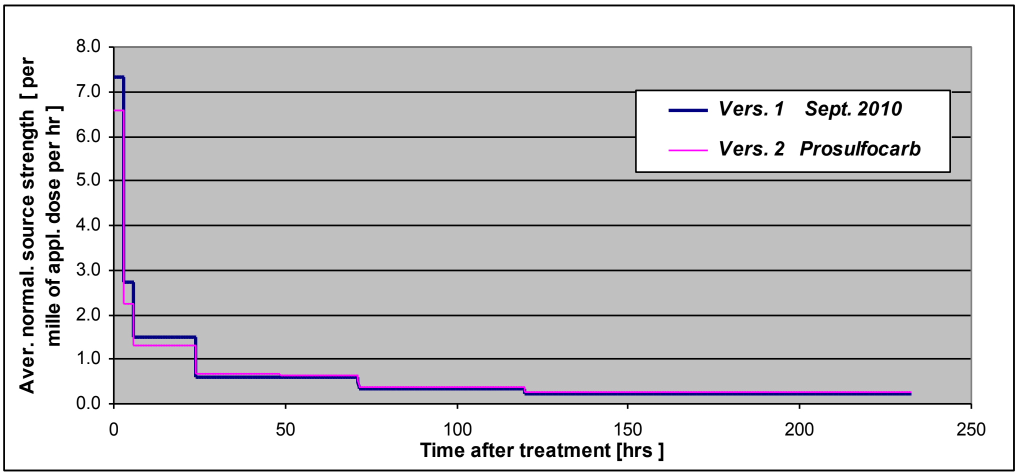

Figure 4.25 *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***prosulfocarb*** *during the seven consecutive sampling periods (~232 hrs in all) following treatment in September 2010.*

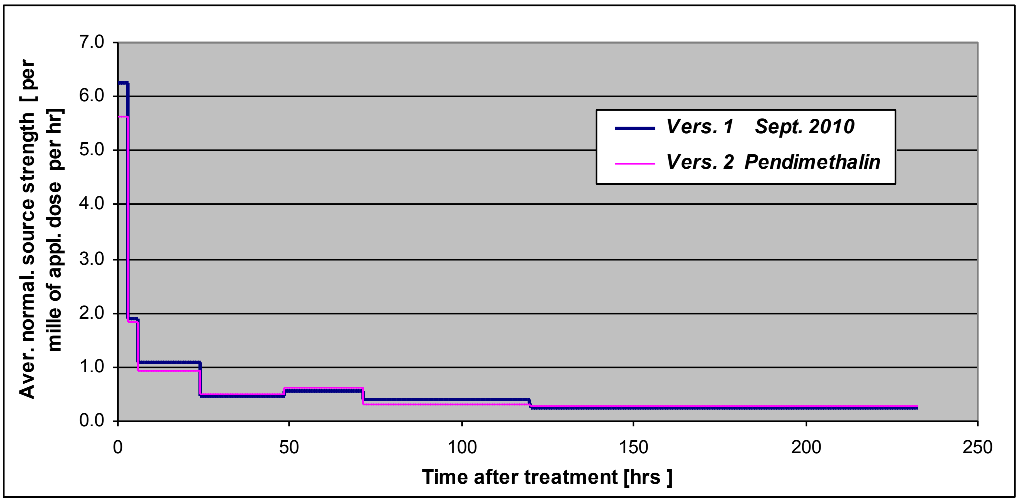

Figure 4.26 *Average normalized source strengths - expressed as per mille of the applied dose per hour - for pendimethalin during the seven consecutive sampling periods (~232 hrs in all) following treatment in September 2010.*

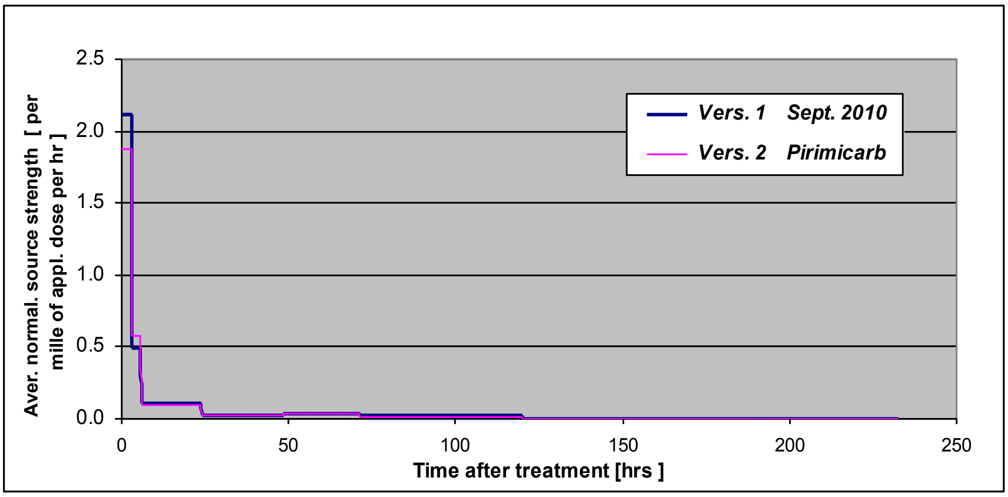

Figure 4.27 *Average normalized source strengths - expressed as per mille of the applied dose per hour - for* ***pirimicarb*** *during the seven consecutive sampling periods (~232 hrs in all) following treatment in September 2010.*

These differences between the years may also be demonstrated by the graphs over the time course of the accumulated horizontal fluxes. In figs. 4.28-4.29 for Sept. 2009 the increase in the flux rates after about 48 hrs (in period 5) is evident (at least in the case of the more volatile compounds).

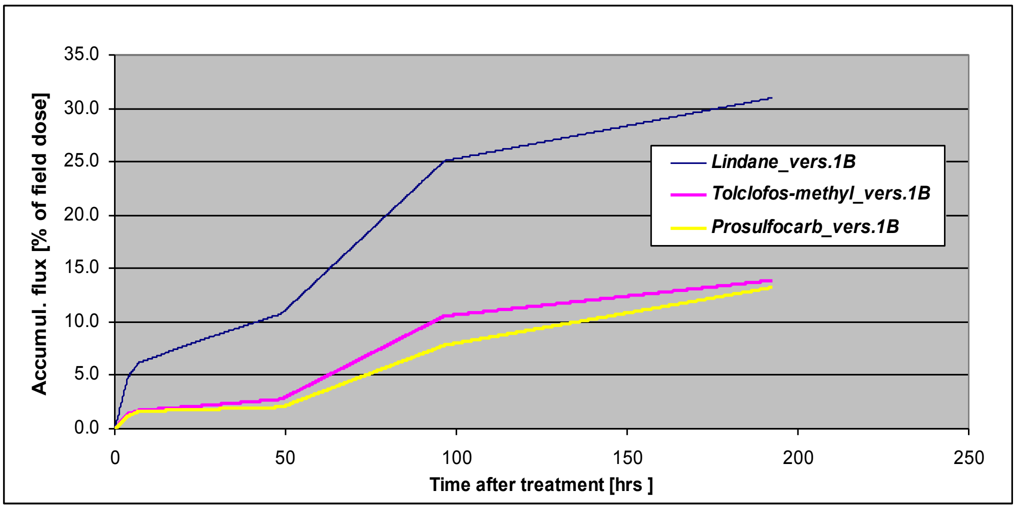

Fig. 4.28 *Accumulated horizontal fluxes (given as percentages of applied dose) of lindane, tolclofos-methyl and prosulfocarb during the first 8 days following spraying in September 2009.*

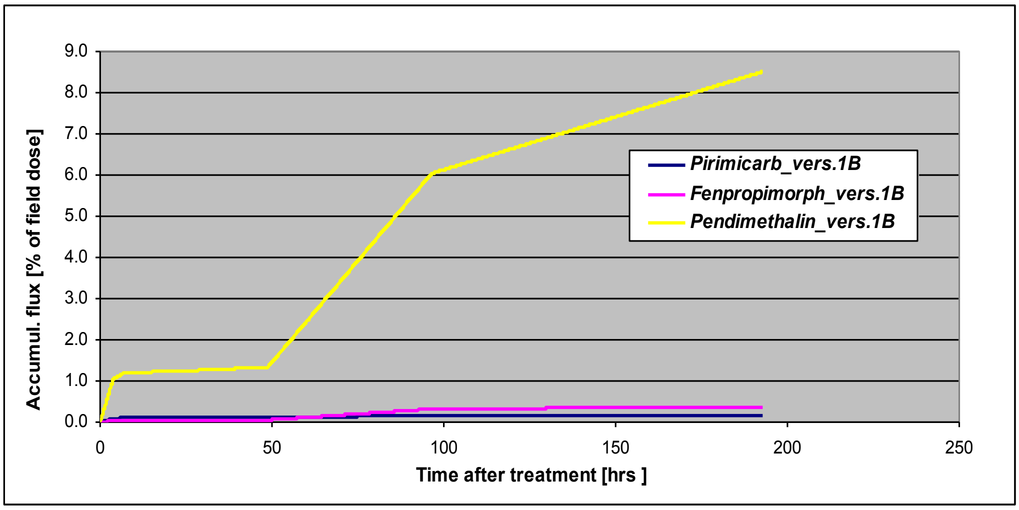

Fig. 4.29 *Accumulated horizontal fluxes (given as percentages of applied dose) of pirimicarb, fenpropimorph and pendimethalin during the first 8 days following spraying in September 2009.*

The relatively low volatilization during the first two days, especially in comparison with the corresponding graphs for the summer conditions (Figs. 4.8-4.10), is evident excepting pirimicarb. In fact, something roughly between 9 and 19 % of the total accumulated flux during the first 168 hours (7 days) occurred during the first 6 hours for all substances (including fenpropimorph) except for pirimicarb where this ratio was in the range 43-58 %. These ratios (i.e. the ratio between accumulated flux during the first 6 hrs in relation to that in 168 hrs) from the July 2010 campaign (the July -09 experiment lasted only 71 hrs) were in the range 82-

86 % for most substances and above 90% in the case of pirimicarb and fenpropimorph (cf. Table 4.8).

The corresponding courses of accumulated fluxes from September 2010 are shown in Figs. 4.30-4.31. To show the mostly relatively small difference in the estimated fluxes resulting from the choice of either version 1 or version 2 of the underlying concentration equation, the curves for both versions are shown in this case. For tolclofos-methyl the accumulated flux after 232 hrs is thus about 10 percent lower with version 2 compared to version 1 and for lindane this figure is less than 2 percent. For prosulfocarb version 2 gives a value less than 2 percent higher than version 1. (These differences between versions are chiefly of the same small magnitude also for the September results from 2008 and 2009 as can be seen from Table 4.4 a-b.)

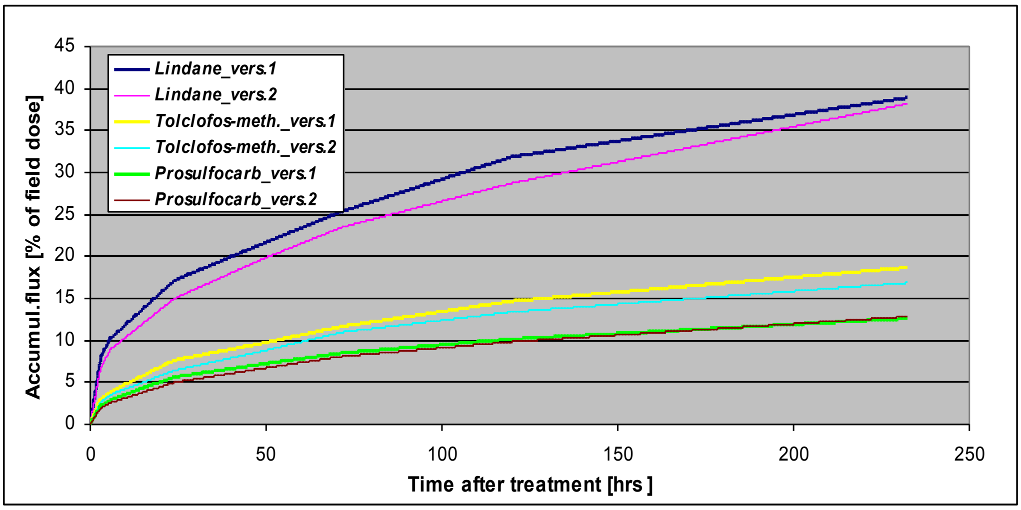

Fig. 4.30 Accumulated horizontal fluxes (given as percentages of applied dose) of Lindane, tolclofos-methyl and prosulfocarb during almost 10 days (232 hrs) following spraying in September 2010.

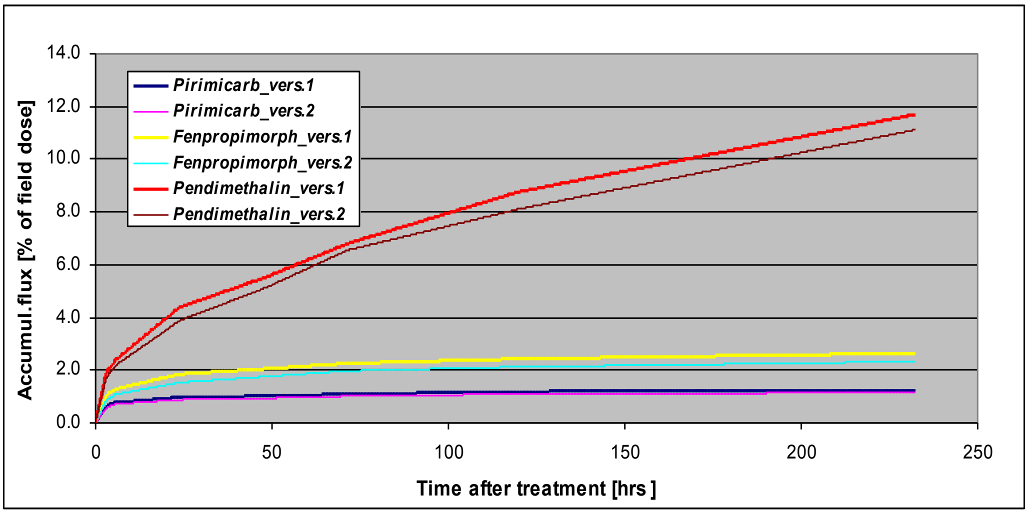

Fig. 4.31 Accumulated horizontal fluxes (given as percentages of applied dose) of pirimicarb, fenpropimorph and pendimethalin during the ~9.7 days (232 hrs) following spraying in September 2010.

In September 2010 the volatilization rates during the early stages were considerably faster than during September 2009 and the ratios of 6hr/168hr - accumulation (as described above) were now of the order of 24 – 29 % for all substances excepting fenpropimorph and pirimicarb for which this ratio was about 50 and 64 %, respectively.

Thus, obviously in Sept. -09 only a minor part of the total accumulation during a longer period, e.g. 168 hrs, occurred during the first 24 hrs after spraying for most of the pesticides, as opposite to the case in Sept. -10 and also to the common pattern for the summer cases.

For several of the pesticides – primarily fenpropimorph, but also tolclofos-methyl, prosulfocarb and pendimethalin – the accumulated flux during the first 6 hrs amounted to 15 % or less of that accumulated in 168 hrs (compared to shares for the first 6 hrs between 24 and 50 % in Sept. 2010, and between 80 and 90% in July 2010 (cf. Table 4.8 below).
A possible explanation to this behaviour might be that many pesticides are more or less strongly adsorbed to the soil particles as long as the soil surface is comparatively dry.
In September 2009 the topsoil layer was fairly dry at the onset of the measurements (on the 18th of Sept.), with a soil moisture content just below 18 %. Under such conditions it is claimed that pesticides tend to be rather strongly adsorbed to the soil particles. Around midnight the 20th about 8 mm of rain was recorded at a nearby station (< 1 km from our experimental site), thus rising the moisture content in the surface layer to ~34 % in the morning of the 21st , about 10 hrs into sampling period 5. This wettening of the dry surface probably diminished the adhesive bonds to the soil particles and thereby reinforced the volatilization. During the latter part of this period, and the following last period (period 6: 96-193 hrs after spraying), no or very little further precipitation fell, resulting in a gradual drying up of the soil surface to a moisture value again around 18 % in the morning of the 26th (i.e. about 3 hours before the end of the Sept. 2009 sampling).
The relatively high vapour flux during the first two sampling periods (together covering the first 7 hours after spraying) should then be explained by vaporization from a ´fresh´ pesticide film on the soil particles, not yet fully or strongly adsorbed to the particles.

In September 2010, on the other hand, the soil surface was comparatively moist already from the beginning, starting with a moisture content about 27 % (percent of dry soil) at the onset of the experiment (in the early afternoon of the 8th of Sept.) and then gradually increasing to ~34% in the middle of the last sampling period (period 7, 120-243 hrs from the onset).This moisture content was apparently sufficient to keep the volatilization going at a comparatively high rate (possibly near or equal to the “potential” rate under the prevailing weather conditions), but gradually and evenly diminishing with time.

Why this explanation does not seem to apply also to pirimicarb – which even under the dry soil conditions in Sept. -09 was the most ´rapidly´ evaporating among the six, with the 6/168 hr- ratio in the range about 43-58 % (the span here reflecting the two versions of conc. equations) – might possibly be due to its very high water solubility, several orders of magnitude greater than the other substances, which then may have led to a more significant leakage into deeper layers of the soil during the rainy episodes in the later parts of the sampling both these years (i.e. in Sept. 2009 and 2010).

(It should be kept in mind in this context that, most certainly, it is important for the outcome of this comparison in which part of the day the first 6-hr period falls. In our experiments – the summer as well as the autumn cases – this 6-hr period practically always was commenced during daylight hours (in 5 of the 6 campaigns the air sampling starts some hour between 10 a.m. and 14 p.m., but at 17 p.m. in June -08). On the other hand, pesticide treatments in regular farming practise are also generally commenced during daylight conditions, quite frequently in the morning or forenoon hours.)

Table 4.8 *Quotient of accumulated flux during the first 6 hrs to that during 168 hrs (71 hrs in July -09)***.** ***(****First figure in each pair refers to vers.1 and the second to vers.2 of the underlying concentration equations.)*

	July 2009	**July 2010**	**Sept. 2009**	**Sept. 2010**
	Acc. flux 6hrs/71hrs	***Acc. flux 6hrs/168hrs***	***Acc. flux 6hrs/168hrs***	***Acc. flux 6hrs/168hrs***
Lindane	0.69 – 0.69	0.83 – 0.82	0.20 – 0.18	0.30 – 0.27
Pirimicarb	0.59 – 0.59	0.92 – 0.92	0.58 – 0.43	0.64 – 0.64
Tolclofos-meth.	0.50 – 0.47	0.86 – 0.86	0.13 – 0.07	0.24 – 0.24
Prosulfocarb	0.47 – 0.42	0.86 – 0.85	0.13 – 0.11	0.27 – 0.24
Fenpropimorph	0.81 – 0.80	0.92 – 0.91	0.11 – 0.09	0.52 – 0.49
Pendimethalin	0.23 – 0.20	0.82 – 0.83	0.15 – 0.09	0.24 – 0.24

4.2 Volatilization flux correlated with physical-chemical properties of the pesticides

Following some methods outlined by Woodrow et al. (1997) regarding modelling techniques for the correlation between pesticide vapour fluxes and their physical/chemical properties, we have applied these methods to the absolute accumulated flux data from both the summer and autumn campaigns in 2009 and 2010, respectively.

A key parameter in these correlations is the vapour pressures of the substances involved. As certainly noticed by other authors in this subject matter, a variety of vapour pressure values, and for which specific temperature they are valid, occurs in the literature. Just as one example of this, the vapour pressure (Vp) of tolclofos-methyl is given to 0.877 mPa (20℃) by EFSA (European Food Safety Authority) but to 57 mPa (also at 20 ℃) by KEMI (the Swedish Chemical Agency). Due to these facts, the results of the correlation calculations carried out are highly dependent on which set of Vp values for the substances involved that is chosen. In fact, more than a dozen of different sets of vapour pressure values have been tested on our data, among them one based on the values given by PPDB (denoted Vp(1) in the following) – which in practice is identical with the values published by EFSA except for the stated temperature, where PPDB says 25 ˚C but EFSA 20 ℃ – and one based on values published by KEMI, but supplemented with data from other sources in the case of lindane and pendimethalin for which substances no Vp data published by KEMI were found. The resulting correlations from the use some of these Vp-sets in the regession calculations will be presented below.

4.2.1 Flux – vapour pressure correlations for the summer experiments

When the volatilization takes place from an assumed inert surface, in this case in fact also from growing leaf surfaces, Woodrow et al. (1997) suggest that the volatilization flux should correlate with the dose corrected vapour pressure of each substance (= dose [kg/ha] xVp[Pa]) when correlated in a ln – ln plot: ln(accum. flux) versus ln(dose*Vp).

Using the vapour pressure values (Vp-set) given by PPDB on the July 2009 flux data results in a fairly moderate correlation between dose corrected vapour pressures and the accumulated vapour flux, both when integrating over the first 24 hrs and over the whole measuring period, ~71 hrs (Fig. 4.32). A slight improvement of the linear relation occurs if the Vp-set taken from KEMI (completed with data from other sources for lindane and pendimethalin as explained above) as evident from Fig. 4.33.

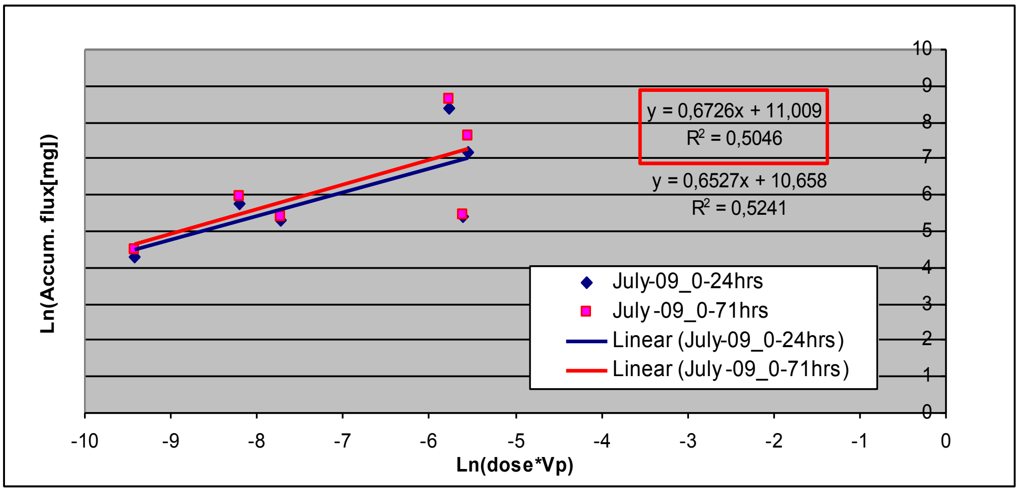

Fig. 4.32. *Accumulated horizontal flux versus dose [kg/ha] corrected vapour pressure [Pa] in July 2009 during the first 24 hrs after spraying, and during 71 hrs (the whole sampling time), respectively. Vapour pressure data according to PPDB.*

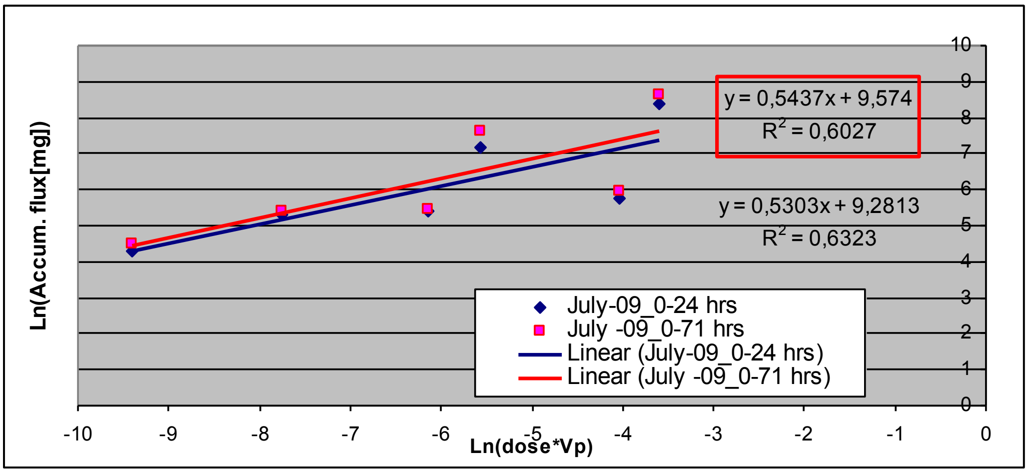

Fig. 4.33. *Accumulated horizontal flux versus dose [kg/ha] corrected vapour pressure [Pa] in July 2009 during the first 24 hrs after spraying, and during 71 hrs (the whole sampling time), respectively. Vapour pressure data according to "KEMI".*

A still better correlation is achieved if the PPDB data are used (as in Fig. 4.32) but excluding fenpropimorph from the regression, which substance in at least some of the campaigns exhibited a rather deviating flux pattern from the remaining ones (Fig. 4.34).

However, an equally high correlation, with all six substances included, may be achieved by using a selection of Vp-values from different sources of published vapour pressure data (Fig. 4.35). This Vp-set ("new4") differs very markedly from the PPDB data and also from the KEMI data in the case of three of the substances as is shown in Table 4.9 (Variations in the ambient temperature will cause a shift of the curves along the vertical axis, and possibly also a shift in their respective inclinations (i.e. gradients) – conf. e.g. the graphs in *Fig. 4.49* representing different years and seasons.)

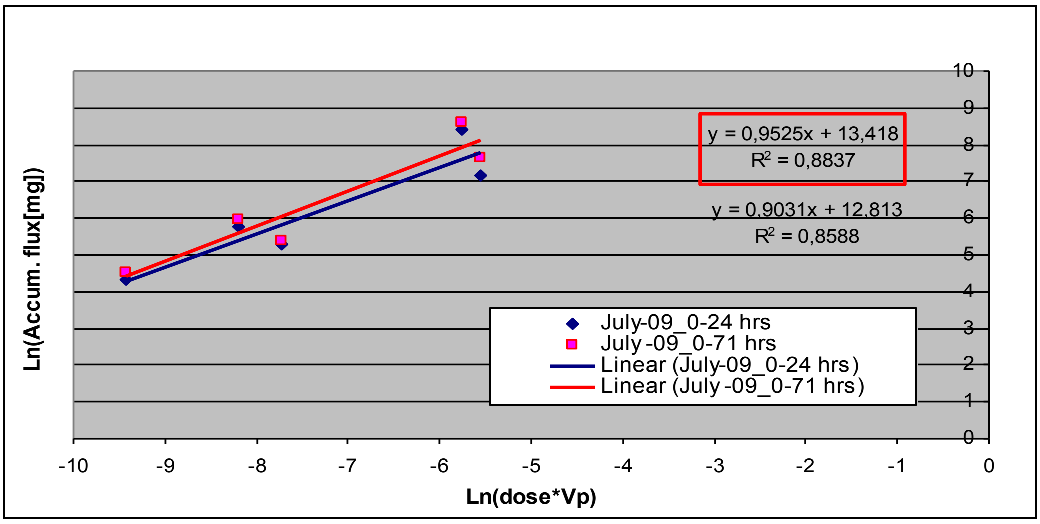

Fig. 4.34. *Accumulated horizontal flux versus dose [kg/ha] corrected vapour pressure [Pa] in July 2009 during the first 24 hrs after spraying, and during 71 hrs (the whole sampling time), respectively. Vapour pressure data according to PPDB but with fenpropimorph excluded.*

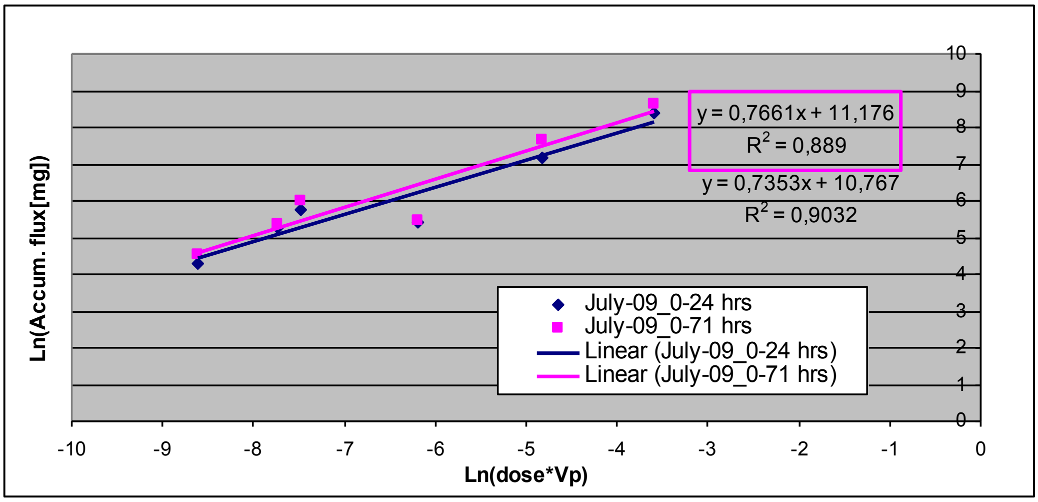

***Fig. 4.35**. Accumulated horizontal flux versus dose [kg/ha] corrected vapour pressure [Pa] in July 2009 during the first 24 hrs after spraying, and during 71 hrs (the whole sampling time), respectively. Vapour pressure data according to the Vp-set "Vp(3)".*

It appears from the examples shown, that the correlation between accumulated flux and dose corrected vapour pressure is almost as good after nearly three days accumulation as after the first day after spraying.

Applying the Vp-set from PPDB to the accumulated fluxes in July 2010 results in about the same, not particularly good, correlation as when used on the July -09 data. And again, also as in July -09, a markedly better fit appears if the "KEMI"-values are used instead (Fig. 4.36).

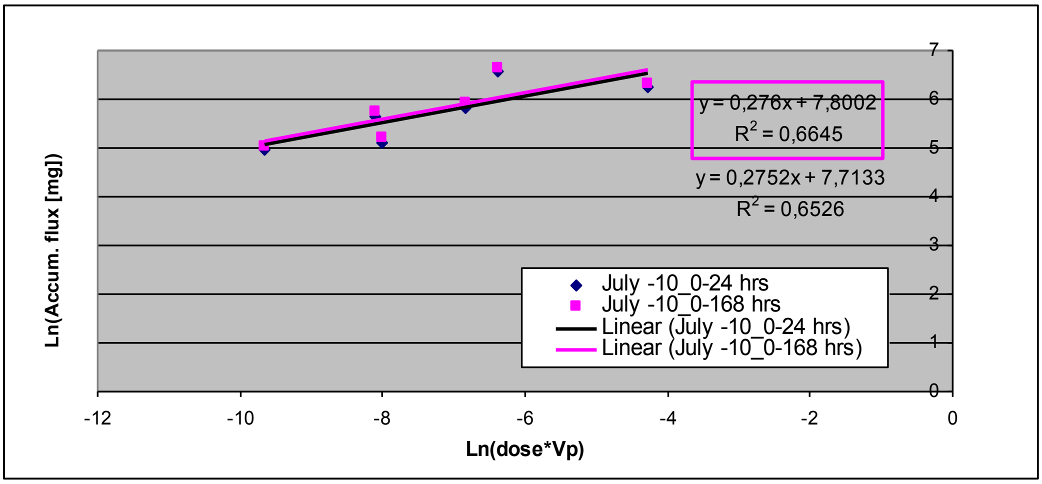

***Fig. 4.36**. Accumulated horizontal flux versus dose [kg/ha] corrected vapour pressure [Pa] in July 2010 during the first 24 hrs after spraying, and after 168 hrs (7 days), respectively. Vapour pressure data according to Vp-set mainly from KEMI (Vp(2)).*

And again like for July-09, a further improvement of the correlation occured if fenpropimorph was excluded (i.e. the point with coordinates [-6.38; 6.64] in *Fig.4.36*).

The highest correlation found, however, resulted from a Vp-set (labeled "Vp(4)" in Table 4.9) selected from different sources and which differs from the PPDB-set for four of the six substances, and which show a high correlation even with all six substances included (Fig. 4.37).

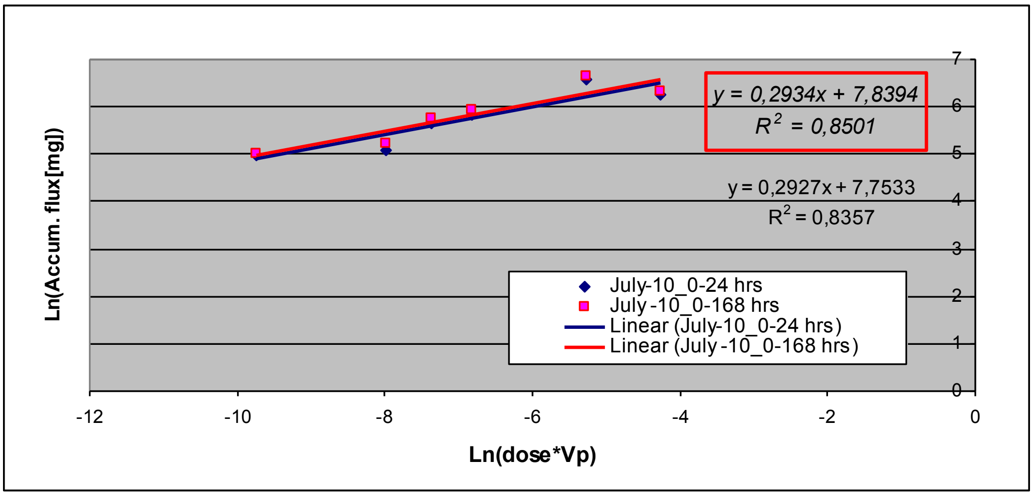

__Fig. 4.37__. Accumulated horizontal flux versus dose [kg/ha] corrected vapour pressure [Pa] in July 2010 during the first 24 hrs after spraying, and after 168 hrs (7 days), respectively. Vapour pressure data according to Vp-set "Vp(4)".

Judging from the examples shown here, the tested relations seem to be quite as good, even over a 7-day accumulation period, as for the first 24 hrs after the spraying.

Table 4.9 *Vapour pressure sets [mPa] according to different sources*

	Vp(1)_"PPDB"[1]	*Vp(2)_"KEMI"[2]*	*Vp(3)*	*Vp(4)*	*Vp(5)*	*Vp(6)*
Lindane	4.4	4.3[3a]	4.4	4.4	8.63[3b]	45.6[9]
Pirimicarb	0.43	0.44	0.97	0.4[4] (20˚C)	0.4	0.44
Tolclofos-methyl	0.877	57 (20˚C)[4]	1.82[5]	57	57	57
Prosulfocarb	0.79	6.9 (25˚C)[4]	6.9	6.9	6.9	6.9
Fenpropimo.	3.9	2.3	2.2[6]	7.0[8]	2.2	2.3
Pendimetha.	1.94	1.94[1,4]	4.0[7]	4.0[7]	4.0	1.94

[1] PPDB [25 ˚C]; [2] KEMI(1997) [20 ˚C]; [3] Spencer and Cliath (1970) 3a: [20 ˚C], 3b: [25 ˚C]
[4] Tomlin, C. (Ed.) (2003); [5] EFSA [25 ˚C]; [6] Kröhl et al.(1998) [20 ˚C]
[7] www.agropages.com/agrodata [25˚C]; [8] EFSA [25 ˚C]; [9] Xiao et al. (2004) [20 ˚C]

4.2.2 Volatilization flux correlated with vapour pressure and other physical-chemical properties – the autumn experiments

During the autumn experiments, the pesticide spraying took place on bare soil. In the case of volatilization from a (bare) soil surface, Woodrow et al. (1997) suggest that the vapour flux probably will be correlated not with the vapour pressure (Pa) alone, but with a combination of this, the water solubility (S_w [mg/l] and the affinity to soil organic matter (K_{oc} [ml/g]), combined to the parameter $R_{surf} = Vp/K_{oc} S_w$ and, finally, also with the applied dose (kg/ha) for each substance which ends up to a dose corrected R_{surf} (labelled R_{inc} by Woodrow): dose corr. R_{surf} = dose*Vp/(K_{oc} S_w). (Note, that we have used the Freundlich variant for the soil absorption coefficient, K_{foc} , instead of K_{oc} in the expression for R_{surf} . The values used, together with the values used for solubility in water, are given in Table 4.3 in sect. 4.1.)

Beside this approach, we also tested the applicability of the simpler relation as used above for the evaporation from plants (i.e. with dose corrected Vp as independent variable).

With the approach suggested by Woodrow for bare soil applied to the September 2009 accumulated fluxes, the use of the Vp(1)-set (PPDB), and all pesticides included, showed no correlation ($R^2 \leq 0.06$) up to 48 hrs of accumulation and then a rather feeble increase at longer accumulation times from 96 hrs onwards (with $R^2 \leq 0.32$).

However, as mentioned before, the substance fenpropimorph during some of the experiments exhibited a more or less deviating volatilization flux from the others (such as, for example, from only half of that from pirimicarb (in July -09) to about the same as pirimicarb (July -10) despite a markedly higher vapour pressure according to both the PPBD and KEMI and also other sources, and only 1/20 of that from pendimethalin in Sept. -09 despite a comparably high (or possibly even higher) Vp than that of pendimethalin). Thus, excluding fenpropimorph from the regression (and keeping the PPDB Vp-set) results in a significant improvement of the correlation (see Fig. 4.38).

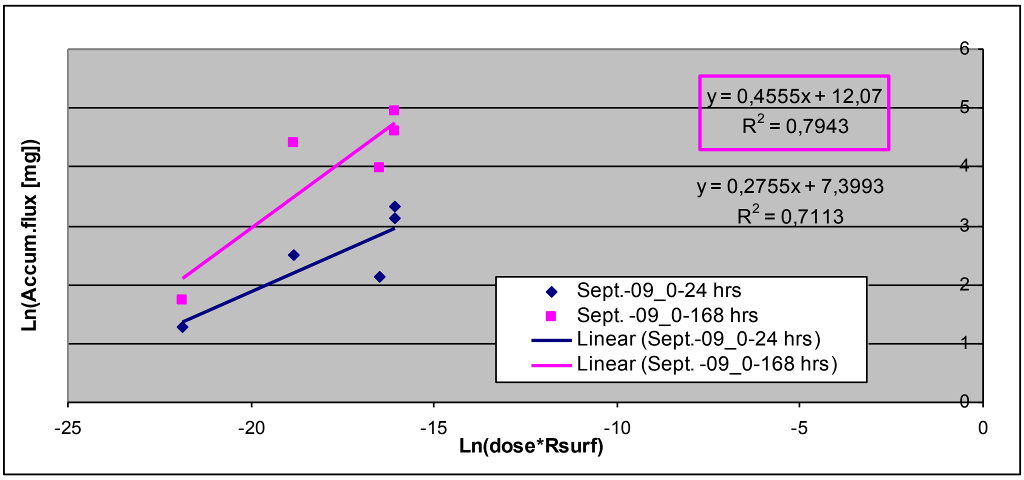

***Fig. 4.38**. Accumulated horizontal flux versus dose corrected Rsurf in Sept. 2009 during the first 24 hrs after spraying, and during 168 hrs ,respectively. Vapour pressure data according to PPDB but with fenpropimorph excluded.*

It may be mentioned, also, that the highest correlation here occurs after an accumulation time around 96 hrs (with $R^2 = 0.833$). This may probably reflect that the surface soil moisture reached a maximum value some days into this September experiment, starting with a fairly dry soil at the beginning of it, and this increased soil moisture seemed to promote the volatilization, as discussed earlier.
A still better correlation may be achieved, however, by using a new set of Vp values (“Vp(5)” in Table 4.9). Just to show the marked difference between the two

cases: with or without fenpropimorph included in the regression, both are shown (Figs. 4.39 and 4.40).

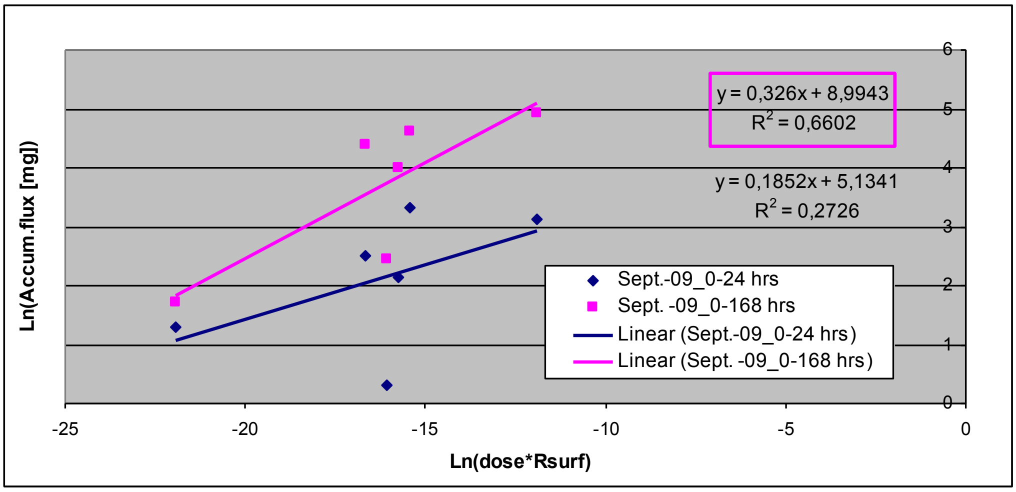

Fig. 4.39. *Accumulated horizontal flux versus dose corrected Rsurf in Sept. 2009 during the first 24 hrs after spraying, and after 168 hrs ,respectively. Vapour pressure data according to Vp-set "Vp(5)"(conf. Table 4.9) – all six substances included.*

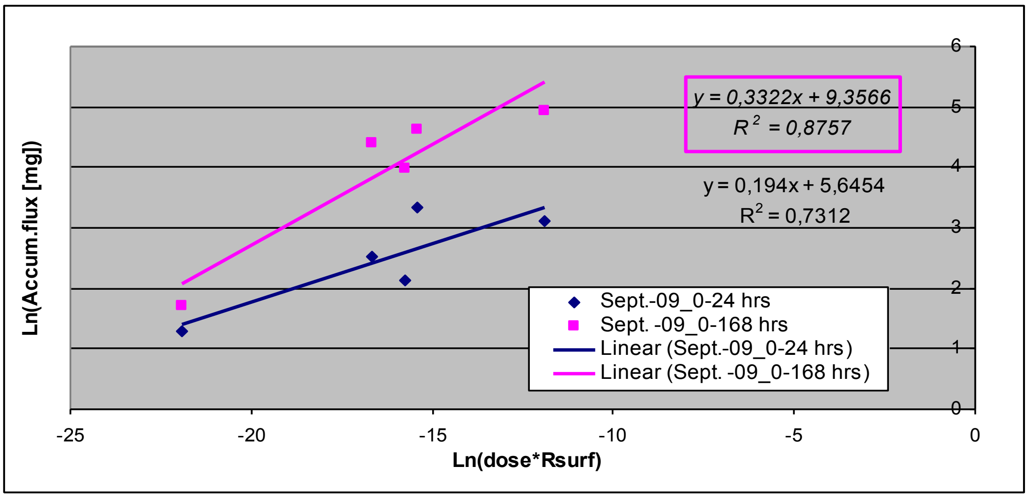

Fig. 4.40*. Accumulated horizontal flux versus dose corrected Rsurf in Sept. 2009 during the first 24 hrs after spraying, and after 168 hrs, respectively. Vapour pressure data according to Vp-set "Vp(5)"(conf. Table 4.9) –* ***fenpropimorph not included****.*

A comparably good correlation as that shown in Fig. 4.40 – on the longer accumulation times (≥ 96hrs) even slightly higher – was achieved when applying the Vp-set that gave the best fit on the July -09 data (labelled Vp(3) in Table 4.9), and with fenpropimorph excluded. (If fenpropimorph also *is* included, on the other hand, this set gives only a moderately good fit, measured in terms of R^2.)

In Sept. 2010 the use of the original PPDB-set (Vp(1), Table 4.9) resulted in a fairly moderate correlation, whereas the set Vp(2) based mainly on ´KEMI´ data gave quite a high fit, especially at longer accumulation times. In fact, even for the flux during the 232 hrs which was the total sampling time during the experiment, as is evident from Fig. 4.41.

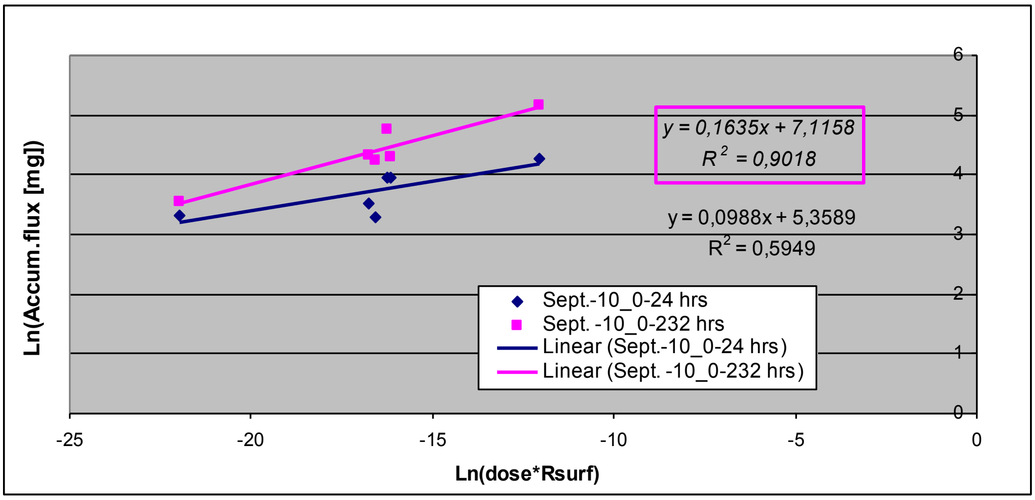

***Fig. 4.41**. Accumulated horizontal flux versus dose corrected Rsurf in Sept. 2010 during the first 24 hrs after spraying, and after 232 hrs (the total sampling time) ,respectively. Vapour pressure data according to Vp-set "Vp(2)"(conf. Table 4.9).*

As mentioned above, no Vp data for lindane (and pendimethalin) published by KEMI was found. In the set labelled Vp(2) therefore, the value for lindane (0,0043 Pa at 20℃) was taken from Spencer and Cliath (1970). However, if the value given as FAV ("finally adjusted value") after a thorough compilation of data from numerous published sources discussing and proposing values for lindane (Ɣ-HCH), viz. 0.0456 Pa at 20℃ (that is, about 10 times higher than that used in "Vp(2)"), is substituted for the earlier value (0,0043 Pa) we get "Vp(6)" in Table 4.9. By using this new Vp-set, the correlation was further increased (see Fig. 4.42).

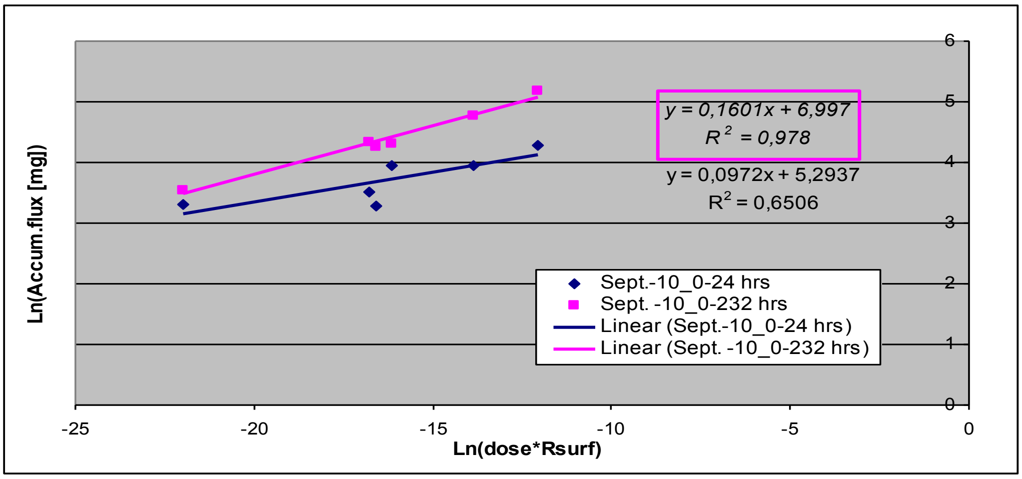

***Fig. 4.42**. Accumulated horizontal flux versus dose corrected Rsurf in Sept. 2010 during the first 24 hrs after spraying, and after 232 hrs (the total sampling time) ,respectively. Vapour pressure data according to Vp-set "Vp(6)"(conf. Table 4.9).*

For comparison of the method now discussed, viz. relating the vapour flux from a bare soil to several physicochemical properties of the substances (accumulated flux versus dose corrected R_{surf}) as suggested by Woodrow et al. (1997), also the simpler relation suggested for volatilization from plants (or "inert" surfaces in general, but assumed to be applicable also to leaf surfaces) – i.e. assuming that the accumulated vapour flux can be correlated to the vapour pressure alone (accumulated flux versus dose corrected Vp, i.e. the same type of relation as used for the summer data) – was applied also for the Sept. 2009 and Sept. 2010 data (thus representing volatilization from bare soil).

When applied to the September 2009 data, neither of the two first Vp-sets from Table 4.9 (Vp(1)_"PPDB" and Vp(2)_"KEMI") gives any high correlation, particularly not Vp(1) which beside fairly low correlation values show a negative slope of the regression line. The result for the set Vp(2), which is the slightly better of the two, is shown in Fig. 4.43. If the, especially during the Sept. -09 campaign, deviating substance fenpropimorph is excluded from the regression (fenpropimorph corresponds to the two points with coordinates (-6.2, 0.3) and (-6.2, 2.5) in the figure, respectively), the correlation increases markedly but still remains at fairly low values, R^2 then being ≤ 0.27 at both 24 and 168 hrs accumulation time.

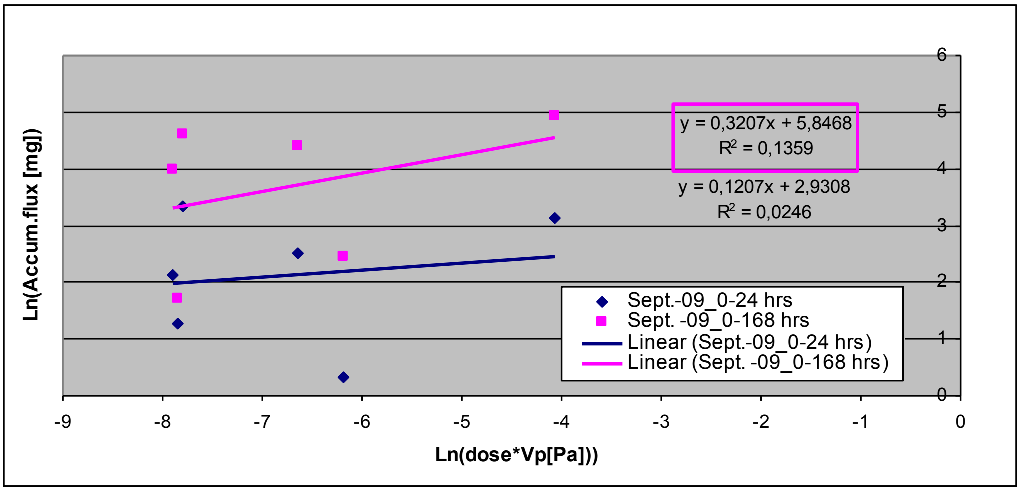

Fig. 4.43. *Accumulated horizontal flux versus dose corrected Vp in Sept. 2009 during the first 24 hrs after spraying, and after 168 hrs, respectively. Vapour pressure data according to Vp-set "Vp(2)" (conf. Table 4.9).*

A slightly higher correlation was achieved by using the vapour pressures in set Vp(6) (Table 4.9), which only differs from Vp(2) by the about 10 times higher value for lindane. This results in R^2 values between 0.25 (after 24 hrs of accumulation) and 0.37 (after 168 hrs) as shown in Fig.4.44. As before, the correlation improved if fenpropimorph was excluded. In this case, R^2 increases to 0.72 (after 24 hrs accum.) and 0.51 (after 168 hrs). The small decline in the correlation from 24 to 168 hrs accumulation might possibly reflect the incidence of precipitation towards the later part of this longer accumulation period (as discussed previously) which in turn may trigger a strengthening of other factors – involving also other physical-chemical properties than vapour pressure – of importance for the volatilization process.

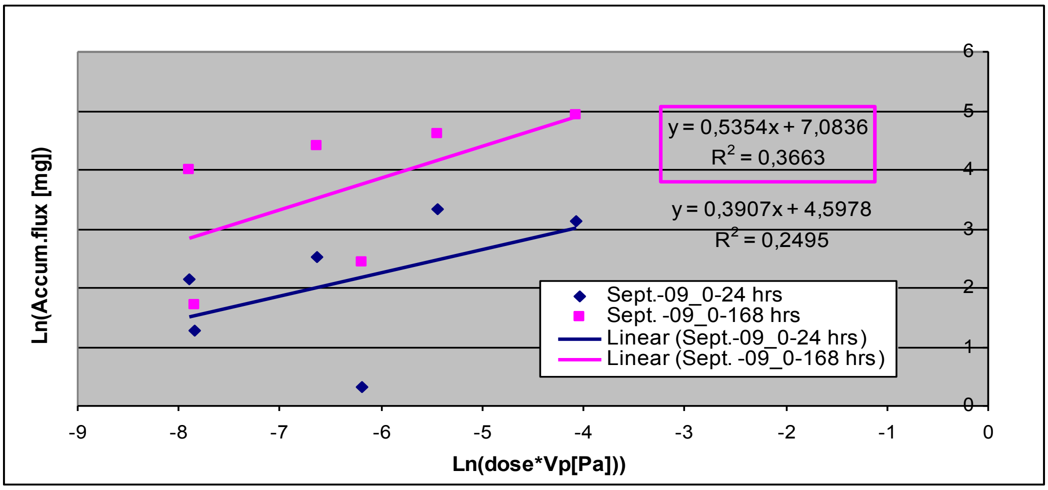

Fig. 4.44. *Accumulated horizontal flux versus dose corrected Vp in Sept. 2009 during the first 24 hrs after spraying, and after 168 hrs, respectively. Vapour pressure data according to Vp-set "Vp(6)" (conf. Table 4.9). (The two points in the figure with an abscissa value of approx. -6.2 correspond to fenpropimorph).*

When exploring the simpler method also on the data from Sept. 2010, it was apparent that the PPDB vapour set (Vp(1)) does not give any useful relation to the accumulated flux (Fig. 4.45).

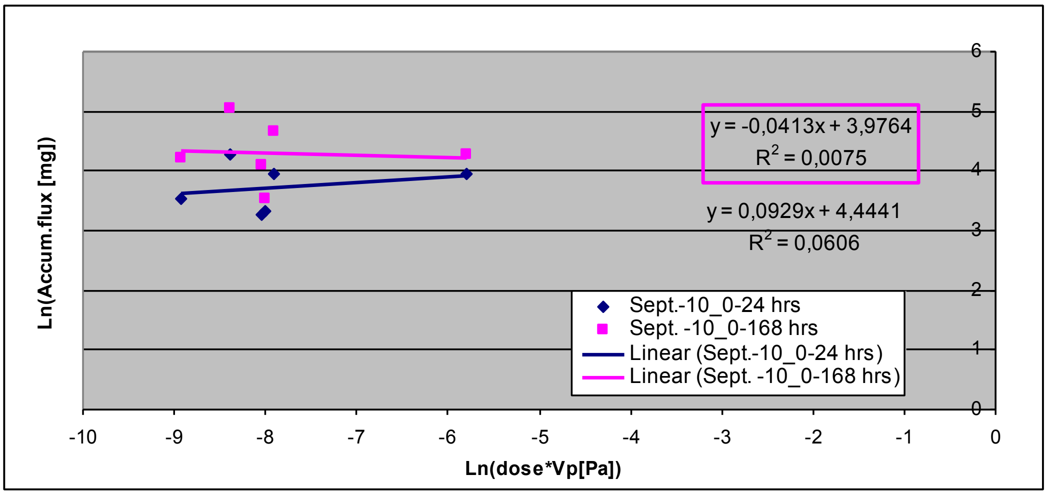

Fig. 4.45. *Accumulated horizontal flux versus dose corrected Vp in Sept. 2010 during the first 24 hrs after spraying, and after 168 hrs, respectively. Vapour pressure data according to the PPDB-set "Vp(1)" (conf. Table 4.9).*

Applying the "KEMI"-set Vp(2) gives a just moderately good correlation (Fig. 4.46), which, on the contrary to many cases in Sept.-09 – not improves but marginally if fenpropimorph is excluded. (However, a very appreciable improvement occurred if lindane was excluded, resulting in values of R^2 in the range 0.85 – 0.96 with the lower limit occurring after 168 hrs of accumulation and the upper value after 48 hrs.

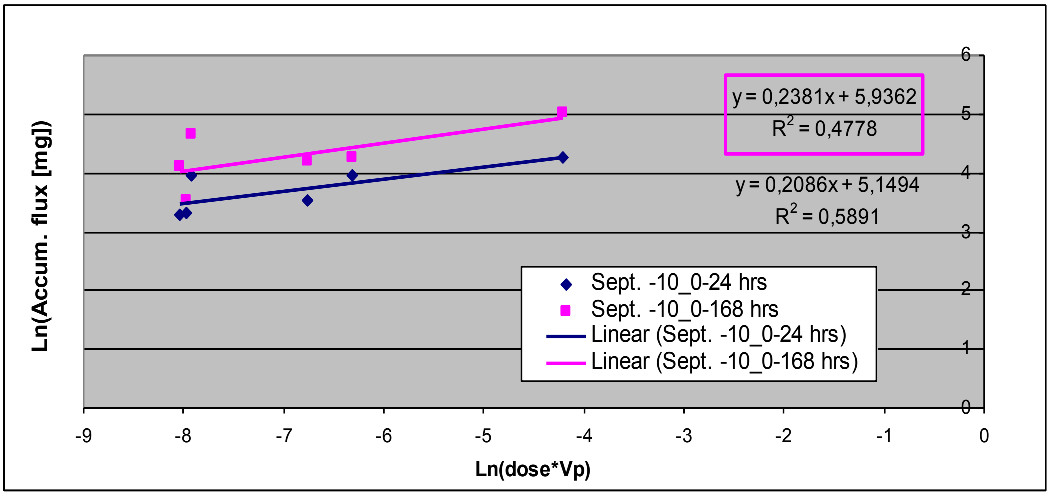

Fig. 4.46. *Accumulated horizontal flux versus dose corrected Vp in Sept. 2010 during the first 24 hrs after spraying, and after 168 hrs, respectively. Vapour pressure data according to Vp-set "Vp(2)" (cf. Table 4.9).*

If the Vp-set labelled Vp(6) in Table 4.9 is applied, finally, the correlation improves markedly – with all six substances kept in the regression – and gets even higher for accumulation times longer than 48 hrs if pendimethalin in this case is excluded (cf. Figs. 4.47 and 4.48). After the total accumulation time for this experiment, 232 hrs, the correlation figures has decreased slightly but still remains rather high with $R^2 = 0.81$ for the case shown in Figure 4.47 and $R^2 = 0.96$ for the case in Figure 4.48 (Table 4.10).
It may also be worth while to compare these results with the outcome of using the same Vp-sets in the more complex parameter R_{surf}, and for the two cases: with and without pendimethalin included. Table 4.10 below shows the resulting correlations from use of the vapour pressure set Vp(6) in both approaches.

Table 4.10. *Comparison of the goodness of correlation for the two approaches of relating accumulated vapour flux from bare soil to physical-chemical properties used on September 2010 data with vapour pressures according to the Vp-set: Vp(6) in Table 4.9*

	Correlation(Vp(6)) : R^2				
Accumulation time for flux [hrs]:	*24*	*48*	*96*	*168*	*232*
Flux vs ***dose*Vp***	*0.932*	*0.965*	*0.928*	*0.859*	*0.807*
Flux vs ***dose*R_{surf}***	*0.651*	*0.800*	*0.921*	*0.967*	*0.978*
Flux vs ***dose*Vp****; with pendimeth. excl.*	*0.907*	*0.964*	*0.981*	*0.973*	*0.963*
Flux vs ***dose*R_{surf}*** *; with pendimeth. excl.*	*0.851*	*0.948*	*0.983*	*0.986*	*0.984*

Thus, it appears that it is possible to achieve a good correlation between accumulated flux and physicochemical properties with both methods (at least with this set of Vp-values, chosen as an example). At longer accumulation times, > 96 hrs, the more complex relation using the parameter R_{surf} seems to better describe the evaporative flux in this case. This may well be caused by increased soil moisture during the later parts of the experiment in connection with the incidence of frequent rain episodes at that time. On the other hand, at shorter accumulation times the simpler relation, only involving the dose corrected vapour pressure, seems to perform better. It also appears in the present case, that the goodness of fit of the more complex relation remains high, or even increase, at fairly long times after the spraying.

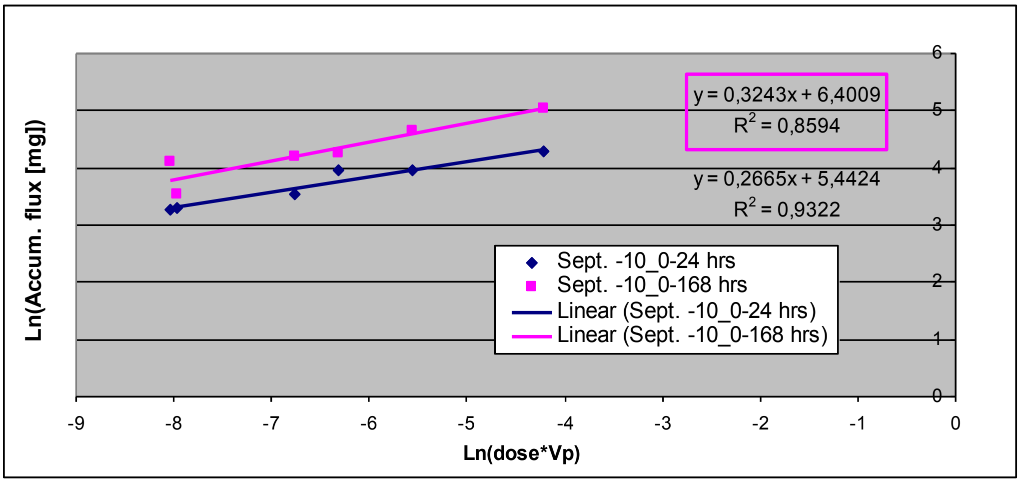

Fig. 4.47. Accumulated horizontal flux versus dose corrected Vp in Sept. 2010 during the first 24 hrs after spraying, and after 168 hrs, respectively. Vapour pressure data according to Vp-set "Vp(6)" (cf. Table 4.9).

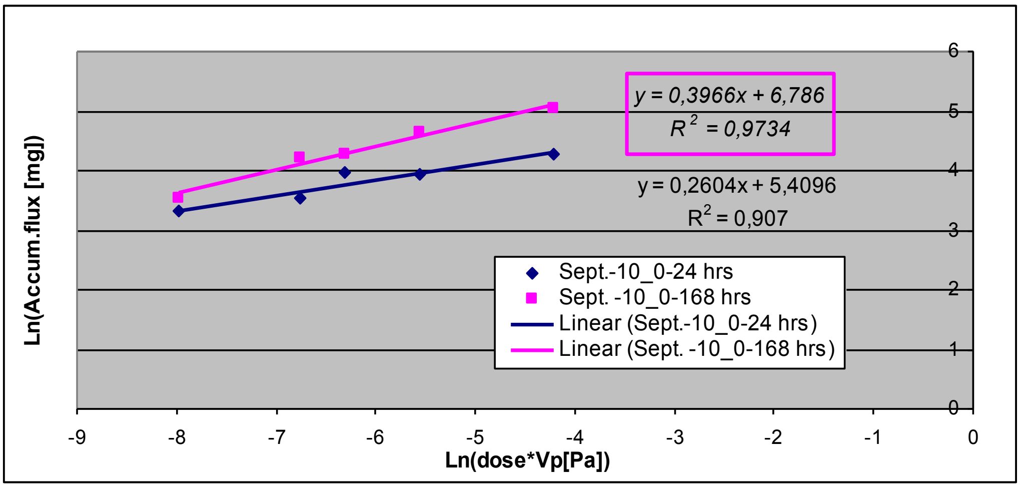

Fig. 4.48. Accumulated horizontal flux versus dose corrected Vp in Sept. 2010 during the first 24 hrs after spraying, and after 168 hrs, respectively. Vapour pressure data according to Vp-set "Vp(6)" (cf. Table 4.9). ***Pendimethalin not included*.**

Finally, some words concerning the evolution of the correlative fit of the investigated relations with increasing accumulation time of the fluxes may be mentioned.

In the summer cases, it was generally found that the goodness of the correlation remained at a more or less constant level for accumulation times spanning from about 24 hrs all the way up to the full duration of the respective experiments (i.e. ~70 hrs in July -09 and ~200 hrs in July -10).

For the September experiments, on the contrary, there was a more or less marked increase in the correlation (measured in terms of R^2) with increasing accumulation time. This was particularly evident in the case of Sept. -09, where the fit increased very markedly from accumulation times roughly ≥ 96 hrs onwards, mainly coinciding with the occurrence of precipitation events this September month.

The foregoing exercise has shown that the outcome of the Woodrow approach in attempting to correlate volatilization flux to physical-chemical properties of the evaporating substances, very much depend on the values chosen for the key variables involved in the suggested relations. In the present case this has been explored regarding the vapour pressure, but also the soil adsorption coefficients (K_{foc}) seem to be a source of uncertainty in this respect (cf. the wide ranges of values given in Table 4.3) though not investigated further in this study. It was also evident that it frequently was possible to achieve rather strong correlations by the tested relations – in some cases particularly after having excluded one of the substances.

A disturbing point, however, will be the fact that those Vp-sets resulting in a good, or even very good, correlation between the variables involved when applied to the flux data from one season of *one* the examined years (2009 or 2010), in many cases performed nothing as good as that when used on data from the same season the other year (or, likewise, on another season of the same or another year). Only in very few cases a relatively high correlation was found for both of the examined years with one and the same Vp-set applied to both.

An example of this problem is shown in Fig. 4.49 below. In this figure, the Vp-set giving the strongest correlation with the September 2010 data (“Vp(6)” in Table 4.8) has also been used for the flux data from Sept. -09 and July -10, respectively. It should be noticed here, that the seemingly fairly low correlation (R^2 =0.69) in the case of Sept. -09 actually is one of the best (if not the best) achieved for this September when all the substances are included, and if the at times deviating fenpropimorh is excluded from the Sept. -09 plot, the correlation improves markedly to R^2 = 0.90 which also is among the best for this category. On the contrary, the correlation outcome of July -10 (R^2 =0.30) is the worst of about 18 tested sets for this season.

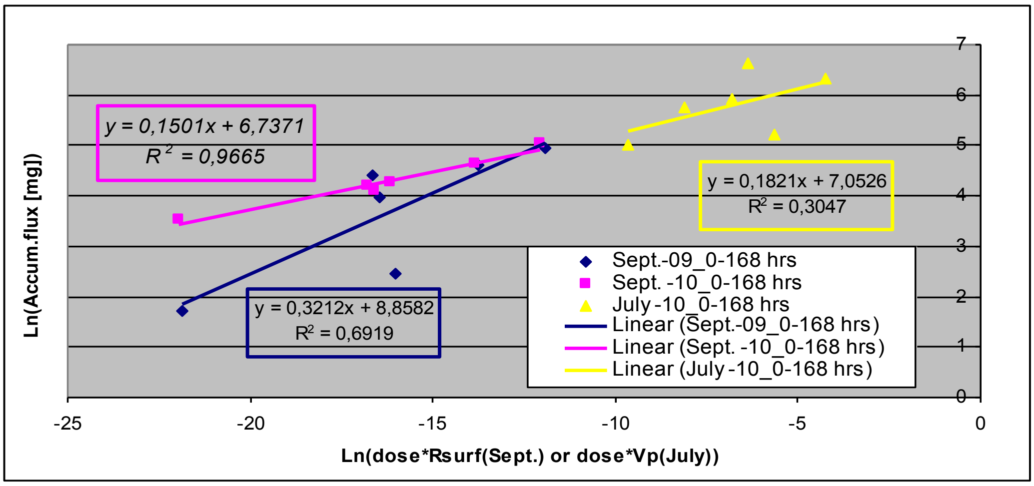

Fig. 4.49. *Accumulated horizontal flux versus dose corrected Rsurf in Sept. 2009 and 2010 and versus dose corrected Vp in July 2010 during the first 168 hrs after spraying. Vapour pressure data according to Vp-set "Vp(6)" (cf. Table 4.9). (Note that* R^2 *for Sept. -09 data improves from 0.69 to 0.895 if fenpropimorph – the dot with coordinates -16;2.5 – is excluded.)*

The findings above may seem confounding and will certainly raise further questions, since only one set of vapour pressure values can reasonably be regarded as ´true´ at a given temperature. This matter is discussed further in Section 5.7.

4.3 Dry deposition on soil

4.3.1 Dry deposition during summer conditions

Collection and analysis of dry deposited pesticides on square shaped Petri dishes, 10x10x1 cm, filled with soil, at several distances from 1 up to 100 m downwind from the outer edge of the sprayed circular area were performed during the summer campaigns in 2008 and 2009. Also, such deposition inside the unsprayed area within the sprayed circle was collected at distances from 1 to 10 m downwind from the *inner edge* of this circle.
Selected data concerning the prevailing weather conditions during the deposition sampling periods in both summers are shown in Table 4.11. The finite difference Ri-numbers over the height interval 0.15-16m are given as separate mean values for daytime and night time hours, respectively.

Table 4.11 *Average values of selected weather variables for the single sampling period (26hrs) for dry deposition in June -08, and for the two periods in July -09*

	$T(2m)$ [˚C]	***T_{surf}*** [˚C]	***$\bar{U}(2m)$*** [m/s]	***RH*** [%]	***P*** [mm]	***$Ri_B(16-0.15)$***	
						daytime	*night*
Mean (sum for P) 24/6 15:00-25/6 17:00 2008	*13.9*	*15.3*	*3.4*	*58*[2]	*0*	*-0.051*	*0.18*
Maximum (the same period)	*19.5*	*25.1*	*5.1*				
Mean (sum for P) 4/7 10:30-5/7 12:00 [1] ***2009 (period 1)***	*15.2*	*17.1*	*2.0*	*73*	*0*	*-0.087*	*0.11*
Maximum (the same period)	*22.0*	*27.9*	*4.0*	*95*			
Mean (sum for P) 5/7 14:00-6/7 17:00 2009 (period 2)	*12.7*	*14.0*	No signal	*73*	*0*	*-0.046*	*0.48*
Maximum (the same period)	*18.0*	*20.9*	No signal	*95*			

[1] Sampling finished at 13:00 but no data from the wind speed sensors after 12:00

[2] Value from Ultuna climate station (~9 km WSW from experimental site)

Table 4.12 shows the analysed results after a 26 hour long sampling period following spraying in June 2008. Both the absolute (in $\mu g/m^2$) and the relative deposition, normalized with the field dose per m^2 (given as per mille of the applied dose per m^2) are shown.

At two of the distances: 3 m downwind from the edge in the inner circle and 1 m downwind from the outer edge, respectively, the deposition on surface wetted soil was also examined (labelled “wet top soil”).

The deposition inside the unsprayed part of the circle (the upper half of the table) does not show any clear variation with distance from the upwind inner edge, except perhaps for a very weak decrease with distance for pirimicarb, which may well be a random effect in this case as the other substances does not support this tendency. What seems to be a clear feature, on the other hand, is a markedly increased deposition on the samplers at 3 m downwind distance with wetted soil. The deposition on these was about a factor 2 greater on average for all substances compared with the dry soil samplers at the same distance.

Concerning the deposition pattern outside and downwind of the treated area, up to a distance of 100 m, this pattern appears to be more consistent and clear. Here, there is a regular decrease with distance in the deposition with values at 100 m mostly in the range 3 to 7.5 % of those at 1m (for pirimicarb this quotient is 14 %). Pirimicarb and fenpropimorph, however, show both almost constant deposition values over the distance interval 3-10m. This may also, of course, be a random outcome of the sampling since both at 5 and 10m there was only one single sample at each distance. The accumulated deposition amounts observed after 26 hours at 100m were all in the range ~0.1-0.3 per mille of the applied dose.
Like the corresponding case above for the depositions inside the unsprayed circle, the deposition on dishes with surface wetted soil were significantly higher than that on dry soil at the same distance (in this case 1m downwind from the outer edge of treated area). In this case however, the observed increase was slightly less and about a factor 1.6 on the average. Thus, it appears that a wet soil surface both promote a higher volatilization of (at least some) pesticides *from* a bare soil, and increase the dry deposition *to* such a surface, compared with a dry surface.

It must be realized here, that the observed deposition in experiments like this will be strongly dependent on the size, geometry and location (distance) of the treated area in relation to the site(s) for sampling, and on the duration of the sampling. This fact makes direct comparisons of the results with other deposition studies more or less difficult, but they may of course be more successfully used for comparisons *within* the actual experimental set-up, e.g. comparisons between the different years and seasons and between different substances etc.

In July 2009 dry deposition was sampled in a similar way on the same type of Petri dishes as in June -09, but now without any sampling on wetted soil. This year three sample repetitions
was used at all distances (in June -08 three repetitions was used only for the short distances 1 and 3m). And in July -09 the deposition was measured during two subsequent periods: 0-26 hrs and 27-48 hrs, respectively, after spraying. The averaged results from each of these periods are shown in Tables 4.14 a-b.

During the first period (0-26 hrs after spraying; Table 4.14a) a more or less regularly decreasing deposition with downwind distance from the treated area was found. Thus, the deposition at the distance of 100m was typically in the range 4 - 6.5 % of that at 1m. Pirimicarb, however, showed a more slow decrease than the others with this value being ~40% of that at 1m. At a distance of 100m the accumulated deposition varied from 0.02 ‰ (fenpropimorph) to 0.30 ‰ (pirimicarb) of the applied dose per m^2. These normalized deposition values (i.e. deposition expressed as per millage of the field dose) are, with an exception for pirimicarb, lower than the corresponding values from June -08 (Table 4.12). In the case of pirimicarb these values are equal (~0.30 ‰) between the two years. These lower deposition values (in most cases) at the 100m distance may be due to a significantly lower mean wind speed during the first sampling period in July -09 compared to the corresponding sampling period in June -08: at the 4-m height the mean speed during this 26-hr period in 2009 was 2.6 m/s but 4.5 m/s in June -08.

During the second period (27-48 hrs after spraying; Table 4.14b) also a more or less regular decrease with distance in the accumulated deposition is mostly observed. In the case for pirimicarb, however, there appears to be a minimum in the values at the intermediate distances 10-25m and beyond that increasing again. Whether this is a random outcome or is the result of some chemical/physical process is not clear (it should be noticed here, that all deposition values in the table are means of three sample repetitions which in this case are reasonably concordant, and that the exclusion of the most deviating single values in each triplet at the actual distances (10, 25, 50 and 100m) does not change the picture appreciably).

Some examples of the dependence of the deposition upon distance are shown in Figures 4.50-4.53. These graphs, which display all sample repetitions at each distance, also will give an impression of the normal spread among the sample repetitions at a given distance. This sample scatter appears generally to be much more pronounced at the shorter distances.

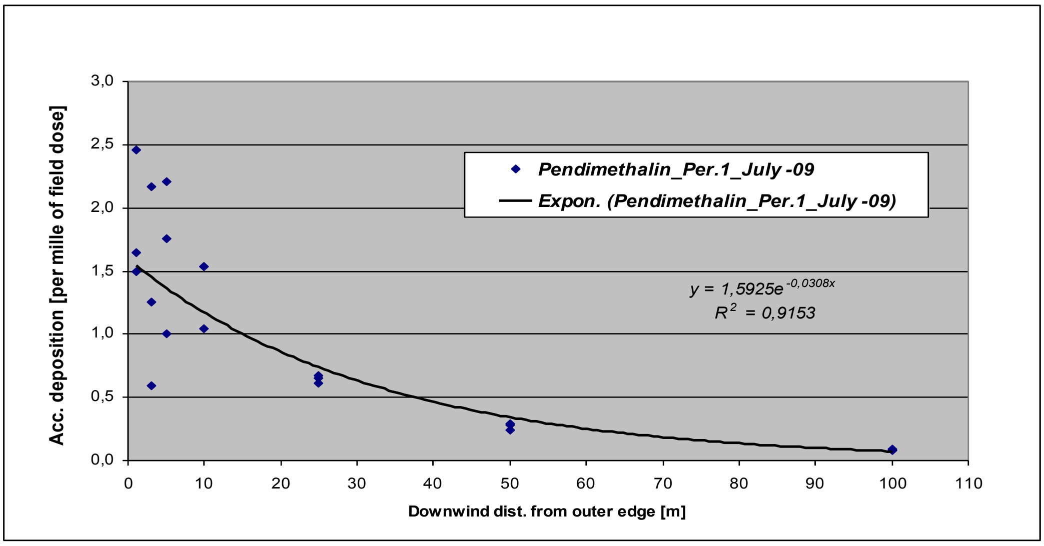

Fig. 4.50. Accumulated dry deposition of pendimethalin during first 26 hrs (= period 1) in July 2009 as a function of downwind distance from outer edge of the sprayed circular area. The three sample values at each distance are shown.

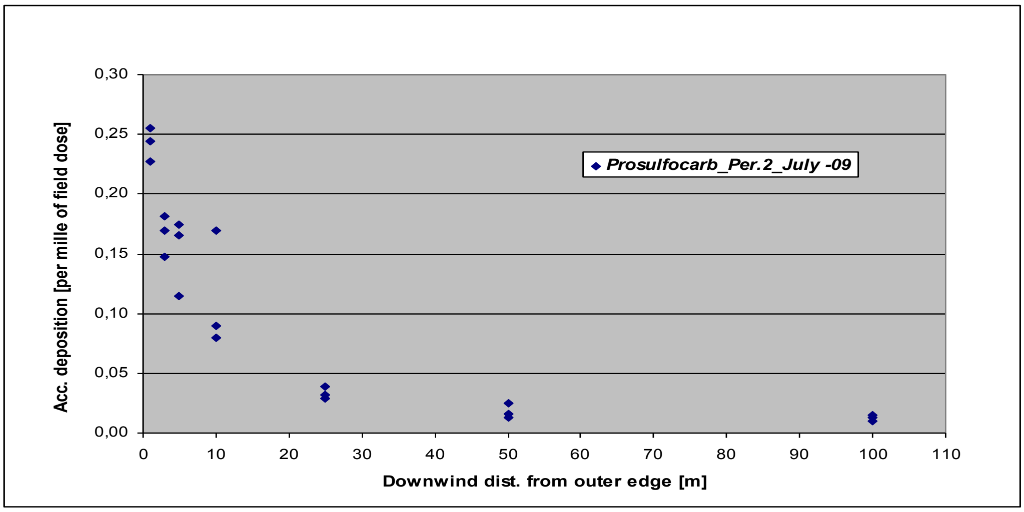

Fig. 4.51. Accumulated dry deposition of prosulfocarb during the second sampling period (27-48 hrs after spraying) in July 2009 as a function of downwind distance from outer edge of the sprayed circular area. The three sample values at each distance are shown.

This dependency on distance is often well described as an exponential decrease with distance (x) as in Fig.4.49, but in other cases (rather more often, judging from both our summer and autumn 2009 results) a logarithmic function of distance gives a better fit to data, particularly in the shorter distance region. An example of the latter case is shown in Fig. 4.52 for tolclofos-methyl from period 2.

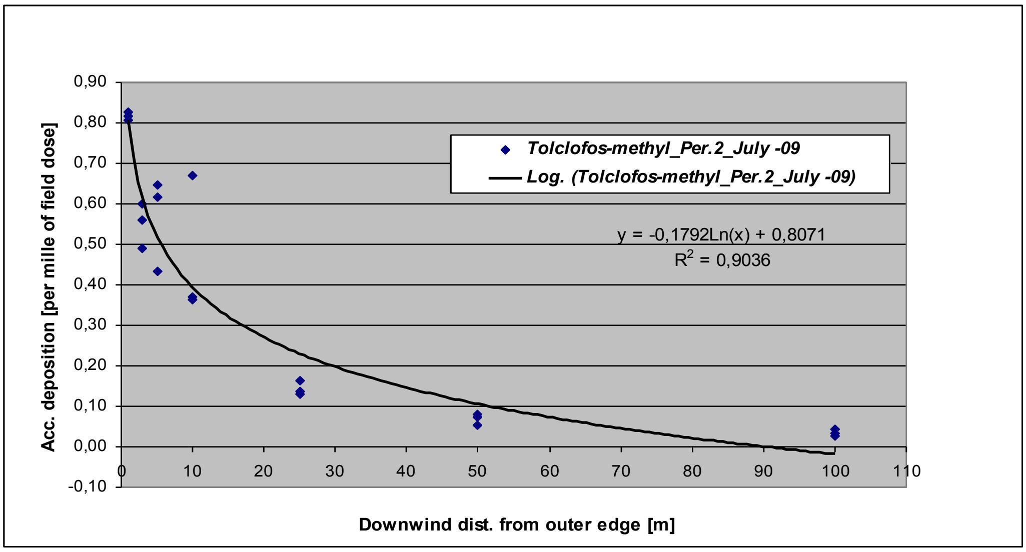

Fig. 4.52. Accumulated dry deposition of tolclofos-methyl during the second sampling period (27-48 hrs after spraying) in July 2009 as a function of downwind distance from outer edge of the sprayed circular area. The three sample values at each distance are shown. The logarithmic, best-fit function of distance (x) is also shown.

The deposition values for pirimicarb from period 1 (0-26 hrs; Fig. 4.53) indicate, if real, a much more slow decrease with distance than for any of the other substances. Thus, the fitted equation implies a relative deposition larger than 0.1 ‰ of applied dose even at distances beyond 400 m – a very small value, but significantly larger than for any of the others. (The deposition results for pirimicarb from period 2 show a very irregular pattern with distance, which may indicate some sampling or analysis problems.)

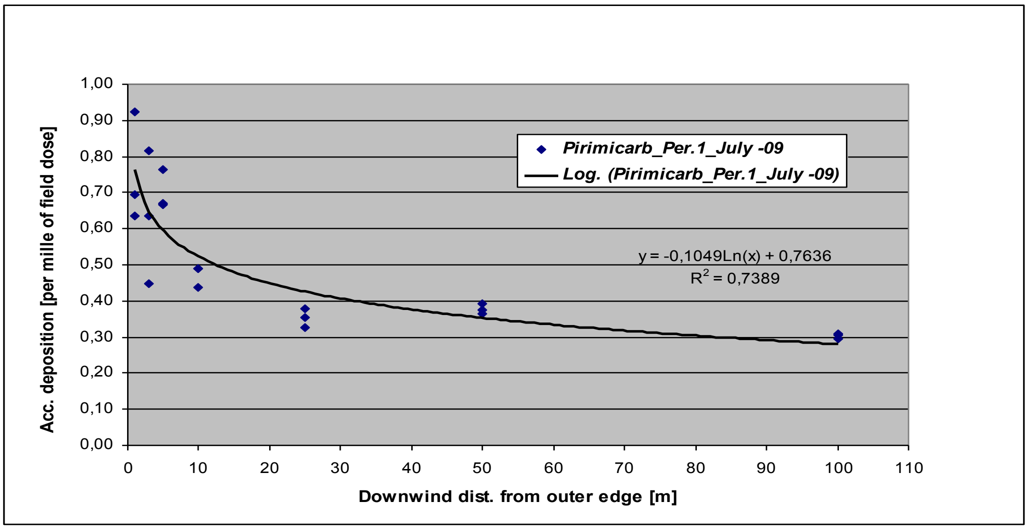

Fig. 4.53. *Accumulated dry deposition of pirimicarb during sampling period 1 (0-26 hrs after spraying) in July 2009 as a function of downwind distance from outer edge of the sprayed circular area. The three sample values at each distance are shown. The logarithmic, best-fit function of distance (x) is also shown.*

Table 4.12 Accumulated dry depositions of pesticides after 26 hrs on passive soil samplers located in the unsprayed inner circle and outside the sprayed outer circle respectively, **June 2008.** (*The relative depositions have been normalized to the dose on **1** m*^{2})

Downwind distance from the upwind inner edge of the circle [m]	**Pendimethalin**				**Prosulfocarb**				**Pirimicarb**				**Fenpropimorph**			
	Deposition on dry top soil		*Deposition on wet top soil*		Deposition on dry top soil		*Deposition on wet top soil*		Deposition on dry top soil		*Deposition on wet top soil*		Deposition on dry top soil		*Deposition on wet top soil*	
	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep- **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose
1 **	218	1.36			350	1.09			22	1.49			41	0.55		
3 **	201	1.25	*394*	*2.5*	303	0.95	*811*	*2.5*	21	1.42	*32*	*2.2*	40	0.53	*76*	*1.0*
5 *	198	1.24			342	1.07			19.2	1.28			41	0.55		
10 *	315	1.97			353	1.1			18.7	1.25			39	0.52		
Downwind distance from the outer edge of the spr. circle [m]	**Pendimethalin**				**Prosulfocarb**				**Pirimicarb**				**Fenpropimorph**			
	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m**	‰ of field dose	Dep. **µg/m²**	‰ of field dose
1 **	499	3.12	*778*	*4.9*	986	3.08	*1537*	*4.8*	30	2.03	*52*	*3.5*	86	1.15	*136*	*1.8*
3 **	305	1.90			493	1.54			21	1.37			35	0.47		
5 *	278	1.74			506	1.58			21	1.41			35	0.47		
10 *	274	1.71			419	1.31			23	1.55			40	0.54		
25 *	113	0.71			172	0.54			11	0.74			14	0.19		
50 *	51.6	0.32			56.4	0.18			6.7	0.45			9.0	0.12		
100 *	37.3	0.23			33.3	0.10			4.3	0.29			4.5	0.06		

When comparing the (absolute) deposition amounts from sampling period 2 (=22hrs; Table 4.14b) with the corresponding values from period 1 (~26 hrs; T 4.14a) it can be seen that at most distances and for most substances the accumulated deposition during the later period, which was almost, but not quit the same duration (22 hours versus 26 for the former; i.e. ~15% shorter), was markedly less. Thus, excluding the shortest (1m) and longest (100m) distances which both seems to deviate appreciably from the intermediate ones, the *avera* depositions over the intermediate distances (3-50m) were of the order 30 to jus above 50% of the deposition values at these distances in period 1 in the case of tolclofos-methyl, fenpropimorph, pirimicarb and lindane (in ascending order fr 32% for tolclofos-methyl). For prosulfocarb this quotient was only 16%, but 80 in the case of pendimethalin. The latter, high value for pendimethalin may seem consistent with the comparatively “slow” volatilization rate during the (at least first six hours after spraying in July 2009 discussed earlier in connection with t time course of the volatilization (conf. Table 4.8, first column). The opposite to reasoning: that a *fast initial* volatilization rate should lead to a (much) lesser deposition during a later stage (here period 2), does not seem readily to apply a explanation to the low deposition value for prosulfocarb during period 2, since of the other substances (except pendimethalin) showed a faster initial vaporizat than prosulfocarb (Table 4.8, first column).

Concerning the deviating pattern at the distances of 1m and 100m, respectively following may be said. The higher relative deposition at 1m, compared to peri (that is: higher than that at the intermediate distances, but yet generally lower t during period 1 (except for pendimethalin(!)) may be coupled to the closeness the source area.

The rather high deposition values at 100m – close to, or in two cases even larg than, 100% of those during the former period 1 – may seem somewhat unexpec and not easily explained. One obvious possibility, of course, would be to take i a random failure of the sampling technique (or an analysis error).

4.3.2 Dry deposition during autumn conditions

In September 2008 dry deposition of the applied pesticides was sampled with t same method as during the summer campaign, i.e. on square shaped Petri dishe (10x10x1 cm) filled with soil, taken from the surrounding field and homogeniz The sampling was carried out during 27 hrs, from 21/9 15:00 to 22/9 18:00. Selected data on the prevailing weather conditions for this period are shown in Table 4.13 (together with data from the campaign in Sept.-09). Also the bulk R number for the 0.15-16m layer is shown (for daytime and night time hours separately). Thus, it is clear that the temperatures, at the 2-m height and at the surface as well, were considerably higher during the second year, and also the speeds, particularly during the last two periods in 2009. During the third sampl period in Sept.-09 (20/9 12:00 – 22/9 12:00), ~8mm of rain was recorded at a nearby station (within 1 km from the experimental site). Periods 1 and 2 this ye like the single sampling period in Sept.-08, passed without rain.

***Table 4.13** Average values of selected weather variables for the respective dry deposition sampling periods: one in September 2008 and three in September 2009 (some noticeably high values marked in red)*

	$T(2m)$ [˚C]	**T_{surf}** [˚C]	**$\bar{u}(2m)$** [m/s]	**RH** [%]	**P** 2) [mm]	**$Ri_B(16\text{-}0.15)$**	
						daytime	*night*
Mean 21/9 15:00 -22/9 18:00 2008	*7.9*	*7.6*	*0.86*	*89*	*0*	*-0.13*	*2.9* 1)
Maximum (the same period)	*14.8*	*15.8*	*2.7*	*98*			
Mean 18/9 12:00 -19/9 12:00 (per.1) 2009	*10.4*	*11.0*	*1.4*	*81*	*0*	*-0.010*	*2.4* 1)
Maximum (the same period)	*18.0*	*19.5*	*5.4*	*99*			
Mean 19/9 12:15 -20/9 11:55 (per.2) 2009	*12.6*	*13.0*	*2.8*	*77*	*0*	*-0.025*	*0.51*
Maximum (the same period)	*20.4*	*21.5*	*7.0*	*98*			
Mean 20/9 12:00 -22/9 12:00 (per.3) 2009	*13.9*	*14.0*	*3.5*	*81*	*8*	*-0.030*	*0.084*
Maximum (the same period)	*19.9*	*20.9*	*8.0*	*98*			

1) Very high Ri-number may occur quite frequently during night time in weak wind situations with small vertical wind speed gradients. 2) Total sum (mm)

Table 4.15 below presents the deposition results from September 2008. The normalized deposition (i.e. in relation to actual field doses) on dry surface soil in Petri dishes placed within the ring-shaped sprayed area at distances 1, 3 and 5m downwind from the inner edge of the sprayed circle, were at all distances and for all substances except fenpropimorph roughly in the range 0.08 – 0.2 ‰ of applied dose, which is about 85 to above 90% lower than the corresponding depositions in June -08 (for fenpropimorph the deposition was mainly below the detection limit).

Downwind the sprayed circular area the normalized, accumulated depositions *on dry soil* (i.e. not especially wetted) out to a distance of 10m were in the range 0.1 – 0.7 ‰ of applied dose (with the highest value at 1m for pendimethalin). At the three more distant sampling points (25, 50 and 100m from the outer edge) the relative depositions varied between not detectable (pendimethalin (at 50 and 100m) and fenpropimorph) to 0.2 ‰ of applied dose. These values are also markedly lower than the corresponding depositions in June; broadly of the order 70 to 90% lower than those.

The deposition on *wetted soil* in Petri dishes at a downwind distance of 1m was (like the case in June -08) noticeably higher than on the dry dishes at the same distance: with a factor ~1.3 for pendimethalin and pirimicarb, and at least with a factor 2 in the case of prosulfocarb and fenpropimorph.

For pendimethalin and prosulfocarb a more or less regular decrease with increasing distance is observed. Pirimicarb, on the other hand, shows an almost constant deposition (~0.2 ‰) over the distance range, at least from 5m and outwards, and fenpropimorph showed no detectable values at any distance, except for the low value (0.04 ‰) at 3m.

Table 4.14a *Accumulated dry depositions of pesticides* ***0-26 hrs after spraying (period 1)*** *on passive soil samplers located in the unsprayed inner circle and outside the sprayed outer circle respectively;* ***July 2009.*** *(The relative depositions have been normalized to the dose on 1* m^2*)*

Downwind distance from the upwind inner edge of the circle [m]	**Lindane**		**Pirimicarb**		**Tolclofos-meth.**		**Prosulfocarb**		**Fenpropimorph**		**Pendimethalin**	
	Deposition on dry top soil		Deposition on dry top soil		Deposition on dry top soil		Deposition on dry top soil		Deposition on dry top soil		Deposition on dry top soil	
	Dep. [µg/m²]	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***
1 ** ***not used***												
3 **	60.9	*6.09*	30.5	*1.63*	123.1	*3.96*	705.6	*1.77*	78.0	*0.83*	704.5	*3.54*
5 * ***not used***												
10 * ***not used***												
Downwind distance from the outer edge of the spr. circle [m]	**Lindane**		**Pirimicarb**		**Tolclofos-meth.**		**Prosulfocarb**		**Fenpropimorph**		**Pendimethalin**	
	Dep. [µg/m²]	***‰ of field dose***	**Dep. [µg/m²]**	***‰of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***
1 **	13.8	*1.38*	14.0	*0.75*	54.9	*1.77*	355.1	*0.89*	18.3	*0.20*	371.8	*1.87*
3 **	16.3	*1.63*	13.6	*0.73*	48.4	*1.56*	300.2	*0.76*	17.4	*0.19*	340.4	*1.71*
5 **	15.4	*1.54*	13.1	*0.70*	42.7	*1.37*	291.0	*0.73*	13.1	*0.14*	329.1	*1.65*
10 **	10.1	*1.01*	8.82	*0.47*	41.0	*1.32*	263.9	*0.66*	10.4	*0.11*	272.8	*1.37*
25 **	4.74	*0.47*	6.60	*0.35*	20.0	*0.64*	125.6	*0.32*	4.95	*0.05*	128.6	*0.65*
50 **	2.68	*0.27*	7.05	*0.38*	8.59	*0.28*	49.9	*0.13*	3.50	*0.04*	54.2	*0.27*
100 **	0.90	*0.09*	5.67	*0.30*	2.68	*0.09*	17.0	*0.04*	1.97	*0.02*	16.7	*0.08*

Table 4.14b *Accumulated dry depositions of pesticides* ***27-48 hrs after spraying (period 2)*** *on passive soil samplers located in he unsprayed inner circle and outside the sprayed outer circle respectively;* ***July 2009.*** *(The relative depositions have been normalized to the dose on 1* m^2*)*

Downwind distance from the upwind inner edge of the circle [m]	**Lindane**		**Pirimicarb**		**Tolclofos-meth.**		**Prosulfocarb**		**Fenpropimorph**		**Pendimethalin**	
	Deposition on dry top soil		Deposition on dry top soil		Deposition on dry top soil		Deposition on dry top soil		Deposition on dry top soil		Deposition on dry top soil	
	Dep. [µg/m²]	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***
1 ** ***not used***												
3 **	9.18	*0.92*	7.37	*0.39*	23.6	*0.76*	92.7	*0.23*	4.28	*0.05*	352.8	*1.77*
5 * ***not used***												
10 * ***not used***												

Downwind distance from the outer edge of the spr. circle [m]	**Lindane**		**Pirimicarb**		**Tolclofos-meth.**		**Prosulfocarb**		**Fenpropimorph**		**Pendimethalin**	
	Dep. [µg/m²]	***‰ of field dose***	**Dep. [µg/m²]**	***‰of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***	**Dep. [µg/m²]**	***‰ of field dose***
1 **	11.2	*1.12*	8.54	*0.46*	25.4	*0.82*	96.4	*0.24*	9.79	*0.10*	466.1	*2.34*
3 **	7.63	*0.76*	7.71	*0.41*	17.2	*0.55*	66.3	*0.17*	6.53	*0.07*	312.8	*1.57*
5 **	8.22	*0.82*	7.41	*0.40*	17.6	*0.57*	60.2	*0.15*	5.57	*0.06*	321.7	*1.62*
10 **	4.61	*0.47*	1.95	*0.10*	14.5	*0.37*	33.7	*0.09*	3.09	*0.03*	202.3	*1.02*
25 **	2.56	*0.26*	2.44	*0.13*	4.49	*0.14*	13.3	*0.03*	1.94	*0.02*	77.8	*0.39*
50 **	1.69	*0.17*	5.81	*0.31*	2.14	*0.07*	7.16	*0.02*	2.12	*0.02*	42.2	*0.21*
100 **	1.49	*0.15*	5.71	*0.31*	1.09	*0.03*	5.08	*0.01*	1.82	*0.02*	20.7	*0.10*

Period of measurement: 27 – 48 hours (=22 hrs) after application: 5/7 14:00 – 6/7 11:30 2009. Applied doses**: Lindane** 10 000 µg/m², **pendimethalin** 199 000 µg/m², **prosulfocarb** 398 000 µg/m², **pirimicarb** 18700 µg/m², ; **fenpropimorph** 93400 µg/m², **tolclofos-methyl** 31100 µg/m² ** = average of three samples

Table 4.15 *Accumulated dry deposition of pesticides during 27 hrs following application on passive soil samplers located in the unsprayed inner circle and outside the sprayed circular area, respectively;* ***September 2008.*** (*The relative depositions are normalized to the dose on* **1 m^2**)

Downwind distance from the upwind inner edge of the circle [m]	**Pendimethalin**				**Prosulfocarb**				**Pirimicarb**				**Fenpropimorph**			
	Deposition on dry top soil		*Deposition on wet top soil*		Deposition on dry top soil		*Deposition on wet top soil*		Deposition on dry top soil		*Deposition on wet top soil*		Deposition on dry top soil		*Deposition on wet top soil*	
	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep- **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose
1 **	29	0.18			22	0.07			3.3	0.22			< 3	<0.05		
3 **	30	0.19			29	0.09			3.3	0.22			<LOD 1)	--		
5 *	27	0.17			26	0.08			3.1	0.21			< LOD	--		
Downwind distance from the outer edge of the sprayed circle [m]	**Pendimethalin**				**Prosulfocarb**				**Pirimicarb**				**Fenpropimorph**			
	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose	Dep. **µg/m²**	‰ of field dose		‰ of field dose	Dep. **µg/m²**	‰ of field dose
1 **	113	0.7	*144*	*0.9*	126	0.4	*259*	*0.8*	4.0	0.25	*5.2*	*0.35*	< LOD	--	*5.8*	*0.08*
3 **	89	0.6			98	0.3			5.4	0.4			3.3	0.04		
5 *	34	0.2			37	0.12			3.0	0.2			< LOD			
10 *	31	0.2			39	0.12			3.4	0.2			< LOD			
25 *	10	0.06			15	0.05			3.2	0.2			< LOD			
50 *	< LOD				6	0.02			2.6	0.2			< LOD			
100 *	< LOD				5	0.02			3.3	0.2			< LOD			

Period of measurement*: 21/9 15:00 – 22/9 18:00 2008*. Applied doses: **pendimethalin** 160 000 µg/m² ; **prosulfocarb** 320 000 µg/m²; **pirimicarb** 15 000 µg/m² ; **fenpropimorph** 75 000 µg/m². * = one single sample and ** = average of three samples; 1) LOD (level of detection) for **fenpropimorph** was 2.9 µg/m²

During the campaign in September 2009 the sampling of dry deposition was extended out to a distance of 200m outside the sprayed area, but the sampling inside the treated circle was restricted to just one distance (3m) and no samplin wet topsoil was used.
The averaged results of absolute deposition (in µg/m^2) are shown in Table 4.16 of the normalized (in per mille of applied dose) in Table 4.17. (The values presented in both tables are mean values of three sample repetitions at each distance unless otherwise noted.)

In September 2009 three consecutive periods was used for deposition sampling period 1 (0-24 hrs after spraying), period 2 (25-48 hrs) and period 3 (49-96 hrs (Note, when comparing results between periods in Sept. -09, that period 3 was twice as long as each of the other two, and when comparing absolute depositio between years that the applied doses were in general very different, e.g.: the dc of prosulfocarb in Sept.-09 was only 6% of that in Sept.-08, whereas that of pirimicarb was almost 6 times larger in Sept.-09 compared with Sept.-08; conf Table 4.1.)
When comparing the normalized deposition values (Table 4.17) from period1 a distance of 3m downwind from *the inner edge of the circle* with the correspond values from the only, and slightly longer, period in September -08 (27 hrs in Se 08 versus 24 hrs in per.1 Sept.-09), it is obvious that the deposition was appreciably much higher during the latter year. For those four substances that v used both years the relative depositions during 2009 were from a factor about 4 (prosulfocarb) to 13 (pendimethalin) higher than the in Sept. -08 (the shorter sampling time disregarded here).
Outside and downwind the sprayed area a more or less regular decrease in the averaged values with increasing distance is observed for most substances (and all three periods; Table 4.16 and 4.17). The spread among the individual sampl repetitions at each distance were mainly reasonably small at the outer distances tended to increase at shorter distances (roughly ≤ 10m downwind the outer edg Figures 4.54 and 4.55 show two examples from period 1 (0-24 hrs after sprayir In these figures both an exponential and a logarithmic curve fitted to the sampl data and describing the distance dependency are given. The logarithmic functic type often gives a better fit, especially at the shorter distances, but may occasionally (as in the case in fig. 4.53 for lindane) reach a zero value at a shor distance than the observations indicate.
Two substances, pirimicarb and pendimethalin, however, appear to deviate fro this general pattern. In the case of pirimicarb the deposition values (whether considering the absolute or the normalized ones) generally show a large scatter among samples at most distances and in all periods, and does not show an obvi decrease with distance (rather being more or less constant over the observed distance range). Figure 4.56 show this behaviour of pirimicarb in period 2 (alm the same pattern is apparent in period 3 for this substance, whereas the sample scatter is worse at almost all distances in period 1). Even if the fitted exponenti curve does indicate some decrease in the deposition with distance, this decreas given by the equation, is so slow that at a 500 m distance it has merely droppec 1.5 ‰ of the applied dose.

Also pendimethalin show a comparatively large scatter among the sample repetitions in period 1 and 3, respectively (but not particularly in period 2) and also here it is hard to discern any decreasing trend with distance (if not disregarding many of the sample repetitions; conf. Fig. 4.57, showing period 2).

Table 4.16 *Accumulated dry depositions of pesticides during three subsequent periods after spraying on dry topsoil in Petri dishes located inside the unsprayed inner circle and outside the sprayed circular area, respectively;* ***18th – 22nd*** *of* ***Sept. 2009. Period 1: 0-24 hrs, per.2: 25-48 hrs and per.3: 49-96 hrs*** *after spraying. The relative depositions have been normalized to the field dose on 1 m^2 and are averages of three samples at each distance unless otherwise remarked.*

	Lindane			**Pirimicarb**			**Tolclofos-methyl**			**Prosulfocarb**			**Fenpropimorph**			**Pendimethalin**		
	Deposition [µg/m^2]			**Deposition [µg/m^2]**			**Deposition [µg/m^2]**			**Deposition [µg/m^2]**			**Deposition [µg/m^2]**			**Deposition [µg/m^2]**		
Downwind dist. from inner edge of circle [m]	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***
1 *not used*																		
3	*47.0 1)*	*20.2*	*17.9*	*137.4*	*118.7*	*192.7*	*32.7 1)*	*10.9*	*14.2*	*6.47*	*4.27*	*7.53*	*34.9*	*17.2*	*18.6*	*46.9*	*39.2*	*50.3*
5 *not used*																		
	Lindane			**Pirimicarb**			**Tolclofos-methyl**			**Prosulfocarb**			**Fenpropimorph**			**Pendimethalin**		
Downw. dist. from outer edge [m]	**Deposition [µg/m^2]**			**Deposition [µg/m^2]**			**Deposition [µg/m^2]**			**Deposition [µg/m^2]**			**Deposition [µg/m^2]**			**Deposition [µg/m^2]**		
	Per.1	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***
1	*106.5 1)*	*28.2*	*13.7*	*276.4 2)*	*206.3*	*224.2*	*41.5*	*16.3*	*16.0*	*4.98*	*1.79*	*5.07*	*47.1*	*5.43*	*8.4*	*13.4 1)*	*30.5*	*23.7*
3	*59.6*	*17.9*	*17.3 1)*	*(17.5)*	*200.6*	*200.0*	*26.7*	*10.2*	*14.7*	*3.68*	*1.48*	*4.60 1)*	*30.2*	*4.52*	*6.5*	*14.9*	*28.5*	*34.7*
5	*51.2*	*17.7*	*10.2*	*261.9 2)*	*225.7*	*165.7*	*25.7*	*11.0*	*13.0*	*3.28*	*1.45*	*4.39*	*27.5 1)*	*4.59*	*5.8*	*15.4 1)*	*24.3 1)*	*21.4*
10	*47.0*	*12.4*	*16.8*	*199.6 2)*	*236.0*	*224.7*	*22.4*	*6.5*	*8.7*	*3.26 1)*	*1.33*	*0.00*	*28.4*	*3.12 1)*	*4.60*	*18.1 1)*	*25.4*	*27.4 1)*
25	*15.5*	*5.6*	***≤ LOD***	*216.6 2)*	*230.5*	*208.0 2)*	*7.7*	*2.47*	*5.0*	*2.87*	*1.09*	***≤ LOD***	*12.7*	*2.85*	*1.80*	*18.9 1)*	*23.5*	*25.5*
50	*8.9 1)*	*3.23*	***≤ LOD***	*63.5 2)*	*195.8*	*(8.8)*	*3.37*	*1.69*	*3.0*	*1.61*	*1.01*	***≤ LOD***	*6.0*	*4.22*	***≤ LOD***	*8.8*	*20.3*	*18.2*

Table 4.17 *Accumulated dry depositions of pesticides during three subsequent periods after spraying on dry topsoil in Petri dishes located inside the unsprayed inner circle and outside the sprayed circular area, respectively;* ***18th – 22nd*** *of* ***Sept. 2009. Period 1: 0-24 hrs, per.2: 25-48 hrs and per.3: 49-96 hrs*** *after spraying. The relative depositions have been normalized to the field dose on 1 m^2 and are averages of three samples at each distance unless otherwise remarked.*
1) Average of two samples with most outlying value omitted; 2) a single sample value

	Lindane			**Pirimicarb**			**Tolclofos-methyl**			**Prosulfocarb**			**Fenpropimorph**			**Pendimethalin**		
	Per.1	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***
Downw. dist. from inner edge of circle [m]	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***
1 *not used*																		
3	5.0 1)	2.13	1.89	1.54	1.33	2.16	1.10 1)	0.37	0.48	0.34	0.23	0.40	0.39	0.19	0.21	2.5	2.1	2.7
5 *not used*																		
	Lindane			**Pirimicarb**			**Tolclofos-methyl**			**Prosulfocarb**			**Fenpropimorph**			**Pendimethalin**		
Downw. dist. from outer edge [m]	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***	***Per.1***	***Per.2***	***Per.3***
	‰ of field dose	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***	***‰ of field dose***
1	11.2 1)	3.0	1.44	3.1 2)	2.3	2.5	1.4	0.55	0.54	0.26	0.094	0.27	0.53	0.061	0.094	0.71 1)	1.60	1.25
3	6.3	1.88	1.82 1)	(0.20)	2.3	2.2	0.90	0.34	0.49	0.19	0.078	0.24 1)	0.34	0.051	0.073	0.78	1.50	1.83
5	5.4	1.86	1.07	2.9 2)	2.5	1.9	0.86	0.37	0.44	0.17	0.077	0.23	0.31 1)	0.052	0.065	0.81 1)	1.28 1)	1.12
10	5.0	1.31	1.77	2.2 2)	2.7	2.5	0.75	0.22	0.29	0.17 1)	0.070	0.00	0.32	0.035 1)	0.052	0.96 1)	1.34	1.44 1)
25	1.63	0.59	**≤ LOD**	2.4 2)	2.6	2.3 2)	0.26	0.08	0.17	0.15	0.057	**≤ LOD**	0.14	0.032	0.020	1.00 1)	1.24	1.34
50	0.94 1)	0.34	**≤ LOD**	0.71 2)	2.2	0.10	0.11	0.06	0.10	0.085	0.053	**≤ LOD**	0.067	0.047	**≤ LOD**	0.46	1.07	0.96
100	0.41	0.28	**≤ LOD**	2.8 2)	2.1	2.4	0.060	0.04	0.05	0.081	0.078	**≤ LOD**	0.041	0.030	(0.037)	0.33 1)	0.83	(2.15)
200	0.24	0.10	**≤ LOD**	3.4 2)	2.05	2.0	0.030	0.02	**≤ LOD**	0.069	0.056	**≤ LOD**	0.024	0.030	**≤ LOD**	0.11 1)	1.38	1.37 1)

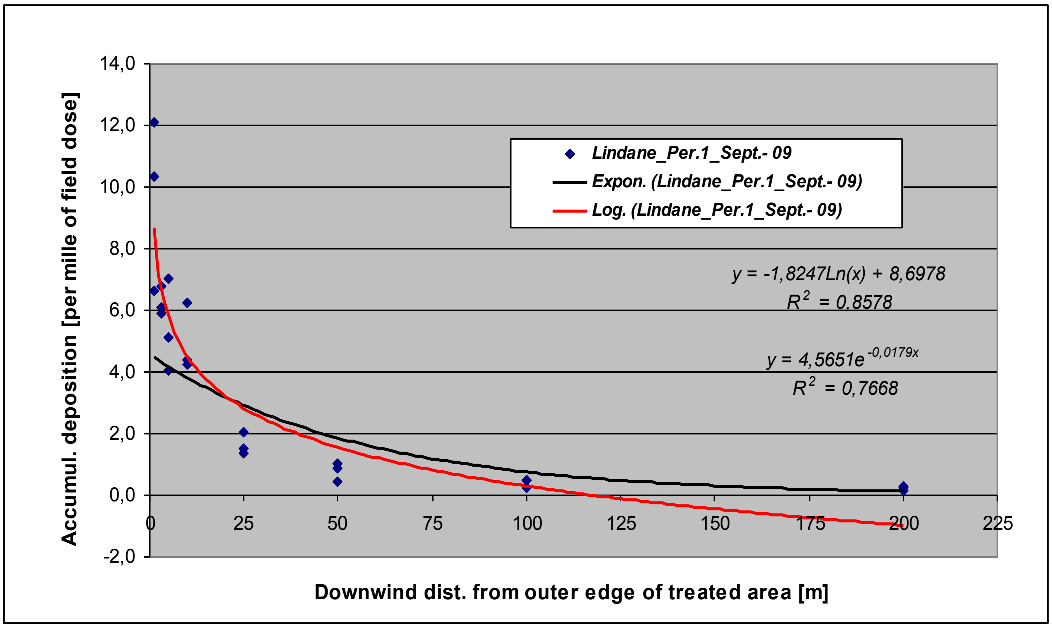

Fig. 4.54. *Accumulated dry deposition of lindane during sampling period 1 (0-24 hrs after spraying) in Sept. 2009 as a function of downwind distance from oute r edge of the sprayed circular area. The three sample repetitions at each distance are shown. Also a logarithmic as well as an exponential curve fit to these data are shown.*

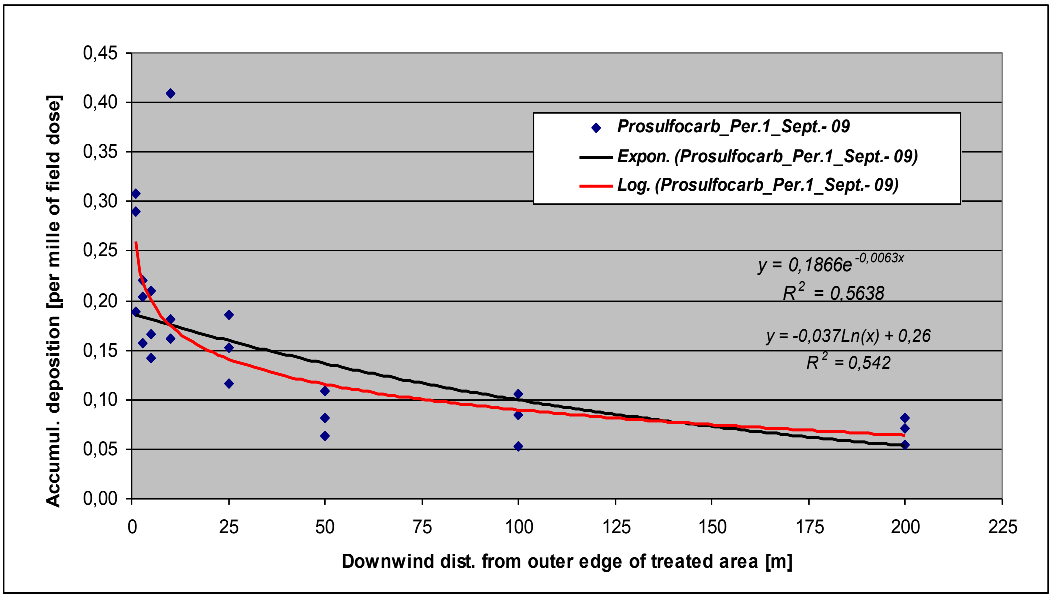

Fig. 4.55. *Accumulated dry deposition of prosulfocarb during sampling period 1 (0-24 hrs after spraying) in Sept. 2009 as a function of downwind distance from outer edge of the sprayed circular area. The three sample repetitions at each distance are shown. Also a logarithmic and an exponential curve fit to the data are shownn.*

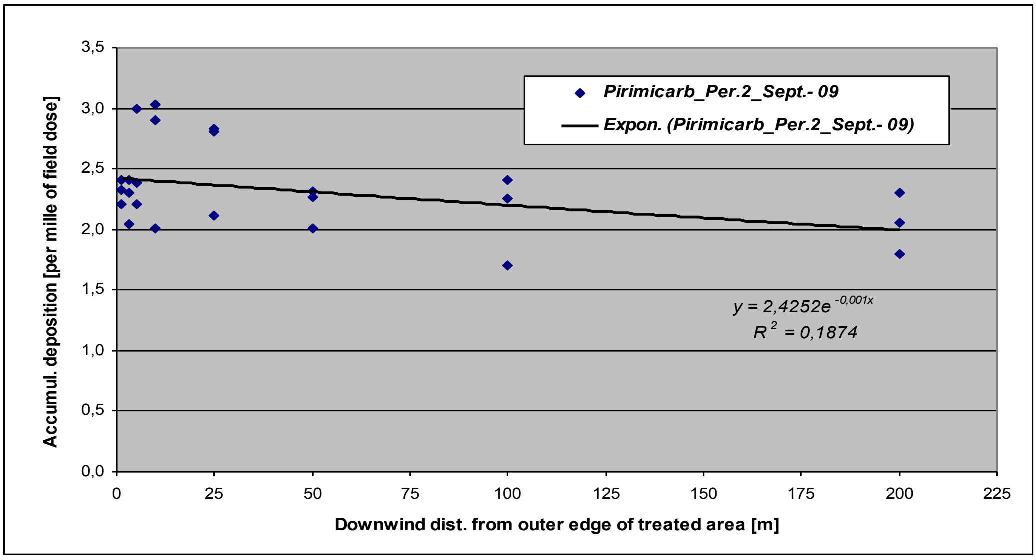

Fig. 4.56. *Accumulated dry deposition of pirimicarb during sampling period 2 (25-48 hrs after spraying) in Sept. 2009 as a function of downwind distance from outer edge of the sprayed circular area. The three sample repetitions at each distance are shown. An exponential curve fit to these data is included for comparison with the two previous figures.*

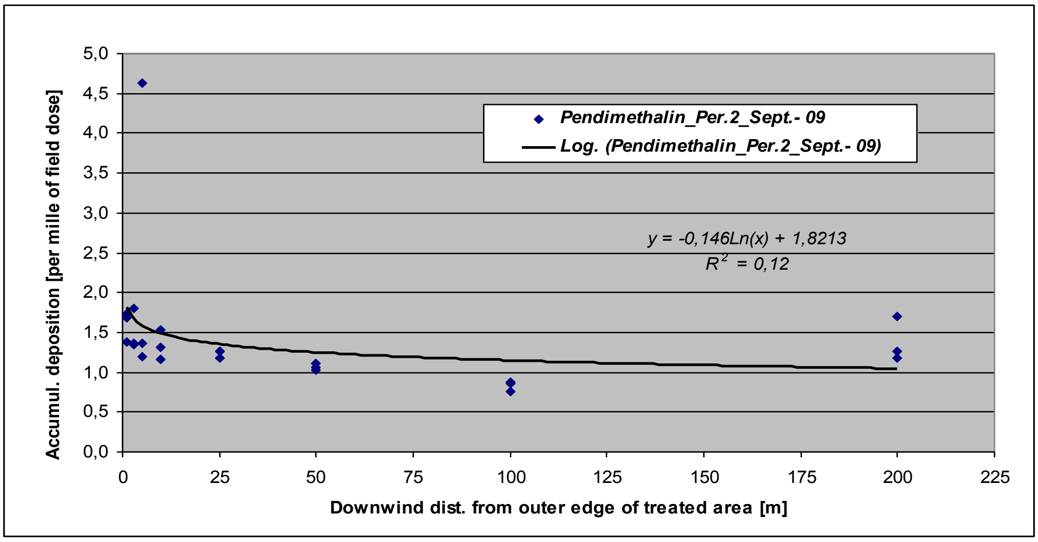

Fig. 4.57. *Accumulated dry deposition of pendimethalin during sampling period 2 (25-48 hrs after spraying) in Sept. 2009 as a function of downwind distance from outer edge of the sprayed circular area. The three sample repetitions at each distance are shown. A logarithmic curve fit to these data is also given.*

4.3.3 Comparisons of deposition between seasons and periods

When comparing the normalized depositions (as permillage of applied doses) during sampling periods of comparable durations (mostly about 24-27 hrs in the present case) between the different seasons (conf. Figs. 4.58-4.63 below, which show the *averaged depositions*, when a few doubtful outlying sample values have been omitted), it is found that the highest deposition values occurred partly during the first (and only) sampling period in June -08 (0-26 hrs after spraying) and partly during the first period in July -09 (0-26 hrs) in at least four cases: in June -08 for prosulfocarb, fenpropimorph and pendimethalin (at short distances, 1-10m; at greater distances, from 25m and beyond, the curve from per.2 in Sept. -09 – if correct and not a result of analysis problems – shows the highest deposition) and in per.1 in July -09 for tolclofos-methyl. Lindane shows the highest deposition in period1 (~0-24 hrs), Sept. -09 (and the second highest during per.2 that month). In the case of pirimicarb, the highest deposition apparently occurred during period 2, Sept. -09 (24-48 hrs after spraying). The deposition curve for pirimicarb in the latter case (Fig. 4.59) may possibly appear doubtful in that it shows an almost constant, and rather high, value with increasing distance. Also the curve from period 1, Sept.-09 (Fig. 4.59) may indicate some sampling or analysis problems. If both these two September periods are considered dubious in some respect or another, and therefore disregarded, also pirimicarb shows the highest deposition in the single period in June -08.

The weather conditions during this period in June (conf. Table 4.11) are characterised by a moderately high mean air temperature (13.9˚C) as well as surface temperature (15.3 ˚C), (both of them yet lower than during period 1 in July -09), a rather high maximum surface temperature (~25 ˚C) and a higher average wind speed (3.4 m/s) than any of the other sampling periods (excepting period 3 in Sept.-09, with about the same average and period 2 in July -09 from which we have no wind speed data). The highest maximum wind speeds (at the height of 2 m) occurred during period 3 (8.0 m/s), period 2 (7.0 m/s) and period 1 (5.4 m/s), respectively, in Sept.-09 (conf. Table 4.13). Thus, it is possible that the combination of a fairly high maximum surface temperature and a moderately high wind speed in June -08 was favourable for the higher dry deposition of at least prosulfocarb, fenpropimorph and pendimethalin that year (and possibly also for pirimicarb according to the discussion regarding the curves for pirimicarb above) – if not other factors, such as the type and properties of the sprayed surface, are more deciding.

Deposition may be seen as the last link in a chain of processes: the ′production′ phase at the source, the transport phase in the atmosphere – during which chemical reactions, degradation or other transformation processes may occur – and subsequently followed by dry or wet deposition (wash-out). All of these processes are more or less strongly governed by the prevailing meteorological conditions. A thorough discussion of this matter is beyond the scope of this report, yet some brief considerations are given in Ch.5.7.

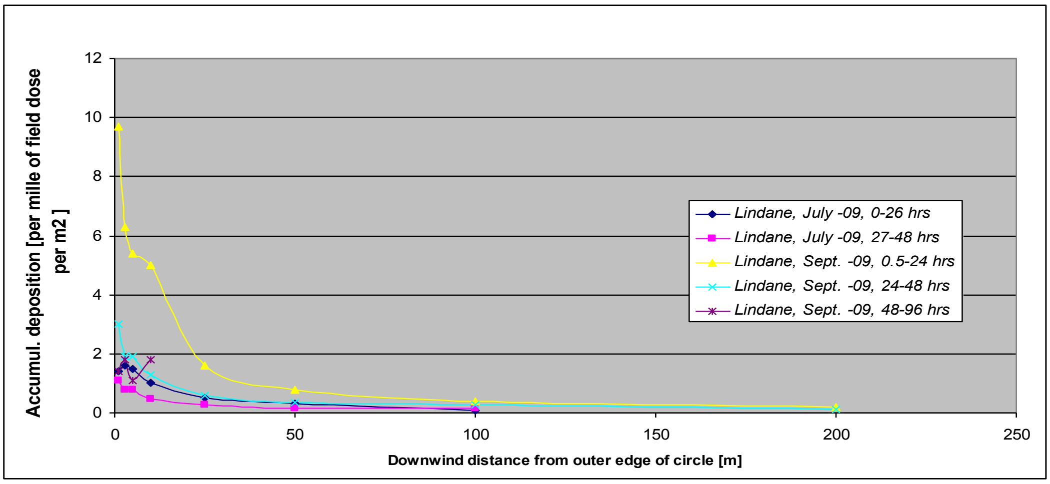

Fig. 4.58. *Accumulated dry deposition of lindane (per mille of applied dose per m^2) during the different seasons and sampling periods (note the double sampling duration (48 hrs) in period 3, Sept.-09).*

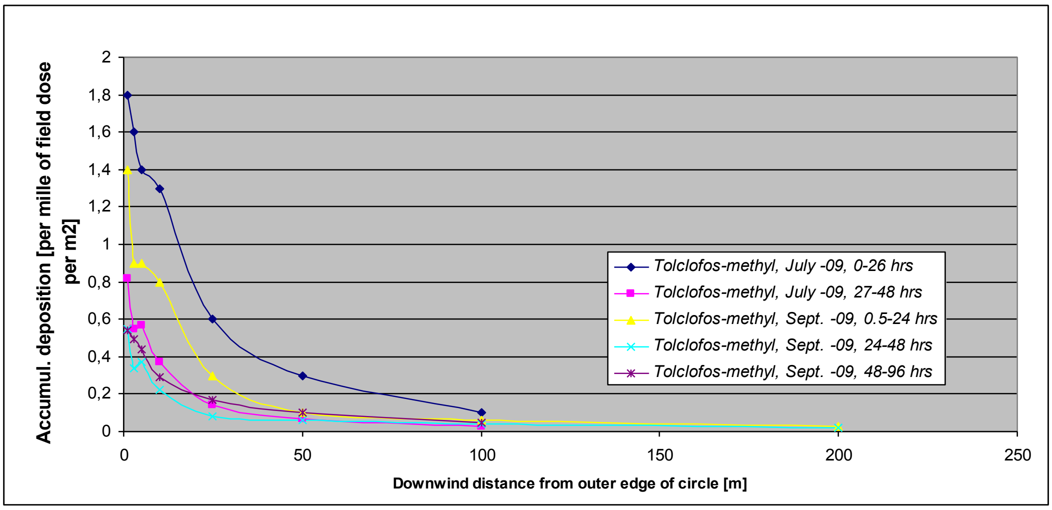

Fig. 4.59. *Accumulated dry deposition of tolclofos-methyl (in per mille of applied dose per m^2) during the different seasons and sampling periods (note the double sampling duration (48 hrs) in period 3, Sept.-09).*

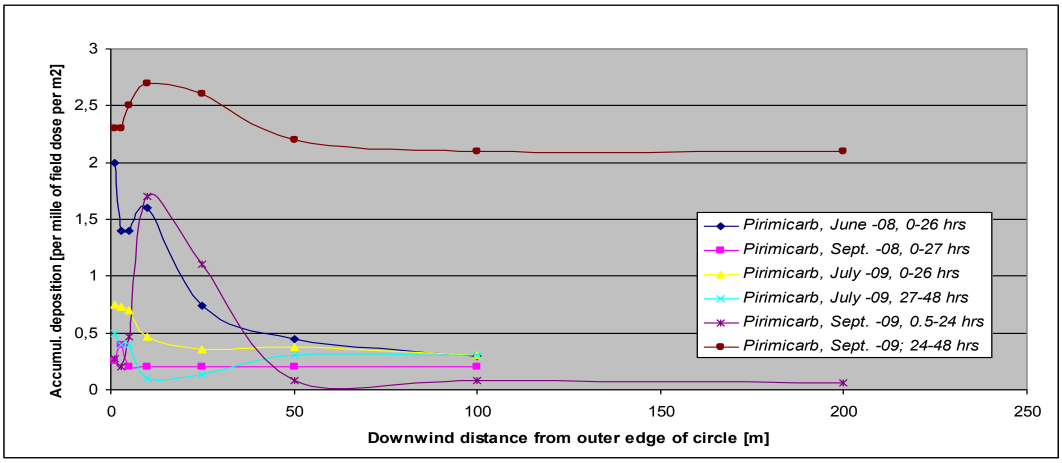

Fig. 4.60. *Accumulated dry deposition of pirimicarb (in per mille of applied dose per m^2) during the different seasons and sampling periods (period 3, Sept.-09 omitted due to different length of this period).*

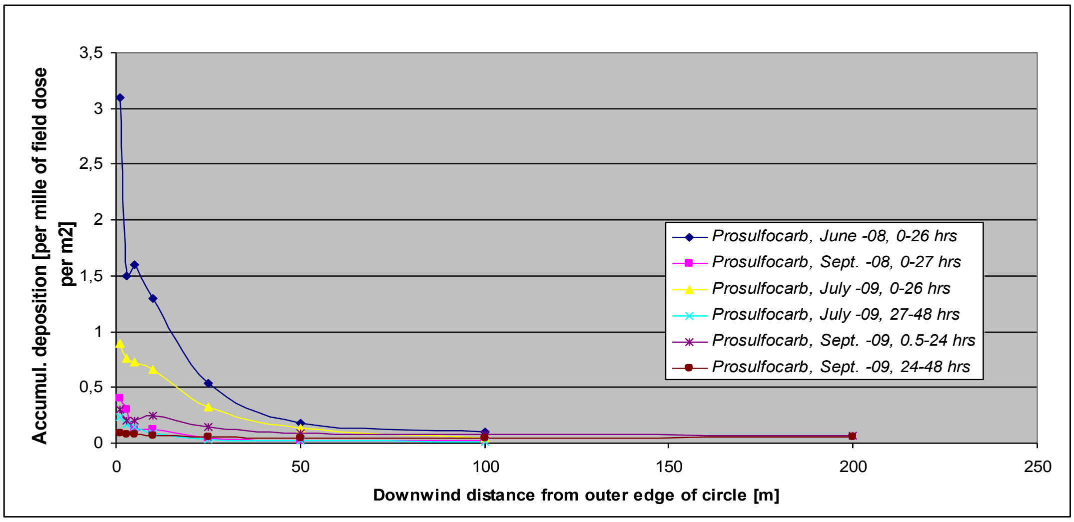

Fig. 4.61. *Accumulated dry deposition of prosulfocarb (in per mille of applied dose per m^2) during the different seasons and sampling periods (period 3, Sept.-09 omitted due to different length of this period).*

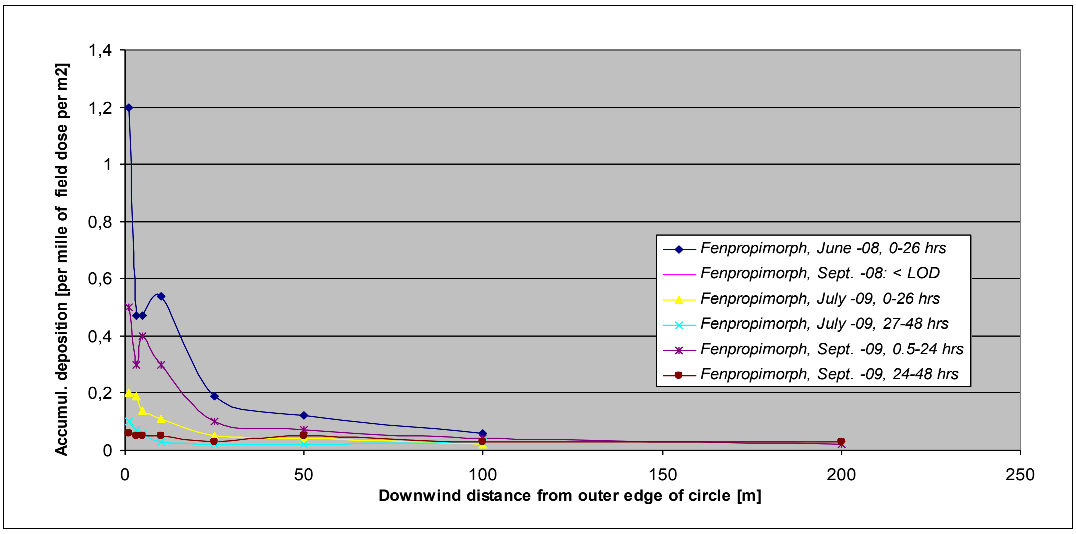

Fig. 4.62. *Accumulated dry deposition of fenpropimorph (in per mille of applied dose per m^2) during the different seasons and sampling periods (period 3, Sept.-09 omitted due to different length of this period).*

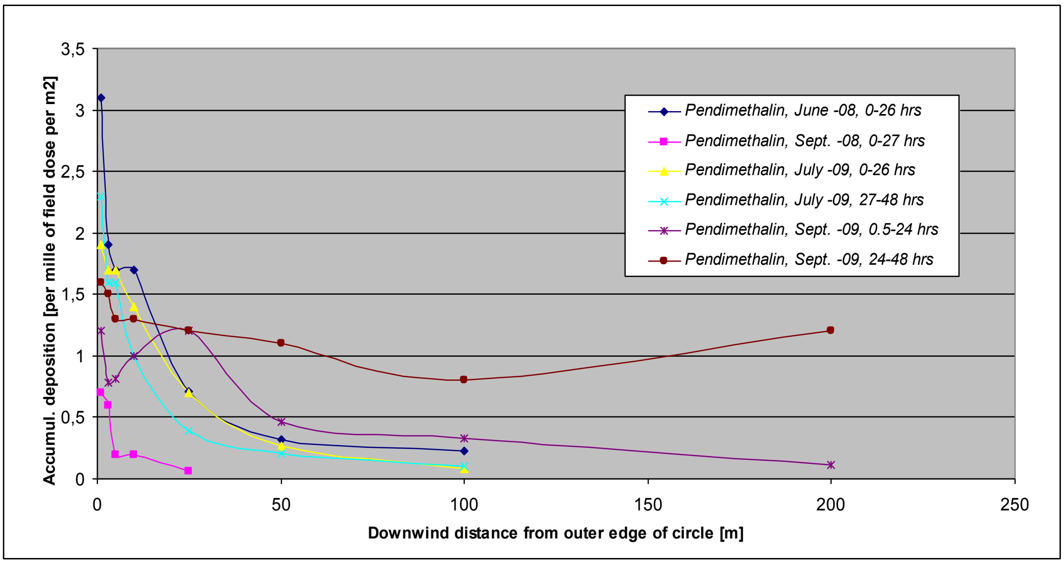

Fig. 4.63. *Accumulated dry deposition of pendimethalin (in per mille of applied dose per m^2) during the different seasons and sampling periods (period 3, Sept.-09 omitted due to different length of this period).*

5 Discussion and conclusions

5.1 Methods and experimental set-up

The method used for measuring the volatile flux of six pesticides, the integrated horizontal flux (IHF) method is a micrometeorological method that relays on accurate vertical profile measurements of horizontal wind speed and concentration of the respective pesticides in air.
The IHF method requires only a rather restricted fetch over treated area and use of a circular plot around the measuring towers makes it independent of changes in wind direction during the experiments. However, two possible sources of error should be recognized: the possibility of a (horizontal) flux above the highest air sampling height in the mast and also a less accurately determined concentration profile, next to the surface, below the lowest sampling height.
The first possibility have mainly been avoided partly by the use of measuring masts with heights (16 m) that are high in proportion to the actual fetch (54 m) and furthermore, when the concentration profiles in spite of this not approached zero concentration at the height of 16 m, the integration of the extrapolated profiles were extended to higher levels (at most 32 m). There is of course an uncertainty implicit in this procedure as the real behaviour of the concentration plume above the 16 m measuring point is not known. (On the other hand, the additional contribution to the total accumulated flux during a sampling period due to the flux above 16 m was mostly of the order 3-5 % of the total.)
The second difficulty was during the summer campaigns handled by assuming a height constant concentration profile below the zero plane displacement height of the crop canopy, and during the September campaigns by extrapolating the profile downwards from the lowest measuring level. In both cases, however, we assume that due to the comparatively low wind speeds close to the surface (or within the crop canopy) a certain degree of inaccuracy in the concentration profile does only cause a comparatively small inaccuracy in the determined flux.

Another issue concerning the IHF method to consider here is the possible overestimation of the flux due to the normal neglect of the turbulent diffusion term ($\overline{u'c'}$). As mentioned earlier, this overestimation has been estimated by several authors to be roughly in the range 0 to about 15 %, varying with the surface roughness and stability conditions. Due to the ambiguous data on this point (and the rather varying weather and other conditions during our experiments), we have not attempted to apply any corrections for this possible error to our accumulated fluxes.

A circumstance that may have acted towards a certain underestimation of the relative fluxes, on the other hand, is the fact that we do not have any direct measurements of the factual dose hitting the target surface (either the standing crop or the bare soil, respectively) due to the problems connected with the tests with a fluorescent dye as a tracer in the tank mixture. That is, we have estimated the applied field dose from the amounts of the respective substances added to the tank mixture (and corrected for the remaining volume in the tank after treatment) and have thus no information about any possible drift by the wind – or the immediate evaporation – during the spraying activity itself of the substances. The drift by wind was perhaps negligible regarding the inner spray swaths (low drift nozzles were used throughout) but maybe not when it comes to the outermost swath (12 m in width, corresponding to ~ 44 % of the total sprayed area). This may lead to a certain underestimation of the determined relative fluxes, calculated as a percentage of the intended applied dose without any corrections for such losses. Thus it may be noticed, for example, that the average wind speed at the 2-m level during (or immediately after) the pesticide spraying in June 2008 was about 5 ms^{-1}, almost 3 ms^{-1} in July -10 and more than 3 ms^{-1} in Sept. -09 (while it was fairly low (≤ 1 ms^{-1}) in July -09 and Sept. -08). The average air temperature was at the same time well above 26 ˚C at the spraying in July -10, almost 20 ˚C in July -09 and above 18 ˚C in Sept. -10. At least at the higher temperature occasions it is not unreasonable that non-negligible amounts of the more volatile substances were vaporized already during the application, before the air sampling commenced.

A more significant source to underestimation of the fluxes during the summer campaigns, however, is certainly the fact that an unspecified share of the dose land upon the ground and not on the leaf surfaces. And as we know, the evaporation from a bare soil surface is generally much more reduced than from plant surfaces. The importance of this naturally varies with the density of the plant stand. Thus, during the experiment in June 2008 the crop was about 75 cm in height but fairly sparse between rows, whereas in July -09 the crop (barley) was slightly lower but now more or less covering the ground. This was also the case in July -10 with a ~90 cm high wheat crop.

5.2 Height of the IBL and the upper limit for vertical integration

The proper upper limit for integration of the horizontal flux expression:

$Q = \int_0^z \overline{uc}\,dz$ should be determined by the new internal boundary layer (IBL) height at the location of the air sampling mast. Numerous formulae regarding the rate of growth of the IBL under different stability and surface roughness conditions have been suggested. Several of them take a rather simple form:

$$\delta(x) = cX^b \qquad (1)$$

where $\delta(x)$ is the height of the IBL at the downwind distance X and the parameters c and b take different values according to stability and surface roughness (z_0). Even in this rather simple form, a number of suggestions concerning the values of the parameters b and c have been suggested during several decades, resulting in quite different height predictions (see e.g. Walmsley, 1989, Garrat, 1990, Savelyev and Taylor, 2005). Most of these formulae predict an IBL height well below 16m at a distance X = 54m (corresponding to our experimental set-up) under neutral conditions. A quite frequently proposed rule of thumb regarding this height is a 1:10 relation: $h(x) \approx X/10$, i.e. the height of the growing IBL should be close to 1/10 of the downwind distance X from the leading edge of the "new" surface in neutral stratification (e.g. Denmead, 2008). It is also clear, however, that in other stratifications, far from neutral, the growth of the IBL may differ significantly from the neutral case. In stable situations the growth is less rapid, and – probably of particular interest in this context – in unstable stratification the growth certainly progress appreciably faster. However, the different formulae suggested, applied to one and the same case, give quite divergent predictions of the IBL. Thus, Savelyev and Taylor (2005) made a comparison of the predictions by 15 different formulae – spanning a time period of almost 50 years regarding their date of appearance, and encompassing a variety of forms and complexities – for an experimental case where the distance X was 90m downwind from a shoreline, the roughness change was from very smooth (Gulf of Mexico) to that of thin grass with height up to 50cm, and near neutral atmospheric stability, the predicted height of the IBL, according to these formulas, varied in magnitude from 3.3 m to 12.4 m, whereas the measured height was 7.2 m. Only five of these predictions fall fairly close to the above mentioned rule-of-thumb value for that case (i.e. 90/10 =9 m), if we tolerate, say, a ±25% deviation from the 9 m estimate: 9 ± 2.3 m). Furthermore, most IBL formulae presented generally refer to flow parameters connected with the wind speed profile and momentum transport (shear stress). However, experimental evidence makes it reasonable to believe that the upward propagation rate of a surface induced modification of various fluid characteristics – such as momentum, heat, water vapour or chemical constituents – may differ from each other (e.g. Dellwik and Jensen, 2000, Savelyev and Taylor, 2005). This question thus adds a further uncertainty to the question of determining the relevant height of the IBL. Anyhow, all of the 15 IBL models included in the above mentioned comparison (and the rule-of-thumb as well) would predict an IBL height well below 16 m for near-neutral (and stable) conditions in our case with X=54m. However, as already mentioned, we regularly carried out the integration up to at least 16 m, and, when subsequent check-ups of the calculated flux profiles indicated a non negligible horizontal flux at that level (compared with that on the level with maximum flux), extended the integration upwards, sometimes even to 28 or 32 m.)

5.3 The wind speed profile

The logarithmic wind profile expression

An issue that certainly may be worth special attention in this context regards the accuracy of the description of the vertical wind profiles, which in our study (partially due to the lack of a sonic anemometer in the instrumental set-up) have been represented by the logarithmic wind profiles, fitted by linear regression to measured data after that a reasonable zero displacement value (d) has been determined for each experimental season, but without any stability dependent

correction terms. This method resulted generally in good or very good linear fit to measured data for the majority of the sampling periods (with R^2 values higher than 0.99 in 21 of the 30 separate sampling periods involved, and with $R^2 > 0.995$ in 14 of these cases). (A few examples of such profiles are shown in Figs. 2.4a-c).
In an attempt to estimate the accuracy (or inaccuracy) of the remaining 9 cases, 4 of the summer profiles and 4 of the autumn profiles with an apparent less good fit than the other profiles within each of the measuring campaigns (selected by visual inspection of all the 30 logarithmic wind profiles) were re-evaluated by "manually" fitting vertical profiles by (subjective) interpolation between the measured values (at the same discrete integration steps (=10 cm) that were used in the ordinary computational routine, as to achieve an as close and "true" fit to measured data as possible. The sampling periods and wind profiles selected for this examination are shown in Table 5.1 together with their respective weight regarding their share of the total time for each sampling campaign (which of course is of importance when estimating the influence of those periods on the determined total accumulated fluxes as presented in Tables 4.2a-b and 4.4a-b etc.).

These re-evaluated wind profiles were then combined with their corresponding concentration profiles (both the equations used for the evaluation alternative labelled "vers.1" in the foregoing, and also the equations pertaining to "vers.2" in each case) to calculate the corresponding horizontal fluxes in the same way as before. The originally determined fluxes (i.e. those determined by use of the logarithmic wind profile equations without stability correction terms) were then compared with these new, "manual", flux determinations (by looking at the quotients of the original and the new determinations, and also averaging over all six (or four in 2008) pesticides *within* each sampling period).

For the four summer periods examined in this way, the result was as follows:

June 2008, per.2 (53% of total sampling time): the original evaluation was on the average 4.4% (for vers.2) to 4.5% (for vers.1) higher than the new one (the variations between pesticides being from 4.1% to 4.8% and thus fairly small), indicating a possible ~4.5% average overestimation of the flux during this period, if the manually evaluated wind profile could be considered to have a higher resemblance to the true profile.

July 2009, per.2 (4.3% of total time): original evaluation gave on the average about 0.55% lower flux (for both versions of concentration) than the new one; thus an almost negligible difference between the two evaluations.

July 2009, per.3 (25.9% of total time): original evaluation was from 0.3% less (together with conc. eq. vers.2) to 0.8% higher (conc. ver.1) on the average than the new one (with very small differences between the pesticides).

July 2010, per.3 (9.4% of total time): original evaluation 6.6 (vers.2) to 6.7% (vers.1) higher than the new (with differences between individual substances from 5.9% to 7.5%), thus indicating a possible overestimation of the flux during this period.

Thus, in summary, the June -08, per.2 case, which also comprise a quite substantial part of the total sampling time this summer, indicate a possible overestimation of the order 4.5% for half of the sampling time. If the remaining two periods, comprising the other ~50% of the total time – in light of these wind profiles apparently quite better fit – may be considered to have a more or less negligible either over or under estimation of the flux, the total horizontal flux during this 24-hr campaign may have been overestimated by roughly 2-3% due to the wind profile equation issue – all other possibilities for over or underestimation discussed earlier disregarded.

For the campaign in July -09 the above results indicate very small, or negligible, over or under estimates of the fluxes due to erroneous wind profiles.

In July -10, period 3, comprising slightly more than 9% of the total time, the fluxes may have been overestimated by about 6.7%. But since the logarithmic wind profiles of the remaining periods in general had a significantly better fit to measured data than per.3 (cf. Table 5.1), we might assume that the overall flux estimate for the July 2010 campaign should be accurate within say 2% with regard to the wind profile issue.

Table 5.1 *Overview over all sampling periods, their respective durations (in hours and share of total sampling time of each campaign (%)) and also the R^2 coefficients for the logarithmic profile equations used routinely in the horizontal flux computations. Red figures indicate those periods selected for "manual" re-evaluation.*

	Period:	***1***	***2***	***3***	***4***	***5***	***6***	***7***
June 2008	Per.length (hrs (%))	4.25 *(17.7%)*	12.75 *(53%)*	7.0 *(29.2%)*				
	R^2 (log wind prof.)	0.9965	0.9845	0.9975				
July 2009	Per.length (hrs (%))	4.0 *(5.8%)*	3.0 *(4.3%)*	18.0 *(25.9%)*	23 *(33%)*	21.5 *(30.9%)*		
	R^2	0.9955	0.9957	0.9947	(1.0)[1]	0.9998		
July 2010	Per.length (hrs (%))	3.0 *(1.5%)*	2.5 *(1.2%)*	19.0 *(9.4%)*	23.5 *(11.6%)*	47.5 *(23.4%)*	48 *(23.6%)*	59 *(29.1%)*
	R^2	0.9985	0.9989	0.9908	0.9936	0.9952	0.9977	0.9985
Sept. 2008	Per.length (hrs (%))	18.0 *(64.3%)*	10.0 *(35.7%)*					
	R^2	0.9976	0.9486					
Sept. 2009	Per.length (hrs (%))	3.77 *(~2%)*	3.35 *(1.7%)*	17.6 *(9.1%)*	24.2 *(12.5%)*	47.6 *(24.7%)*	96.2 *(49.9%)*	
	R^2	0.9638	0.9843	0.9764	0.9606	0.9933	0.9966	
Sept.	Per.length (hrs (%))	3.0 *(1.3%)*	2.5 *(1.1%)*	18.0 *(7.75%)*	24.75 *(10.6%)*	23.0 *(9.9%)*	48.5 *(20.9%)*	112.8 *(48.5%)*

2010								
	R^2	0.9903	0.9925	0.9934	0.9968	0.9883	0.9879	0.9910

1) The profile was reconstructed with the logarithmic equation from measurements at another site (the climate station at Ultuna campus) due to measurement failure of wind speed (pulse counters hit by flash-over) at the experimental site during this sampling period.

Two examples of the cases discussed above are shown in Figs. 5.1 and 5.2 below.

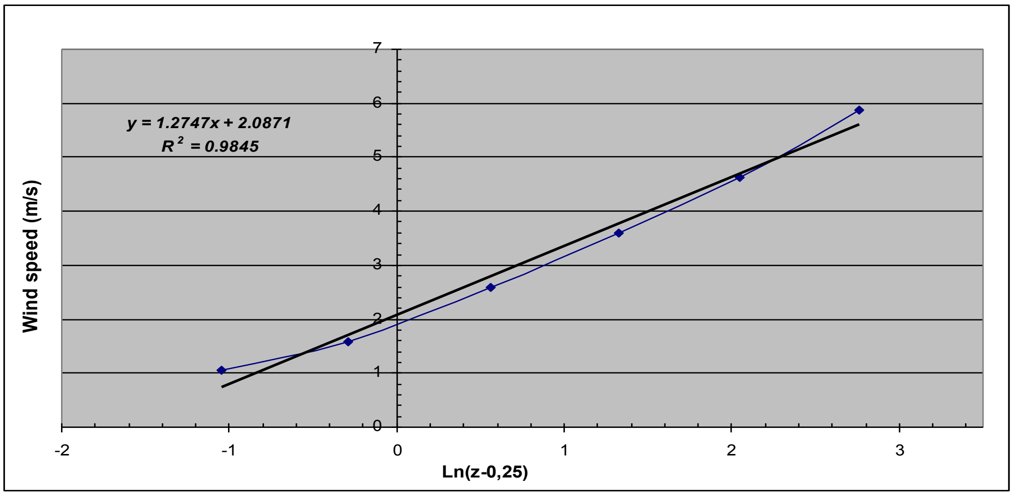

Fig.5.1 *Logarithmic wind profile (d =0.25m) and measured wind speeds (dots) for period 2, June 2008. The logarithmic profile fit may cause an overestimation of the horizontal flux by ~4.5% according to the re-evaluation (cf. text)*

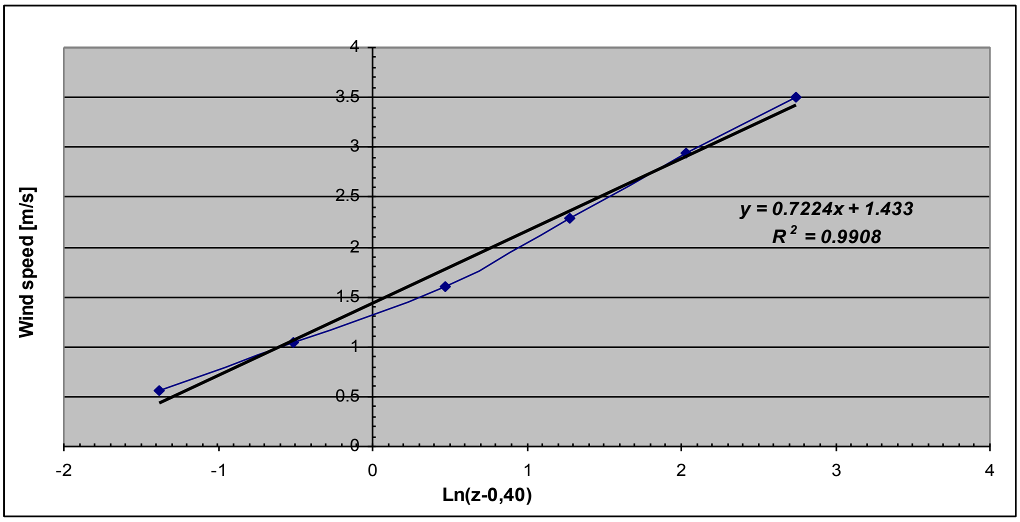

Fig.5.2 *Logarithmic wind profile (d=0.40m) and measured wind speeds (dots) for period 3, July 2010. The logarithmic profile fit may cause an overestimation of the horizontal flux by about 7% according to the re-evaluation (cf. text)*

The re-assessment of the four September cases examined gave the following results:

Sept. 2008, per.2 (35.7% of total sampling time): the original (logarithmic wind equation fit) produced on the average 1.4 % (vers.2) to 1.5 % (vers.1) higher fluxes than the new evaluation for two of the substances (prosulfocarb and pendimethalin). However, in the case of pirimicarb – for which the horizontal flux was entirely confined to a very shallow layer close to the ground – with non-detectable concentrations in the air at heights already above the 2-m level (cf. Fig. 5.3b) – the use of the original wind profile gives from 34 (vers.2) to 37% (vers.1) higher flux estimates than the new, subjectively fitted, profile. For fenpropimorph, with a similar shape of the flux profile, though not equally pronounced (the highest level with detectable concentration now being at 4 m, the corresponding figures are 21-22% higher flux (during the period) with use of the original wind equation. These apparent overestimates of the flux in these two cases are a consequence of the fact that the original, logarithmic profile fit overestimate the wind speed at heights below ~0.75 m, and also over a height interval from ~1.35 to 2.6 m (the simultaneous *under*estimate of the wind speed between heights 2.6 and ~11 m does obviously not compensate for this overestimate, since very little of the flux remains at these levels for the two substances in question; cf. Figs. 5.3a-b below).

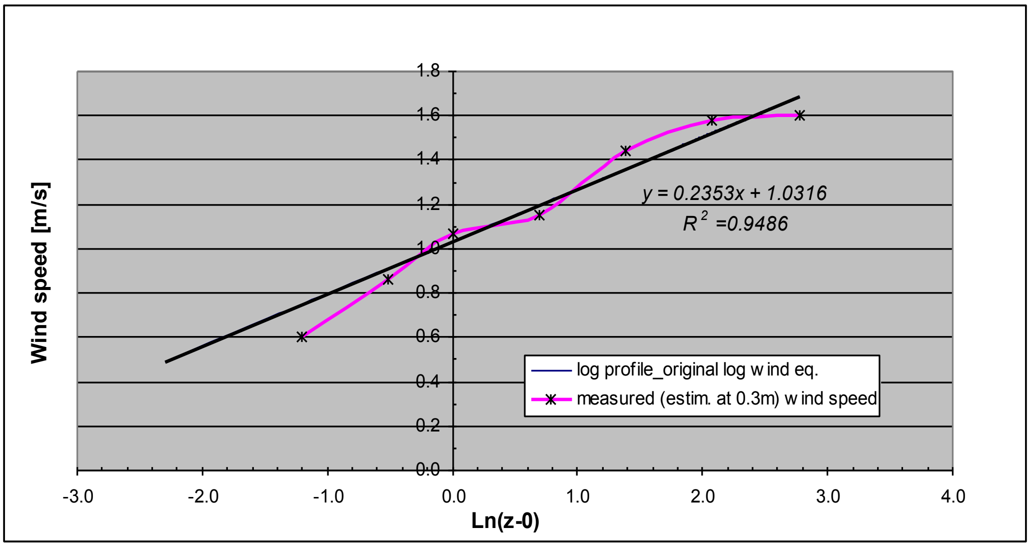

Fig.5.3a *Logarithmic wind profile (d=0m) and measured wind speeds (dots) for period 2, Sept. 2008. The original logarithmic profile fit will probably cause a significant overestimate of the horizontal flux for pirimicarb and fenpropimorph according to the re-evaluation due to the shape of the vertical concentration profile of these substances in this case (cf. main text). (The lowest point of the measured (red) curve (at z=0.30m) is estimated; the remaining cross marks are measured wind speed averages.)*

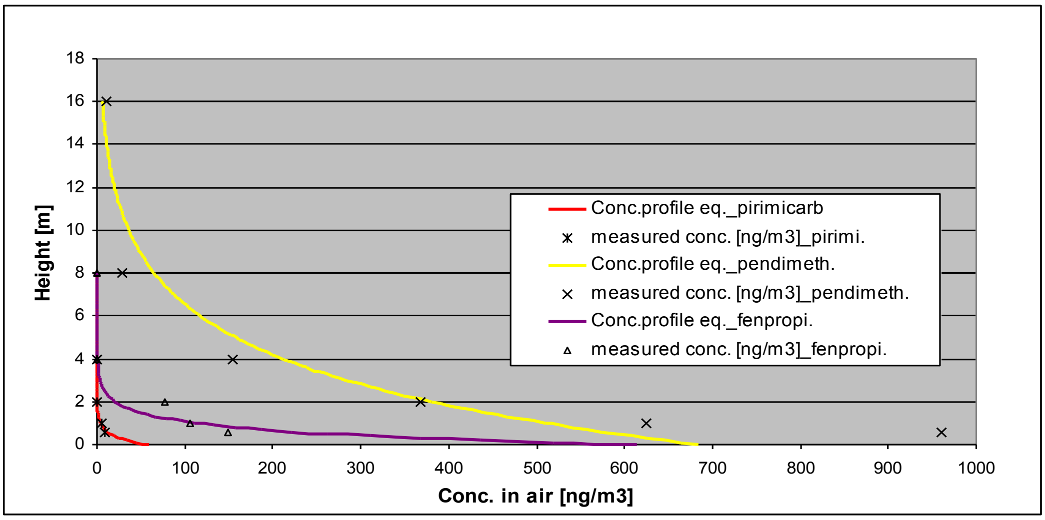

Fig.5.3b *Vertical concentration profiles from period 2, Sept. 2008 for three of the substances (the profile for prosulfocarb, though not shown, lies well to the right of that for pendimeth.with C(16m)=34ng/m3). Measured concentration at the height of 4m is 0 (pirimicarb), 0.2 (fenpropimorph) and ~155ng/m3(pendimethalin), respectively.*

Sept.2009, per.1 (< 2% of total time): use of the original logarithmic profile equation seemed to cause a negligible overestimation (~0.1%) together with vers.1 of conc. profiles (with rather small differences between pesticides and estimated wind profile shapes below 0.35m), but almost 5% as an average together with conc. vers.2 (with rather marked differences both between the different pesticides, but also between the two different alternatives of profile fit below the lowest measuring height (at 0.35m) that was tested: from practically no difference at all between original log. equation and new, subjective fit with "moderate" decrease of speed at levels below 0.35m (though significantly faster than that given by the logarithmic equation) for prosulfocarb, to about 11% for pirimicarb, conc. vers.2 and the alternative with an even faster decrease of wind speed below the 0.35-m level).
Thus, in summary, for the main alternative regarding used concentration equations (i.e. vers.1) there seems to be a negligible risk for over- (or under-)estimation of the flux with use of the standard logarithmic form of wind equation, whereas an overestimation somewhere between 5 and 10% is possible in connection with vers.2 of concentration profiles for this sampling period. (It should be remembered though, that this period constitutes slightly less than 2% of the total sampling time during this season).

Sept. 2009, per.4 (12.5% of total time): together with vers.1 of concentration profiles the original logarithmic profile resulted in an average overestimate of flux of ~0.5% (with individual variations between a 0.8% underestimation to about 1.8% overestimation (for tolclofos-methyl), while together with vers.2 the logarithmic profile on the average produced a 4.7% overestimation of the flux (compared to the subjectively fitted profile) with variations between the substances from ~2% (pirimicarb) to 7.5% (tolclofos-methyl). This case is shown in Fig. 5.4.

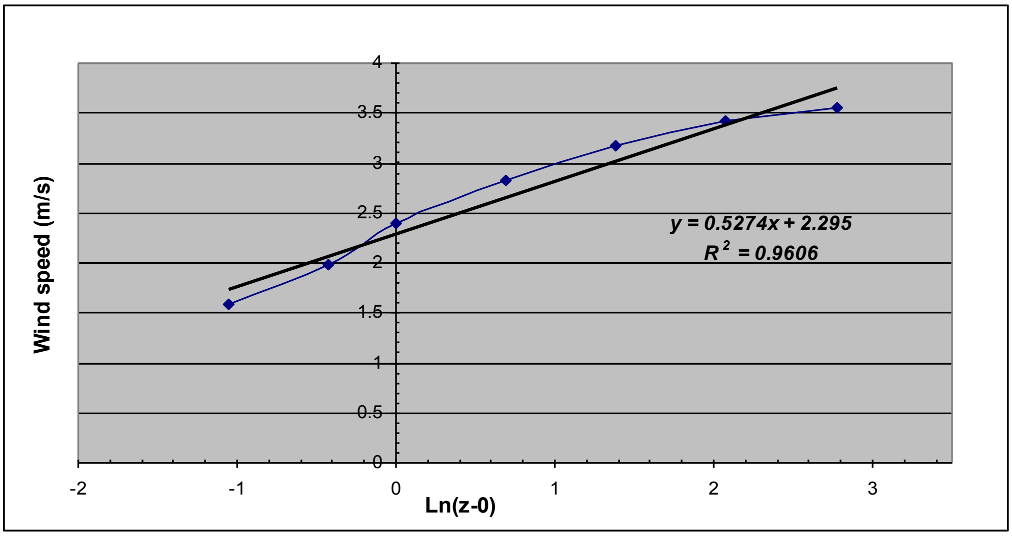

Fig.5.4 *Logarithmic wind profile (d=0.40m) and measured wind speeds (dots) for period 4, Sept. 2009. The logarithmic profile fit may cause an overestimation of the horizontal flux by up to ~7.5% for some of the pesticides in vers.2, but considerably less (≤ 2%) with vers.1 of the conc. equations, according to the re-assessment (cf. main text)*

Sept. 2010, per.6 (20.9% of total sampling time): in combination with vers.1 of concentration profiles the logarithmic profile equation gave on the average a 3.8% overestimation of flux (compared with manually re-evaluated profile) with rather small variations (±0.7%) between the pesticides. With vers.2 of concentration profiles the apparent overestimation was slightly less: 3.0% on average with individual variations between 1.8 and 4.4% between different pesticides and different assumptions for the wind profile shape at the lower height levels (below 0.35m).

Thus, this examination of eight of the sampling periods with, as it appears, less good fit of the logarithmic wind profile equations to measured wind speeds, indicates that this may have caused a measurable overestimation of the accumulated fluxes in some of these periods but mostly quite moderate in magnitude. (In combination with the main concentration equation alternative (“vers.1”) the estimated possible overestimation was of the order 0-2%, as the average over all substances, in 5 of the eight examined periods, and above 5% in only one of them.) And furthermore, since these possible overestimates refer to individual sampling periods, each comprising only a smaller or bigger share of the total sampling time during each measuring campaign, the factual implications for the estimated fluxes, accumulated in total, during each experimental campaign as given in Tables 4.2 and 4.4 will be even less pronounced.
Thus, if we choose those periods which are shown in Figs. 5.1-5.4 above and from each of them take the pesticide with the largest (possible) overestimation, as examples of the final, total effect on the earlier calculated fluxes:

In June 2008 (Fig.5.1), the overestimate of the order 4.8% for *prosulfocarb* (with conc.vers.1) or 4.6% (vers.2) in period 2 would change the figures in Table 4.2b for the relative accumulated flux during the total 23.5 hrs, from 24.7 to 24.5% (vers.1) and from 23.5 to 23.3% (vers.2).

In July 2010 (Fig.5.2), a possible overestimate of 7.5% found for *pirimicarb* (vers.1) (or 7.2% with vers.2) in period 3 (comprising 9.4% of total time) results in a change of 0.2 percentage units of the figures in Table 4.2a for pirimicarb: from 28.8 to 28.6% (vers.1) and from 26.8 to 26.6% (vers.2).
In Sept. 2008 (Fig.5.3), the possible overestimate for *pirimicarb* with ~37% (vers.1) or 34% (vers.2) in period 2 (compr. ~36% of total time) would result in a change from 0.41 to 0.36% (vers.1) and from 0.36 to 0.32% (vers.2) of the accumulated flux during the full period of 27.5 hrs (Table 4.4a). The corresponding figures for *fenpropinorph* during the same period, with a possible overestimate of the order 21-22% (vers.2 and vers.1, resp.) would be: from 1.29 to 1.20% (vers.1) and 0.90 to 0.84% (vers.2), respectively (Table 4.4b).
In Sept. 2009 (Fig.5.4), the overestimate for *tolclofos-methyl* with 7.5% (vers.2) (1.8% in vers.1) in period 4 (compr. just above 6% of total time) leads again to negligible adjustments of the earlier figures in Table 4.4a: from 15.4 to 15.38% (vers.1) and from 16.3 to 16.2% (vers.2).

The re-assessment of the wind profile descriptions using the logarithmic wind equation accounted for above cover eight of the individual sampling periods with the least good linear fit to measured data as mentioned. Among the remaining 22 periods, 6 has logarithmic wind profile shapes (and formal fits) more or less resembling the better half of the 8 examined, 15 has a significantly better fit (with $R^2 \geq 0.997$ in a majority of these cases) and with one period, finally, (per.4 in July - 09) where the wind profile was established from wind data from the most nearby climate station (at Ultuna campus ~8 km W of the experimental site) and should therefore probably be regarded as less accurate than the others.

Our conclusion therefore is, that even in those cases with apparently less good fit of the used wind profile expressions to measured data, the use of these profiles (i.e. without stability correction terms) seems not to lead to any more serious over- or underestimations of the calculated total vapour fluxes – possibly with the exception for pirimicarb and fenpropimorph in September 2008 (although even then with very small *absolute* amounts).

The wind profile within a crop canopy

The shape of *the within-canopy part of the wind profile* also constitutes an uncertainty in the flux computations, the logarithmic wind law expression being invalid below the top of the crop (and less accurate already from some level above the top in the so called *roughness sublayer* which may extend 1-2 canopy heights above the canopy itself, e.g. Harman and Finnigan, 2007).
Several authors have suggested that the wind profile in a (dense) canopy may be described by some form of an exponential function of height. Cionco (1972) e.g. suggests the following expression for the wind speed u(z): $u(z) = u_h e^{a(z/h - 1)}$ with u_h = wind speed at the top of the canopy of height h, z height above ground ($z \leq h$) and where the attenuation coefficient *a* depends on the type of canopy, its

density and flexibility and is assumed to be (quasi-)constant for a given canopy and has to be empirically determined.

Massman (1997) presents the results from an analytical model for momentum transfer and wind speed in vegetation canopies where the wind speed also is modelled as an exponential function, but now as a function of the cumulative leaf drag area according to the following expression: $u(z)/u(h) = e^{-n(1-\zeta(z)/\zeta(h))}$ where $\zeta(z)$ is the cumulative leaf drag area per unit planform area (which in turn depends on the foliage drag coefficient and foliage leaf area density which are functions of height z), $\zeta(h)$ is the drag area index at height h and where the parameter n depends on $\zeta(h)$, u(h) and the friction velocity u_* .

In an earlier review, however, Massman (1987) suggested a hyperbolic cosine-like wind speed profile of the following form: $u(z)/u_h = [(\cosh\beta\xi)/\cosh\beta]^{1/2}$ where u(z) is the wind speed at a height z within the canopy, u_h is the speed at the top of the canopy, $\xi = z/h$ and β is a compound parameter incorporating a foliage drag coefficient (C_d), the leaf area index (LAI) and the vertical foliage area density distribution. Massman claims that this latter, hyperbolic cosine form of the profile will be more consistent with the zero wind speed gradient frequently observed in the lower part of a canopy (roughly below z = 0.5h – 0.6h; cf. e.g. Shaw (1977), and Massman (1997, Fig.2 in particular) but where the actual shape of the profile and the magnitude of the wind speed thus basically depends on the density and vertical distribution of the foliage.

However, such a zero wind speed gradient over a substantial height layer in the canopy seems not always to be present (for example in the wind tunnel study of a modelled wheat canopy reported by Brunet *et al.*, 1994).

In the present study we have chosen to assume a constant wind speed, equal to the above canopy friction velocity (u_*), below the top of the canopy (i.e. $u(z) = u_*$ for $z < h$), like e.g. Andersen *et al.*, 2006. This assumption is supposed to give an average profile not too far from the average of a hyperbolic cosine-shaped profile which starts with $u = u_h$ at the top of the canopy and then gradually decreases to a nearly constant value for u of the order $0.13u_h – 0.25u_h$ at heights roughly below 0.5h – 0.6h (according to measurements in wheat and corn presented in Shaw (1977) or of the order $\sim 0.05u_h – 0.35u_h$ for modelled canopies with variable foliage distributions and with LAI going from 1.0 (giving $u=0.35u_h$) to 3.0 (giving $u=0.05u_h$) given by Massman (1997)). This follows if we assume h = 0.7 m, $z_0 = 0.07$ m and d = 0.45m as was the typical conditions during the July -09 campaign, and then applying the log wind law which gives the magnitude of u_h at the top of the canopy to roughly $u_h \approx 0.26u(10m)$. And further, with the friction velocity being of the order $u_* \approx 1/10$ of u(10m) according to a common rule of thumb – or using the actual average value of $u_*/u(10)$ for all three summer campaigns in our case which rather was ~0.087 – and if we assume $u(z) \approx 0.13u_h$ (referring to the lower value from Shaw(1977) as an example we get: $0.13u_h[= 0.13(0.26u(10))] = 0.034u(10) < u_*$. Or if we choose $u(z) \approx 0.25u_h$ (the higher value from Shaw, 1977 as the constant value for u in the zero-gradient layer of the profile) instead, we get: $u(z) = 0.25(0.26u(10)) = 0.065u(10)$ which also is slightly less than $u_* \approx 0.087u(10)$ but at least fairly close.

Thus, the use of a constant wind speed equal to the friction velocity (u_*) seems to imply some overestimation of the speed in this region of the canopy.

However, these example values taken from Shaw (1977) (and also those cited from Massman (1997)), are the approximate values for heights $z \leq 0.6h$ roughly. In the uppermost region of a fairly dense canopy, from about $z = 0.6h$ to the top of it, there is a steep increase of the profile to the velocity u(h) (≈ 0.26 u(10m) in our example) at the canopy top. In this region u_* is probably an underestimate of the *average* speed through this layer. Thus in conclusion, our use of u_* as (a constant) wind speed through the whole of the canopy may imply some overestimation in the lower parts and a certain underestimation in the upper region. With an assumed constant concentration profile in the canopy and with the two height intervals with opposing errors fairly equal in magnitude the net resulting average error should be quite moderate.
(It may be noted, that the friction velocity used here has been determined from the neutral form of the logarithmic wind profile fitted by linear regression as discussed above [$u_{*(\text{prof.})}$] – without any stability correction and– and not by direct measurement of the mean shear stress $\overline{u'w'}$ (i.e. the turbulent vertical flux of horizontal momentum) by sonic anemometry according to the definition:
$u_* = (-\overline{u'w'})^{1/2}$).

5.4 The concentration profiles

Closely connected to the foregoing issue is of course the corresponding question regarding the accuracy of the equations describing the concentration profiles. However, as already argued in *Sect. 2.6* in connection with the description of calculation procedures, and also in *Sect. 4.1.2* (the summer results), we consider that the parallel use of two alternative sets of concentration equations (denoted ′vers.1′ and ′vers.2′, resp.) – with the main alternative given as “vers.1” – to a good extent capture the possible limits for the resulting flux, and thereby also give some assessment of the associated accuracy.

As already described in *Sect. 2.6*, it was found that the concentration profile most closely fitting the observed concentrations in some cases was of the kind we have used to denote ′type 2′, i.e. $\ln(c)= a\ln(z) + b$, whereas the common, expected exponential type, $\ln(c) = a_1z + b_1$ was denoted ′type1′.
The ′type2′ concentration equation has been judged as preferable in about 8 of the 30 sampling periods in all (viz. period 3 (18hrs) and period 4 (23hrs) in July -09, per.3 (17hrs) and 6 (96hrs) in Sept. -09, period 5 (48hrs) and 7 (59hrs) in July -10 and per. 4 (24hrs) and 5 (23hrs) in Sept. -10, with a few more possible cases) – half of them among the summer periods, half among the autumn cases. We have so far not found a fully conclusive explanation to these cases but some common features for these cases may be noticed here:
Their period lengths are quite long; 6 of the 8 periods are ≥ 23 hrs (3 of them even ≥ 48 hrs), 2 have duration of 17-18 hrs. The majority of these periods are week wind situations, the average wind speed at the height of 8 m being $\leq 3.3\ ms^{-1}$ (in one case $u(8) = 5.5\ ms^{-1}$). 5 of these 8 sampling periods have an average Richardson number for the height layer 0.15-16 m and taken over the night-time

parts of the total respective periods that was Ri_B (16-0.15) ≥ 0.48, i.e. very stable stratification (and in all these cases this night-time part was of about comparable length, or longer, than the daytime parts of the respective period). In 3 of the 8 cases $0 < Ri_B (16-0.15) \leq 0.15$ on the average for the night-time parts (in these 3 cases the night time parts dominated over the daytime parts in duration; cf. Appendix 1a-e for details about Ri_B , period lengths etc.).

All these characteristics seem to indicate situations with fairly weak or even suppressed vertical mixing in the lower layers of the atmosphere. This will certainly have a decisive influence on the concentration profiles – at least when considering the night-time and daytime sub periods separately. Thus, it seems not unreasonable that a weak vertical mixing should enhance the concentration gradient in the lowest layers but reduce it higher up away from the surface, resulting in a convex-shaped profile when displayed in a ln c versus z - plot – i.e. the characteristic ´type 2´- profile shape which apparently gets a more close fit in the ln(c) = f[ln(z)] representation (cf. the typical example in Fig. 5.5). The figure shows the profile for prosulfocarb. However, the occurrence of profiles of ´Type 2´ is *not bound to particular pesticides* but to all substances, more or less, within such a ´Type 2´- *period*.

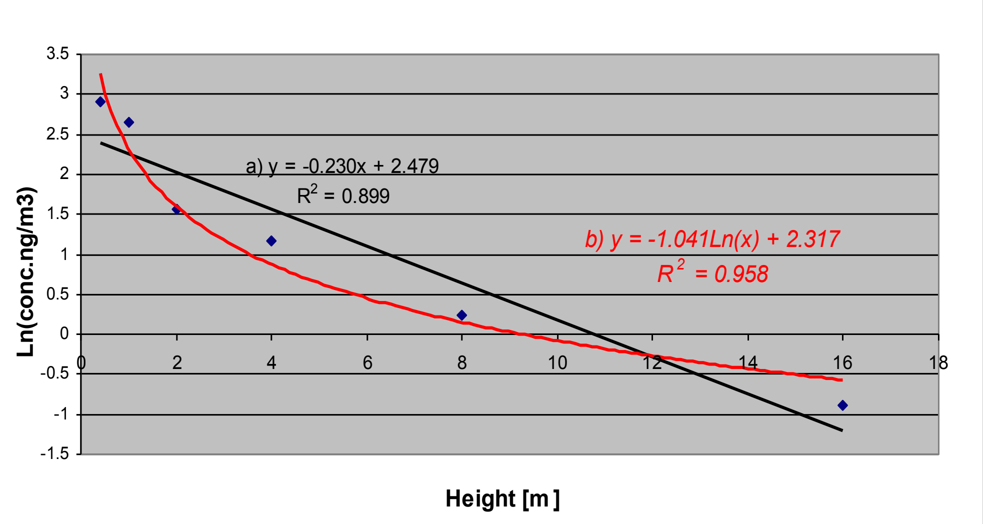

Fig.5.5 *Concentration profile for* ***prosulfocarb*** *in period 5, Sept.-10 represented with a) a conventional ´Type1´equation (ln(c) = az + b, black line) and b) a ´Type2´ equation:* $\ln(c) = a_2 \ln(z) + b_2$ *(red curve; x in the regression equations in the figure stands for height z above ground).*

However, what shape the resulting, *overall average*, profile will take over longer sampling periods – with varying atmospheric stability between several consecutive daytime and night-time sub periods, where more vigorous mixing during the daytime periods ($Ri_B < 0$) alternates with suppressed mixing ($Ri_B > 0$) during the night-time parts – seems not quite obvious.

The second type of concentration equation (i.e. ´type 2´) frequently implies an exaggerated increase of the concentration in the very lowest heights, i.e. when the concentration profile approaches the ground (z =0), compared to the common, purely exponential, type of equation.

This implies a potential risk for overestimation of the concentration very close to the ground (chiefly below the lowest sampling height).
In the bare ground cases, this risk for overestimation is counteracted, however, by forcing the concentration to take a constant value in the lowest levels (usually below 0.3-0.5m, depending on the actual profile shape). This may, on the other hand, imply a possible underestimation of the concentration in a shallow layer next to the ground, but it should at the same time be recognized that the wind speeds in this layer are very low. Altogether, the possible inaccuracy in the calculated flux in this shallow layer due to this procedure may probably be well compensated for by a much better fit over the remaining major part of the profile compared to what would be the case by using a purely exponential ´type1´ equation in these cases.
In the summer occasions, when an equation of ´type 2´ came in question, this potential problem is basically avoided by the fact that in the summer cases, the concentration was always held constant below a height of ~0.5 m, i.e. through the major part of the crop canopy.

5.5 Accumulated horizontal fluxes during the summer campaigns

With reference to temperature – both the air temp. at the 2-m height and the surface temperature – the two campaigns in June -08 and July -09 were very similar taking the overall averages over the whole measuring period for each year as an indicator, with the 2-m average temperature (T(2)) being13.9 ˚C in both years and average surface temperature around 15 ˚C, whereas the campaign in July -10 was significantly warmer with the total average 2-m level temperature just below 21 ˚C and the corresponding surface temp. ~22 ˚C.
Concerning the wind conditions, the total, overall average wind speed at a height of 2 m (ū(2)) was 3.4 ms^{-1} in June -08, 2.2 ms^{-1} in July -09 and 1.8 ms^{-1} in July -10 and with maximum wind speeds (at the 2-m height) between 4 and 5 ms^{-1} all of these years.
The conditions during the first 24 hours after spraying show a similar pattern with average temperatures T(2) = 13.5 ˚C (2008), 15 ˚C (2009) and 22.5 ˚C (2010), respectively and wind speeds at the 2-m height ū(2) = 3.3 ms^{-1} (2008), 2.0 ms^{-1} (2009) and 1.1 ms^{-1} (2010).
None of these summer campaigns was exposed to rain.

Four of the pesticides were used in all three years: pirimicarb, prosulfocarb, fenpropimorph and pendimethalin; lindane and tolclofos-methyl only in 2009 and 2010.
If we consider the accumulated horizontal flux during the first 24 hrs after spraying, expressed as percentages of (intended) applied dose, the outcome may be summarized as follows (cf. Table 4.2):

<u>*June 2008*</u> (24hrs): Prosulfocarb (~28%) > pendimeth.(19%) > pirimi.(9%) > fenpropi. (<3%)

July 2009 (24hrs): Lindane (~54%) > prosulfo.(31%) > tolclofos. (29%) > pendimeth.(18%) > pirimicarb (11%) > fenpropimorph (~6.5%)

July 2010 (24hrs): Prosulfo. (~60%) > lindane (58%) ≈ tolclofos.(58%) > pendimeth.(50%) > pirimicarb (~27.5%) ≥ fenpropimorph (27%)

Regarding the four substances common to all three years, it is obvious that whereas the accumulated flux of these in 2008 and 2009 were mainly rather similar (with an apparent exception for fenpropimorph), it was much higher (with a factor 2 or more) in 2010. This pattern seems to be in good accordance with the corresponding variations in the average temperature conditions between these years. (The quite moderate differences in wind speed, on the other hand, with the slightly strongest winds in 2008 and the weakest in 2010, do not seem to have had any obvious influence on these fluxes.)

When comparing all 6 substances, it is evident that lindane seems to be one of the most volatile irrespective of the weather conditions but in high temperature situations prosulfocarb, and also tolclofos-methyl, seems to have about the same volatility potential.

At the other end of the scale, we find fenpropimorph and pirimicarb, but whereas there was a marked difference between the two both in 2008 and 2009 – the two summers with fairly moderate temperatures, scarcely 14 ˚C at grand average – they showed almost identical fluxes in the warm summer 2010.

This outcome should reasonably to a significant extent be a consequence of the different vapour pressures of the pesticides, but quite naturally also of other factors (besides the weather) such as e.g. chemical-physiological interactions with the crop itself (adhesion on or absorption in plant tissue etc.). These interactions certainly vary with weather conditions and type of crop but also between different pesticides. It may therefore be more or less confounding to compare and evaluate the pattern obtained in these accumulated fluxes (though normalized with respect to their varying doses) in terms of their different vapour pressures alone – in particular since reported data on these values are far from being consistent with each other (cf. Table 4.9 and the discussion in Sect. 4.2).

Thus, for example, a comparison starting from the set of values given by PPDB (2012) (set "Vp(1)" in Table 4.9), it seems quite reasonable that *lindane*, with the highest Vp-value according to this set of values, generally gave among the highest fluxes, and that *pirimicarb* show up in the low-flux end (having the lowest Vp-value, irrespective of which of the Vp-sets in the table you choose). It is more remarkable that *prosulfocarb* – with the second lowest Vp-value – in reality showed the highest, or second highest flux, and *fenpropimorph* (with second highest Vp according to the PPDB-set) turned out to give the smallest fluxes in all the three cases. In the case of prosulfocarb, this result may indicate that the almost 9 times higher vapour pressure given by KEMI (1997) (viz. 6.9 mPa) is more reliable.

Regarding the very low accumulated fluxes of fenpropimorph in June -08 and July -09 – about half or even less of that for pirimicarb (but almost identical as that from pirimicarb in July-10), despite a markedly higher Vp for fenpropimorph (irrespective of which of the Vp-sets given in Table 4.9 you choose) – we can only speculate due to the lack of residue measurements (on and within plant tissue) in our case. One possibility might be a markedly higher penetration into the plants for fenpropimorph – at least during certain weather conditions. Thus, computations by Leistra *et al* (2005) pointed to an accumulated penetration of this substance into the leaves of a sugar beet crop of the order 50% after 3 days compared with a volatilized flux of about 11% and a transformed part of ~12% (of their intended dosage, 76.5% was initially ´found´ on the plants). The deviating relation between the fluxes of these substances found in July -10 (viz. almost identical fluxes this year) might then be due to an overall substantially decreased absorption by the plants that year due to e.g. increased stomatal resistance (though some minor penetration through the cuticle may also occur in parallel) at the fairly high air and leaf surface temperatures during this sampling episode (the maximum surface temperature being above 30 ˚C in 6 of the 7 consecutive sampling periods in July - 10; cf. Appendix 1d).

These accumulated fluxes increased only slightly when the accumulation period increased to 48 hr, mostly with a few percentage units both in July 2009 and July 2010 (cf. Table 4.2) and in July 2010, when the sampling continued for more than a week, the accumulated fluxes after 7 days (168hrs) increased to the following amounts:

July 2010 (168hrs): Prosulfocarb (~66%) > lindane (65%) ≈ tolclofos-methyl (63%) > pendimethalin (56%) > pirimicarb (~29%) ≥ fenpropimorph (29%)

In other words, under such conditions that prevailed during these experimental periods, the very major part of the evaporation seems to take place within a rather few hours following the pesticide spraying, in particular under very warm conditions as in July 2010, which also appears most reasonable.

It was also noticed, that the accumulated fluxes during the 168-hr period in July - 10 (the only of the summer campaigns of that duration) are in rough agreement – with 1-2 possible exceptions – with those predicted by an empirical method for estimation of volatilization fluxes from plants described by Smit *et al* (1998) and with predicted cumulative values 7 days (168hrs) after spraying, given in "Annex 4" (*ibid.*) – (our estimates in brackets):
Lindane 75% (65%), pirimicarb 35% (29%), tolclofos-methyl 100% (63%), fenpropimorph 50% (29%), pendimethalin 47% (51-56%) and prosulfocarb 7% (66%). The estimation method suggested by Smit et al. (*ibid.*) is ´expected to overestimate the cumulative fluxes for compounds subject to fast transformation´ (*ibid.*). This might explain some of the mostly higher estimates from this model. Thus were the external conditions for photolysis, as an example, apparently favourable during the July -10 campaign, with very high surface temperatures and incoming solar radiation above the average for this time of the year during a major part of the total sampling time (cf. Table 3.1). (The large discrepancy in the opposite direction between the two estimates for prosulfocarb might be due to a misprint in "Annex 4".)

The general conclusion from the summer measurements is, that the evaporative flux from a standing crop may reach 50 % or more of the applied dose for several of the investigated pesticides within the first day after application under warm (and dry) conditions (viz. July 2010) and then increase further the following days, but at a (much) slower rate. It is noteworthy that even pirimicarb, with a comparatively low vapour pressure, showed an accumulated flux of almost 30 % within a week after application.

5.6 Accumulated horizontal fluxes from bare soil – the autumn experiments

The autumn measurements of fluxes from a bare soil surface took place in September 2008, 2009 and 2010, respectively. The overall weather conditions, taken as the grand average over the total measuring period each year, were characterized of rather low temperature, very low wind speed and no rain in Sept. 2008:

Sept. -08: $\bar{u}(2)$ =0.9 ms^{-1} , $T(2)$ = 8.7 ˚C and T_{surf}= 7.6 ˚C

September 2009 and 2010 were slightly warmer, more windy and with significant amounts of rain (in both years the rain spells occurred towards the later parts of each campaign, in sampling period 5, about 60 hrs from start, in Sept. -09, and in periods 6 (71-120 hrs from start: 1.4 mm) and 7 (120-243 hrs after spraying: 19 mm):

Sept. -09: $\bar{u}(2)$ =3.5 ms^{-1} , $T(2)$ = 12.3 ˚C , T_{surf}= 12.5 ˚C, precipitation: ~8 mm
Sept. -10: $\bar{u}(2)$ =2.5 ms^{-1} , $T(2)$ = 13.0 ˚C , T_{surf}= 13.2 ˚C, precipitation: ~20 mm

The corresponding conditions during the first 24 hours after spraying were:
Sept. -08 (0-24hrs): $\bar{u}(2)$ =0.8 ms^{-1} , $T(2)$ = 7.2 ˚C, T_{surf}= 7.0 ˚C, precipitation: 0 mm
Sept. -09 (0-24hrs): $\bar{u}(2)$ =1.4 ms^{-1} , $T(2)$ = 10.4 ˚C, T_{surf}= 11.0 ˚C, precipitation: 0 mm
Sept. -10 (0-24hrs): $\bar{u}(2)$ =1.8 ms^{-1} , $T(2)$ = 13.6 ˚C, T_{surf}= 13.8 ˚C, precipitation: 0 mm

Regarding the accumulated flux during the first 24 hours in each year, the observed result was the following:

Sept. 2008 (24hrs): Prosulfocarb (~6%) > pendimeth.(2.5%) > fenpropi.(~1%) >pirimi.(0.4%)

Sept. 2009 (24hrs): Lindane (~8%) > tolclofos. (~2%) > prosulfo.(1.8%) > pendimeth.(1.2%) > pirimicarb (0.1%) > fenpropimorph (~0.04%)

Sept. 2010 (24hrs): Lindane (17%) > tolclofos.(~7.7%) > prosulfocarb (~5.7%) > pendimeth.(4.4%) > fenpropimorph (1.9%) > pirimicarb (~0.9-1%)

These accumulated fluxes increased mostly very marginally, especially in Sept. 2009, when the accumulation period was increased to 48 hours (cf. Table 4.4a-b). It should be noticed here, that during this 48 hrs no rain fell in neither year, and in Sept. -09 the topsoil was fairly dry, but markedly more moist in Sept. 2010.

When the accumulation period is extended up to 96 hrs from the spraying, the accumulated fluxes increase markedly, however (in Sept.-08 the total sampling lasted only ~28 hrs):

Sept. 2009 (0-96hrs): Lindane (~27%) > tolclofos-meth. (~12%) > prosulfocarb(~8%) > pendimeth.(~7%) > fenpropimorph (~0.4%) > pirimicarb (0.16%)

Sept. 2010 (0-96hrs): Lindane (~28%) > tolclofos.(13%) >prosulfo.(~9%) >pendimeth.(7-8%) > fenpropimorph (≤ 2.4%) > pirimicarb (~1.1%)

The fluxes continued to accumulate beyond the first four days at a quite substantial rate in both years – apparently with the smallest rates for pirimicarb and fenpropimorph, and the highest in the case of prosulfocarb and pendimethalin – and after the first week (196 hrs) the determined accumulated fluxes were as follows:

Sept. 2009 (0-168hrs): Lindane (~32%) > tolclofos-meth. (~15%) > prosulfocarb(~12%) > pendimeth.(8-9%) > fenpropimorph (~0.42%) > pirimicarb (0.18%)

Sept. 2010 (0-168hrs): Lindane (~35%) > tolclofos-meth. (~16%) > prosulfocarb (~11%) > pendimeth.(10%) > fenpropimorph (~2.5%) > pirimicarb (~1.2%)

Thus, obviously in Sept. -09 only a minor part of the total accumulation during a longer period, e.g. 168 hrs, occurred during the first 24 hrs after spraying for most of the pesticides, as opposite to the case in Sept. -10 and also to the common pattern for the summer cases.

A possible explanation to this behaviour might be, that several of the pesticides – apparently foremost fenpropimorph but also pendimethalin, tolclofos-methyl and prosulfocarb for all of which the accumulated flux during the first 24 hrs only amounted to 15 % or less of that accumulated in 168 hrs (compared to shares for the first 6 hrs between 80 and 90% in July -10 (cf. Table 4.8) – is more or less strongly adsorbed to the soil particles as long as the soil surface is comparatively dry. In Sept. -09 this was the case before the rain showers occurring around midnight of the 20th this month, about 60 hrs from start of the sampling, raised the topsoil moisture, from scarcely 18 % before this rain to about 33 % after.

In September 2010, on the other hand, the moisture content of the soil surface increased from about 27 % at the onset of the experiment to 34 % in the middle of

the last sampling period (period 7, 120-243 hrs from start). This soil moisture was apparently enough to keep the volatilization going on at a higher , possibly near the "potential", rate under the prevailing weather conditions this year. Not even the rather abundant raining during the last period in Sept. -10 (~19 mm in total) seems to have had any obvious effect on the volatilization.
Why this explanation does not seem to apply also to pirimicarb – which even under the dry soil conditions in Sept. -09 was the most "rapidly" evaporating among the six (although on a very low relative level), with the "24/168 hr"- ratio in the range about 55-60 % - may possibly be due to its very high water solubility, several orders of magnitude greater than for the other substances.

A possible sufficiently high soil moisture content might also be the reason why the fluxes (during 24 hrs) in Sept. -08 were significantly higher than in Sept. -09, despite the lower temperature during the first year. Unfortunately, no soil moisture measurements, which could verify this assumption, exist from that month.

In conclusion: When comparing these results with the corresponding from the summer experiments, some differences will be apparent.
First, the accumulated fluxes from the bare soil were consistently much smaller than those from a standing crop under summer conditions, but with a rather similar order in volatility potential among the substances under both types of conditions – with lindane, prosulfocarb and tolclofos-methyl at the higher end of the scale and pirimicarb and fenpropimorph at the lower end. Yet, sizeable amounts in the range 8 to 30 % or more of applied dose – excepting fenpropimorph and pirimicarb – were accumulated within the first week after application. The comparatively high flux of lindane from bare soil, at accumulation times longer than 24 hrs is in fair agreement with the findings of e.g. Haenel and Siebers (1995) who estimated this flux of lindane to be less than 30 % of the dosage after 2 days during field measurements on bare soil (comprising 3 trials in the month of May, and one in early September and with soil moisture contents below 20% by weight in all cases) at Braunschweig, Germany.

Secondly, whereas in the summer cases the very major part of the total evaporation took place within the first few hours after the application, the evaporation process generally tended to be more gradual from the bare soil, with the major contribution to the total accumulation for most of the substances (excepting pirimicarb) occurring after the initial 3-6 hrs after treatment (cf. Figs. 4.28-4.31 and Table 4.8).

Finally, the volatilization from bare soil apparently is largely depending on the soil moisture conditions, where a dry soil seems to reduce the evaporation rate markedly.

5.7 Accumulated horizontal flux correlated with physical-chemical properties

The methods suggested by Woodrow et al (1997) for correlating accumulated fluxes of volatilized pesticides were investigated in this study, using flux data from the summer experiments and from the bare soil conditions in autumn as well.
For the summer cases, with evaporation from a growing crop (wheat and barley, respectively), the accumulated fluxes during increasing time of accumulation (24, 48, 96 hrs and until the full time of sampling (or nearly so) at each experiment were correlated to the "dose corrected" vapour pressure for each pesticide (viz. vapour pressure, Vp, multiplied with intended field dose).
In this way, it was generally possible to achieve a high, or at least fairly high, correlation to the dose corrected Vp for both the July 2009 and 2010 data (data from the much shorter experiment in June 2008 was not utilized in these tests) and this correlation was in general almost as good for longer accumulation times (up to 7 days or even longer) as for the first 24 hrs (cf. Fig. 4.34-4.37).
However, to achieve a very high correlation it was necessary to use different sets of vapour pressures (Vp-sets) for the different years – or, alternatively, exclude one of the pesticides from the regression. Thus, for example, when using a Vp-set based on data given by PPDB (cf. Table 4.9) with all six pesticides included, the resulting fit to data may possibly be considered acceptable but are not particularly good (Fig. 4.32) but if fenpropimorph was excluded (Fig. 4.34) the correlation increased significantly. An equally good correlation, however, could be achieved if a quite different Vp-set ("Vp(3)", Table 4.9) was used instead.

In the case of volatilization from bare soil, Woodrow et al (1997) suggest that the accumulated flux should be correlated to a compound parameter (R_{surf}), including the dose corrected vapour pressure, the water solubility and the affinity to organic carbon (K_{oc}) for each substance (in this study we have used the Freundlich adsorption coefficient K_{foc} in place of K_{oc}). The general patterns found from the summer cases were basically similar also for the autumn cases:
Thus, it was possible to achieve quite good correlations to the accumulated flux data from the September campaigns in 2009 and 2010 with this compound R_{surf} parameter, but generally not by using the ´best performing´ Vp-set(s) from the summer cases – or by using any other *single,* specific Vp-set for that matter – for correlation with data from both Sept. -09 and Sept. -10 as well unless you accept a just moderately good fit (cf. for example Fig. 4.49).

Concerning evaporation from the bare soil cases, it was also found that under certain circumstances (i.e. the use of a "suitable" Vp-set) an almost comparably high correlation as that given by use of the dose corrected R_{surf} parameter, could be achieved by using the simpler dose corrected Vp as a predictor (cf. Table 4.10 and Figs. 4.47 and 4.48).

However, only one set of vapour pressure values can reasonably be regarded as ´true´ at each specific temperature (which temperature you choose for this specification, within a reasonably normal temperature range, say 15-25 °C, will probably not be crucial here). But this seems to imply for the present case:
If one, and only one, of the Vp-sets we have tested is a ´correct´ set of values (for a given temperature), and since that single set of Vp-values seldom resulted in a high goodness of fit of the regression equation for more than one season and one year at

a time – as we have shown above, neither of the two relations investigated are very dependable under all the varying conditions encountered in the study. Rather, the evaporative flux for certain also depends on other factors, not included in these equations and whose influence not fully will be grasped through their implicit influence on the rather few physicochemical parameters included in these condensed relations. Thus, these relations become too rough or incomplete to accurately model the volatilization flux under too varied conditions. Such external factors – weather, plant and soil conditions etc. – are of course always present, but the relations investigated might be more apt for some ´constellations´ and magnitudes of these parameters than for others. And therefore, the ´normal´ state of performance for these relations would be to produce linear regressions with a rather significant scatter (and lower correlation) in general, but may occasionally be tuned to the state of the external parameters to give a quite high correlation.
The other possibility would be, that none of the Vp-sets explored in the present study (about a dozen combinations in connection with September data and even more for the summer cases) could be regarded as being ´correct´, but due to random coincidences some of them yet produced regression results with a fairly high goodness of fit for some of the examined periods.

Actually, a more extended examination of this matter showed, that when the 4 ´best performing´ Vp-sets from the summer cases were used on the September 2009 and 2010 data (i.e. 4x2 different cases), respectively, the overall outcome turned out as follows:

- none of these 4 Vp-sets gave a particularly high correlation together with the Sept.-09 data (if all the 6 pesticides were included in the regression)
- two of them produced fairly good results (with R^2 values about 0.80 for accumulation times ≥ 96 hrs) together with Sept.-10 data
- these 4 sets gave a significantly higher correlation together with the Sept.-09 data if fenpropimorph were excluded from the regression, raising the R^2 coefficients to > 0.92 in two cases for the longer accumulation times
- exclusion of fenpropimorph from the Sept.-10 data resulted in a better fit worth mentioning only with two of the Vp-sets (to R^2 ~0.89 , but in both cases from already rather high values).

Nor it was generally the case, that a Vp-set that resulted in a comparatively high correlation a specific season one year produced a correspondingly good result when applied to the same season the other year. The correlation the other year could even be quite poor; so e.g. in the case of set “Vp(4)” which gave the best fit to the July -10 data among all the tested sets, but a fairly low fit together with the July -09 data (cf. Fig. 5.6).
Exceptions to this pattern also occurred, however. So e.g. with the set “Vp(6)” which produced fairly good correlations both when used on the Sept.-09 and on the Sept.-10 flux data. In fact, this was the Vp-set that gave the best fit among more than 15 tested for the September cases, both when applied to the Sept.-09 and Sept.-10 fluxes. (Though when used on the Sept. -09 data the correlation R^2 was just about 0.70 for accumulation times ≥ 96hrs, whereas the same set when applied to Sept.-10 gave values of R^2 increasing from 0.80 to 0.98 for accumulation times increasing from 48 to 232 hrs when all 6 pesticides were included. If fenpropimorph was excluded, the goodness of fit increased very

markedly for the Sept. -09 cases (giving R^2 values in the range 0.88-0.94 even for the shortest accumulation times (i.e. from 12 to 193 hrs) but only marginally in the Sept.-10 case. It should also be mentioned that for 17 different Vp-sets tested on the September data, a majority of them (14 cases) resulted in a better, or sometimes much better, fit to the Sept. -10 than to the Sept.-09 data.

This latter feature – the increasing goodness of fit that frequently could be achieved by excluding one of the pesticides (in general fenpropimorph) from the regression – was common for a majority of the tested Vp-sets, both for the summer and the September experiments. However, there was a noticeable difference between the experimental years in this respect.
Thus, the exclusion of fenpropimorph from the calculations resulted in an improvement of the fit for as much as 18 out of 23 tested Vp-sets when applied to the July -09 data – in 7 of these cases this improvement was quite appreciable. With the same 23 sets applied to the data from July -10, the exclusion of fenpropimorph gave a higher correlation ´only´ in 9 cases (of which 5 involved a rather significant increase of the fit) whereas in the reminding 14 cases, there were basically no change at all or even a decrease in the value of R^2.
When it comes to the September cases, the exclusion of fenpropimorph from the calculations resulted in a marked improvement of the fit for all of the 17 Vp-sets tested on data from Sept. -09, but only for one of the sets when used on the Sept. -10 data (for the other sets the fit was mostly roughly the same). However, concerning the Sept. -10 data (but apparently not in the case of the Sept. -09) an even stronger improvement of the correlation could be achieved by the exclusion of pendimethalin, but keeping fenpropimorph (this was the case for all of the 14 Vp-sets tested in this respect).
It should be mentioned here, that these cases, where the exclusion of either fenpropimorph or pendimethalin resulted in notable improvements of the fit, involved Vp-sets that in both cases spanned all the different vapour pressure values investigated here for these substances, viz. 2.2 (and 2.3), 3.9 and 7.0 mPa for fenpropimorph and 1.94 and 4.0 mPa for pendimethalin, respectively. Also the exclusion of lindane resulted in a significant improvement (compared with the case with all 6 pesticides kept in the calculation) of the correlation together with the Sept.-10 data for about half of all tested Vp-sets and encompassing different values for the vapour pressure of lindane (viz. 4.4 and 8.63 mPa). The other half of the Vp-sets that remained roughly unchanged at the exclusion also encompassed two different values for lindane: 4.4 and 45.6 mPa, respectively. However, this improvement was generally slightly less than that when excluding pendimethalin.

This observed difference between the two years might either indicate that the external (weather) conditions in July 2009 were not favourable for a ´normal´ or ´expected´ evaporation rate of fenpropimorph to the same extent as in July 2010, or it might indicate some unreliability in the data for that substance due to some experimental or analysis problems or mistakes this year. The possibility that the 5 Vp-sets that *not* gave an improved fit to the Sept.-09 data already ´produced´ so high correlations (with all six pesticides included) – including the possibility that this couple of Vp-sets indeed includes a truly correct set of values – and therefore further improvements by any alterations should not be expected, seems not to be the case since the corresponding original correlation values are fairly low or just moderately high with $R^2 \leq 0.68$ at most.

The difficulty of finding clear and unambiguous correlations between accumulated evaporation and vapour pressure for pesticides have been pointed out also by other authors. Thus Carlsen *et al.* (2005), in reporting the results from five field experiments with 10 herbicides (including pendimethalin and prosulfocarb) in Denmark, states that: *´the evaporation did not immediately correlate to the vapour pressure, although the vapour pressure could explain some of the tendencies.´* These authors argue that the influence of the additives to the pure, active ingredient may be the reason for this lack of absolute fit, compared to the case when the evaporation from the pure active ingredient is tested.

Rüdel (1997), though finding that volatilization and vapour pressure seemed to correlate (in a wind tunnel experiment with evaporation of five pesticides, both from bare soil and plant surfaces), states that: *´When discussing the data one has to assume that vapour pressure data are difficult to determine. Different methods are yielding differing values for the same substance [---]. Therefore, the correlation depends on the quality of the vapour pressure data.´* (*ibid.*)

It may be mentioned here, that more than 20 different Vp-sets (i.e. combinations of a fewer number of individual Vp-values) were tested together with the summer 2009 and 2010 data and slightly fewer (around 16) with the September flux data.

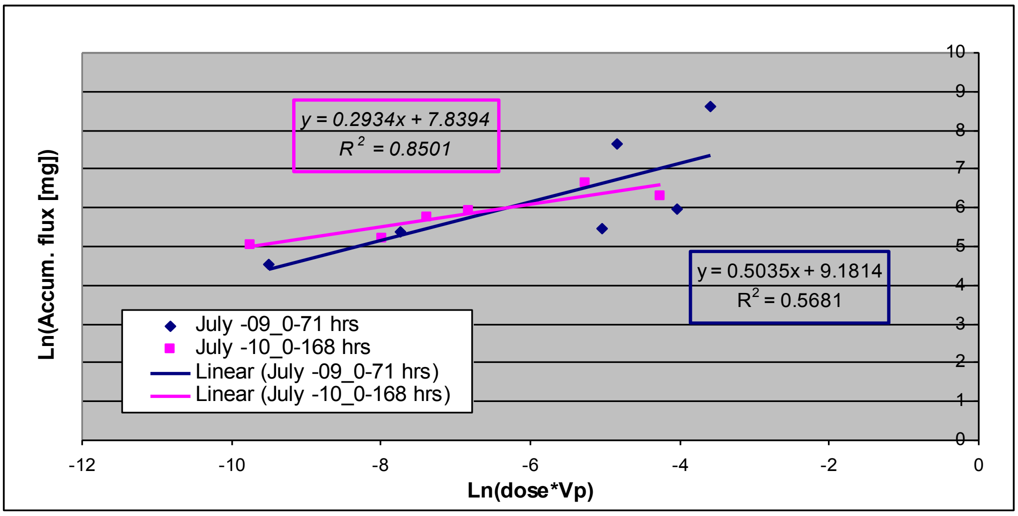

Fig. 5.6. Accumulated horizontal flux versus dose [kg/ha] corrected vapour pressure [Pa] in July 2010 versus July 2009. The shorter accumulation time in July-09 is the total sampling time this year. Vapour pressure data according to Vp-set “Vp(4)” – the set giving the best fit to the July -10 data.

Conclusion: It was possible, in general, to achieve a high correlation between the accumulated vapour flux and either of the two parameters suggested by Woodrow et al (1997), both of which incorporating the dose corrected vapour pressures of the substances.
The goodness of fit in these relations, however, was strongly dependent on the choice of vapour pressure values, and none of the combinations of Vp-values examined showed an equally high correlation when applied to different sets of flux data.
Moreover, the strength of the achieved correlation could, at least in some cases, be significantly increased by excluding one of the six pesticides from the regression (most frequently fenpropimorph, but occasionally also e.g. lindane).

5.8 Dry deposition sampling

Although deposition of pesticides (dry deposition as well as wet) should be an equally important process to study as the volatilization since it comprise the natural next step in the dispersion process (leaving it open here for possible chemical transformation and degradation processes in the air during the atmospheric transport), the sampling and quantification of deposition – and generalization of the results – is connected with a number of difficulties.

Deposition may be seen as the last link in a chain of processes: the ´production´ phase at the source, the transport phase in the atmosphere – during which chemical reactions, degradation or other transformation processes may occur – and subsequently followed by dry or wet deposition, either through absorption/adsorption of the vapour phase at a surface or by sedimentation of aerosol particles (dry deposition), raindrops or fog droplets (wet deposition).
All of these processes are partly dependent on the physicochemical properties of the substances involved and of the properties of the sink, but they are also more or less strongly governed by the prevailing meteorological conditions.

In most model schemes developed for describing atmospheric dry deposition, the mass flux to the surface (whether vegetation covered or not) usually is quantified as $F_i = - V_d\ C_a$ where C_a is the concentration of the substance in the air at a reference height, and where the deposition velocity V_d frequently is calculated as: $V_{d,i} =(R_a + R_b + R_c)^{-1}$ where the right hand terms represent different "resistances", using an electrical analogy. Here, R_a represents the aerodynamic resistance to vertical transport through turbulent diffusion and is thus dependent on the atmospheric stability (and surface roughness), R_b represents the resistance to diffusive transport through the thin, (quasi) laminar layer in the immediate vicinity of the depositing surface and varies with the molecular diffusivity of the specific substance (through the Schmidt number), but is also dependent on the atmospheric stability (through the friction velocity u_*) and the surface roughness. R_c is the total surface resistance to uptake by the surface and depends strongly on the properties of the depositing gas and the surface. In the case of a vegetation cover this is the resulting resistance of several (chiefly biological) resistances working in parallel. In the case of particle deposition, the last two resistances must be replaced by a surface deposition velocity also including the effect of gravitational sedimentation (e.g. Hicks, B.B. *et al*, 1987, Wesely, M.L. and Hicks, B.B., 2000, Petroff, A., *et al*, 2008).

Some meteorological conditions which seem favourable for enhancing the volatilization of a pesticide (i.e. increasing the source strength) have already been discussed above; such as high air or surface temperature, high wind speeds and an unstable stratification. The atmospheric stability (preferably quantified by the Monin-Obukhov length L, or, as in this report, by the Richardson number) will be an important factor both for the volatilization process and the airborne transport, but also for the deposition, in that the stability influences both the concentration of an airborne substance at a given point ($C_a(x,z)$) and also the deposition velocity (V_d) through the aerodynamic and boundary layer resistances (R_a and R_b in the equation for V_d given above). At unstable stratification ($Ri < 0$) the turbulence intensity and thereby turbulent diffusion is comparatively large which leads to a faster dilution of the concentration in the "plume", which in turn acts to decrease the deposition flux according to Asman (1998). In stable stratification ($Ri > 0$) the turbulence intensity is more or less suppressed and the turbulent diffusion lower which acts to maintain a higher concentration in the plume over longer distances, thus potentially increasing the deposition according to the model results by Asman (1998). On the other hand, low turbulence intensity increases the aerodynamic resistance (R_a) which reduces the deposition velocity and should thereby, apparently, partially counteract the increase of the deposition just mentioned and caused by the higher concentration in air. However, this hampering effect on the deposition may possibly be of more importance with elevated sources (such as chimneys) and less important for sources at the ground.

Regarding the impact of wind speed (apart from the apparently trivial statement that more local deposition occurs at low wind speeds, and more long way transport takes place at higher) it should be noted that the wind speed is influencing both the concentration in air, and the turbulent intensity and diffusion in opposing ways (which the surface depletion/deposition model developed by Asman (1998) shows: on one hand the concentration in the air "plume" (C_a) decreases with increasing wind speed, but on the other the turbulent diffusion capacity increase at the same time, thus acting to decrease the aerodynamic and boundary layer resistances $R_a + R_b$. At very small (vanishing) surface resistances (R_s) these two effects more or less cancel each other, and the accumulated amount of the substance that has deposited up to a given distance from the source will be (almost) independent of wind speed. When R_s is *not* negligible compared to the sum of $R_a + R_b$, there will be an interplay between the air bound resistances, the surface resistance and the influence of wind speed on air concentration, resulting in a situation where the accumulated deposition within a given distance from the source *decreases* with increasing wind speed (and to a higher degree the higher the surface resistance).

The relative humidity (RH) may primarily be important for the evolution and fate of aerosols in the atmosphere, and for the potential to dew formation at the ground, thereby possibly decreasing the surface resistance to gaseous uptake markedly.

Our field experiments included sampling of dry deposition only, collected on small passive samplers (square-shaped Petri dishes, 10 x10x1 cm in size) filled to the brim with soil from the experimental site. These dishes were placed on supporting cresset holders with thin shafts. During the summer sampling, these samplers were placed within the standing crop (at different distances from the treated area; cf. Sect. 2.3) and adjusted in height so their upper part was situated just below the top of the crop canopy. During the September sampling, the Petri dishes were placed 10-12 cm roughly above the ground surface. Such an arrangement may probably imply a risk for some disturbance of the wind field and if so, causing more or less different conditions for the deposition process itself than in an undisturbed wind field.

In the summer cases, with the rather slender shaped samplers immersed within the crop canopy, this undesired disturbance is probably reduced by the “shielding” effect of the crop itself, but may possibly be more present during the sampling over bare soil during the autumn experiments.

A second difficulty concerns the interpretation and generalisation of the results. To relate (or `normalize`) the deposited amounts of pesticides (e.g. expressed as μg/m^2 of sampler area) to the dose applied of the substances – as is done in the present and many other studies – seems difficult to avoid. However, the deposition is really not dependant on the dose alone, but to an equal, or in many situations probably even higher, extent also on the size, geometry and location of the treated area in relation to the site of the samplers. To incorporate all such factors in a `normalized` measure of the deposition amounts received during a field study like the present seems difficult however. Thus, it seems rather difficult, if not even impossible, to exactly determine the `footprint source area` for the depositing substances, partly because of the quite pronounced risk for meandering or veering of the wind direction during the course of the sampling (although the possibility for veering of the wind during each sampling period was tried to partly compensate for, by using simultaneous sampling along three directions simultaneously: one main direction, with bearing along the expected wind direction, and two side directions at angles of 45˚ on each side of the main direction.

(The possibility of a so called `grasshopper effect`, might possibly be another complicating factor to consider at the interpretation of deposition results. However, this opposing process, meaning a cyclic process of deposition, re-volatilization of already deposited substance followed by deposition (at another site) again, possibly with repeated steps, may supposedly be a factor to take into account in studies dealing with long-range, trans-boundary dispersion, but in studies confined to comparatively small horizontal scales, like the present, this process is certainly of minor importance if not even entirely negligible (cf. e.g. Gouin *et al*., 2004).)

Therefore, in summary, results of many deposition studies like the present are very site and study lay-out specific and hazardous to generalize. But despite this, they may certainly be valuable for internal (intra-study) comparisons, such as concerning differences in the deposition pattern at increasing distance from the source area, and between different pesticides, different weather conditions or different seasons.

Conclusion

The overall conclusion must *be, that despite several, and certainly partly inevitable, uncertainties, the present study shows that under normal Scandinavian weather conditions, both in the summer and early autumn seasons, a considerable fraction of the applied doses of the several pesticides investigated, is volatilized and diffused into the environment – in some cases and for some substances this fraction amounted to more than 60% under summer conditions during the course of seven days after the application, and up to ~18% (excepting the not permitted lindane, which reached well above 30% within seven days) under bare soil conditions in the autumn.*
This volatilization process was strongly temperature dependent, particularly during the summer experiments.

Under fallow conditions, with evaporation from bare soil, the soil moisture conditions appear to play an important role (possibly more important than the temperature) in the vaporization process – a higher soil wetness promoting the vaporization.

Thus, this investigation strongly supports the presumption put forward in the Preface*: Volatilization is one of the major – and in many cases obviously the dominating – post-application dispersion pathway for pesticides into the environment.*

Nevertheless, further investigations of this kind – under varying weather and crop conditions, and preferably including a range of different pesticides – would be needed to more fully understand the various aspects of pesticide volatilization after spraying. And – not the least – investigations into the subsequent faith of the pesticides, well having entered into the air (with possible chemical degradation and/or possible long range transport, dry and wet deposition etc.), seems to be an equally demanding but logical continuation of the present study.

List of symbols and abbreviations

(Mainly arranged topic-wise – with items mainly referring to measuring techniques and related matter in the first block, those pertaining to meteorological subjects and weather characterization in the second group and notations mainly used in Ch. 4.2 and Ch.5.7 (volatilization as a function of the physical-chemical properties of compounds) in the third – and therefore not strictly in alphabetical order.)

Measuring methods and related items:

APM	Aerodynamic profile method and
IHF	Integrated horizontal flux method: micrometeorological methods for determination of (horizontal) fluxes of air contaminants
EFSA	European Food Safety Authority
KEMI	Kemikalieinspektionen (Swedish Chemicals Agency)
PPDB	Pesticide Properties Data Base (Agricultural and Environment Unit,University of Hertfordshire, UK)
IBL	Internal boundary layer (surface-bound atmospheric layer in equilibrium with new upstream surface conditions)
LOD	Level of detection (i.e. < LOD: value below this level)
PUF	Polyurethan foam (used as an adsorbent)
XAD-4	Polymer resin (used as adsorbent for pesticides or other organic compounds)
Vers.1	Generally the first hand choice of (several possible) concentration profile equation (for each sampling period)
Vers.2	Generally the second hand choice of a concentration profile equation
F	Average source strength of emitting surface per unit area [e.g. µg s-1 m-2]
Q	Average horizontal flux across a vertical plane of unit width [e.g. µg s-1 m-1]
X	Fetch (= horizontal distance swept by the wind) over specified surface area
c	Concentration in air of specified compound
c´	Momentarily deviation of concentration from its time average (i.e. the concentration at any moment can be represented by c= $\bar{c} + c'$)
C(z)	Concentration in air of a specified compound at height z
d	Displacement height [m]: a measure of the vertical displacement (upwards) of the apparent surface with respect to the wind

$\delta(x)$	Height of the internal boundary layer (IBL) at downwind distance x from leading edge of ´new´ surface
h	Average height [m] of the surface ´roughness elements´, here mainly the mean height of standing crop
k	von Kármán´s constant (≈ 0.40)
z	Height above the soil surface [m]
zo	Roughness length [m] – parameter expressing the aerodynamic friction (roughness) exerted by a surface

Meteorological items:

P	Precipitation sum [mm] (also denoted ´Precip.´)
RH	Relative humidity of the air [%]
Ri_B(16-0.15m)	Bulk Richardson number (finite difference calculated) between the heights 16 and 0.15 m
Ri_B(2m-surf.)	Bulk Richardson number (finite difference calculated) between the heights 2 m and the ´surface´ (in the summer cases the ´surface´ is taken as the top of the crop)
Rsol	Incoming solar radiation [Wm-2]
T(2)	Air temperature at the height of 2 m [˚C]
Tsoil(-5cm)	Soil temperature at a depth of approximately 5 cm [˚C]
Tsurf	Average temperature at the surface: the upper side of the crop canopy in summer and the bare soil surface in the autumn cases [˚C]

(T_0m, T_2m and T_16m appearing in some of the tables in Appendix 1 refer to the more correct heights 0.15 m, 2 m and 15.5 m, respectively, for the temperature sensors)

$\bar{u}$	Average horizontal wind speed [ms-1]
$\bar{u}(2)$	Mean wind speed at the height of 2 m
u´	Momentarily (turbulent) deviation of wind speed from the time average [ms-1]
u_h	Wind speed at the top of crop canopy of height h
u_*	Friction velocity [ms-1] – scaling parameter in the logarithmic wind law

Chemical-physical properties of pesticides:

K_H	Henry´s constant
Koc	Adsorption coefficient to organic carbon [ml/g]
Kfoc	Adsorption coefficient to organic carbon [ml/g] according to Freundlich method
Rsurf	Dose corrected parameter characterizing physico-chemical properties of a pesticide (Rsurf = dose* Vp/ Kfoc Sw)
Sw	Water solubility [mg/l] of actual pesticide
Vp	Vapour pressure [Pa or mPa]

Vp(1),Vp(2) etc	Different sets (i.e. combinations) of vapour pressure values for the six pesticides used in the present experiments

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Appendix 1a-e: Average, max. and min. values of weather variables recorded at the experimental site at Lövsta, incl. Ri-number, 2008-2010

Appendix 1a:

June and Sept. 2008

	Wind Spe. 16 m [m/s]	Wind Spe. 8 m [m/s]	Wind Spe. 4 m [m/s]	Wind Spe. 2 m [m/s]	Wind Spe. 1 m [m/s]	Wind Spe. 0,65 m [m/s]	Wind Spe 0,35 m	Wind vect WVc(1) [m/s]	Wind vec WVc(2) [m/s]	Wind dir. mean [0-360˚]	Wind dir. std dev. [0-360˚]	Sol_Wm2_ solar rad. [W/m2]	Rel_Hum (2m) [%]	Air_Temp_ Rotr. (2m) [˚C]	Temp(2m) ("T_2m") [˚C]	Temp(0.15m) ("T_0m") [˚C]	Temp Surf. ("T_surf.") [˚C]
Per.1 **air sampl. June -08:**																	
Meanvalue 24/6 17:00 - 21:00:	8.35	6.97	5.77	4.38	2.81	1.94	x	4.38	3.65	~280[1]	~25[1]	NOS[2]	(58)[1]		16.5	16.5	16.0
Max. value 24/6 17:00 - 21:00:	9.14	7.58	6.32	4.79	3.09	2.23	x	4.79	4.75			NOS		NOS	17.1	17.2	17.2
Min. value 24/6 17:00 - 21:00:	6.76	5.61	4.62	3.50	2.25	1.37	x	3.50	1.11			NOS		NOS	15.2	14.9	14.4
Per.2 **air sampl. June -08:**																	
Meanvalue 24/6 21:30 - 25/6 09:30:	5.88	4.63	3.57	2.58	1.58	1.04	x	2.58	2.55	~280	~25	NOS	(58)[1]	NOS	9.8	9.5	9.4
Max. value 24/6 21:30 - 25/6 09:30:	7.35	6.25	5.28	4.03	2.62	1.82	x	4.03	3.94			NOS		NOS	14.9	15.3	19.5
Min. value 24/6 21:30 - 25/6 09:30:	4.16	2.94	1.94	1.14	0.55	0.27	x	1.14	1.12			NOS		NOS	5.0	4.1	3.7
Per.3 **air sampl. June -08:**																	
Meanvalue 25/6 10:30 - 25/6 17:00:	6.58	5.81	4.96	3.86	2.54	1.57	x	3.86	3.78	~265	~30	NOS	(48)[1]	NOS	18.2	19.4	23.7
Max.value 25/6 10:30 - 25/6 17:00:	7.45	6.57	5.61	4.36	2.84	1.80	x	4.36	4.29			NOS		NOS	19.5	20.8	25.1
Min.value 25/6 10:30 - 25/6 17:00:	4.99	4.28	3.58	2.74	1.75	1.02	x	2.74	2.69			NOS		NOS	16.0	17.3	19.9
Per. 26 hrs **soil depos. June -08:**																	
Mean 24/6 15:00 24/6 - 25/6 17:00:	6.68	5.54	4.52	3.40	2.16	1.42	x	3.40	3.25	~275	~25	NOS	(58)[1]	NOS	13.9	14.1	15.3
Max. 24/6 15:00 24/6 - 25/6 17:00:	9.17	7.90	6.66	5.10	3.25	2.29	x	5.10	5.04			NOS		NOS	19.5	20.8	25.1
Min. 24/6 15:00 24/6 - 25/6 17:00:	4.16	2.94	1.94	1.14	0.55	0.27	x	1.14	1.11			NOS		NOS	5.0	4.1	3.7
Per.1 **air sampling; Sept. -08**																	
Mean 21/9 14:00 -22/9 07:30:	1.22	1.06	0.92	0.74	0.63	0.50	x	0.74	0.68	~90[1]	~20[1]	19.0	90	6.3	6.1	5.4	5.2
Max. 21/9 14:00 -22/9 07:30:	3.61	3.30	2.96	2.65	2.25	1.89	x	2.65	2.63			129.0	98	15.0	15.2	15.1	15.8
Min. 21/9 14:00 -22/9 07:30:	0.20	0.24	0.11	<0.1	<0.1	<0.1	x	<0.1	<0.1			0.0	64	0.8	0.6	0.1	0.1
Per.2 **air sampling; Sept. -08**																	
Mean 22/9 08:30 -22/9 18:00:	1.60	1.58	1.44	1.15	1.07	0.86	x	1.15	0.88	~45	~15	99.6	83	12.0	11.8	12.0	12.6
Max. 22/9 08:30 -22/9 18:00:	2.66	2.50	2.28	1.91	1.76	1.46	x	1.91	1.49			192.6	96	14.3	14.4	14.7	15.8
Min. 22/9 08:30 -22/9 18:00:	0.25	0.27	0.26	0.24	0.18	0.15	x	0.24	0.22			33.7	74	5.3	4.6	5.1	6.4
Per. 27 hrs **soil depos. Sept.-08:**																	

[1] **Wind direction and RH values are from Ultuna climate station ca 9 km WSW from the experimental site at Lövsta**

[2] **No signal from sensor**

Appendix 1a, continued

	Temp(15.5m) ("T_16m") [?C]	Soil_Temp_ T_{soil}(-5 cm) [?C]	Precip. sum [mm]	Ri_B (16-0.15m)			Ri_B (2 m-surf.) [3]		
				mean for whole period	mean for daytime hrs	mean for nightfall and night time hrs	mean for whole period	mean for daytime hrs	mean for nightfall and night time hrs
Per.1 **_air sampl. June -08:**									
Meanvalue 24/6 17:00 - 21:00:	16.6	16.3	0.0	0.0025			0.0051		
Max. value 24/6 17:00 - 21:00:	17.0	17.3	0.0						
Min. value 24/6 17:00 - 21:00:	15.4	15.1	0.0						
Per.2 **_air sampl. June -08:**									
Meanvalue 24/6 21:30 - 25/6 09:30:	11.0	11.8	0.0	0.120	-0.048	0.189	0.028	-0.026	0.050
Max. value 24/6 21:30 - 25/6 09:30:	15.2	14.5	0.0						
Min. value 24/6 21:30 - 25/6 09:30:	7.7	9.7	0.0						
Per.3 **_air sampl. June -08:**									
Meanvalue 25/6 10:30 - 25/6 17:00:	17.0	23.6	0.0	-0.087	-0.087		-0.047	-0.047	
Max.value 25/6 10:30 - 25/6 17:00:	18.4	27.4	0.0						
Min.value 25/6 10:30 - 25/6 17:00:	14.8	18.4	0.0						
Per. 26 hrs **_soil depos. June -08:**									
Mean 24/6 15:00 24/6 - 25/6 17:00:	14.1	16.2	0.0	0.030	-0.051	0.181	-0.0017	-0.028	0.048
Max. 24/6 15:00 24/6 - 25/6 17:00:	18.4	27.4	0.0						
Min. 24/6 15:00 24/6 - 25/6 17:00:	7.7	9.7	0.0						

[3] "surf" ? 0.65 m for June and July periods

				Ri_B (16-0.15m)			Ri_B (2 m-surf.) [3]		
				mean for whole period	mean for daytime hrs	mean for nightfall and night time hrs	mean for whole period	mean for daytime hrs	mean for nightfall and night time hrs
Per.1 **_air sampling; Sept. -08**									
Mean 21/9 14:00 -22/9 07:30:	7.5	9.3	0.0	1.95	-0.245	2.9	0.202	-0.036	0.281
Max. 21/9 14:00 -22/9 07:30:	14.1	12.6	0.0						
Min. 21/9 14:00 -22/9 07:30:	2.2	6.7	0.0						
Per.2 **_air sampling; Sept. -08**									
Mean 22/9 08:30 -22/9 18:00:	11.3	9.8	0.0	-0.082	-0.082		-0.115	-0.115	
Max. 22/9 08:30 -22/9 18:00:	13.6	11.1	0.0						
Min. 22/9 08:30 -22/9 18:00:	4.5	7.0	0.0						
Per. 27 hrs **_soil depos. Sept.-08:**									
Mean 21/9 15:00 -22/9 18:00:	8.7	9.4	0.0	1.16	-0.130	2.9	0.079	-0.092	0.281
Max. 21/9 15:00 -22/9 18:00:	14.1	12.5	0.0						
Min. 21/9 15:00 -22/9 18:00:	2.2	6.7	0.0						

[3] "surf" ? 0.0 m for September periods

Note: All values given here (mean, max. and min.) from the experimental site at Lövsta are based on primary 30-min. mean values delivered as the output "raw" data by the Campbell CR1000 logger system.

Appendix 1b:

July 2009

	Wind Sp. ū(16m) [m/s]	Wind Sp. ū(8m) [m/s]	Wind Sp. ū(4m) [m/s]	Wind Sp. ū(2m) [m/s]	Wind Sp. ū(1.0m) [m/s]	Wind Sp. ū(0.65m) [m/s]	Wind Sp. ū(0.35m) [m/s]	Wind Dir. mean [0-360]	Wind Dir. std dev. [0-360]	Solar rad. R_{sol} [W/m2]	Rel.Hum. 2 m [%]	Air_Temp. Rotr.(2m) [deg.C]	Temp(2m) ("T_2m") [deg.C]	Temp(0.15m) ("T_0m") [deg.C]	Temp. Surf. ("T_surf.") [deg.C]	Temp(15.5m) ("T_16m") [deg.C]	T_{soil}(-5cm) "Tsoil" [deg.C]
Per.1 **_air sampling July -09:**																	
Mean value 4/7 10:30 - 14:30:	3.54	3.21	2.83	2.31	1.54	0.97	x[*]	~10	~60	640.5	61	21.4	21.1	22.1	25.6	20.2	28.0
Max. 4/7 10:30 - 14:30:	4.70	4.18	3.69	2.97	1.97	1.25				797.2	66	22.4	22.0	23.6	27.9	21.0	33.4
Min. 4/7 10:30 - 14:30:	1.33	1.35	1.28	1.11	0.81	0.45				354.2	57	21.0	20.5	21.3	23.6	19.4	24.2
Per.2 **_air sampling July -09:**																	
Mean value 4/7 14:30 - 17:30:	3.04	2.73	2.40	1.88	1.27	0.69	x	~10	~40	279.7	67	20.5	20.4	20.6	22.6	19.8	22.4
Max. 4/7 14:30 - 17:30:	3.92	3.50	3.13	2.56	1.66	1.08				593.4	71	22.1	21.8	22.8	25.7	21.1	26.4
Min. 4/7 14:30 - 17:30:	2.20	2.06	1.87	1.51	1.02	0.37				93.1	63	19.5	19.5	19.2	20.5	18.9	20.2
Per.3 **_air sampling July -09:**																	
Mean 4/7 17:30 - 11:30 5/7:	3.33	3.08	2.57	1.95	1.31	0.72	x	~25	~50	148.2	77	13.3	12.9	12.7	14.2	13.3	15.2
Max. 4/7 17:30 - 11:30 5/7:	5.79	5.87	5.05	4.02	2.94	1.74				607.2	95	20.8	20.8	20.6	23.1	20.0	26.7
Min. 4/7 17:30 - 11:30 5/7:	0.95	0.89	0.81	0.65	0.33	0.14				0.0	54	6.5	6.5	6.0	6.7	8.6	7.9
Per.4 **_air sampling July -09:**																	
Mean 5/7 12:00 - 6/7 11:00:	NOS[3]	NOS	NOS	NOS	NOS	NOS	x	NOS	NOS	198.0	72	13.1	12.9	12.8	14.1	13.1	14.2
Max. 5/7 12:00 - 6/7 11:00:	NOS	NOS	NOS	NOS	NOS	NOS		NOS	NOS	631.3	95	18.2	18.0	18.1	20.9	16.7	21.2
Min. 5/7 12:00 - 6/7 11:00:	NOS	NOS	NOS	NOS	NOS	NOS		NOS	NOS	0.0	47	7.2	6.8	6.7	7.0	8.6	8.3
Per.5 **_air sampling July -09:**																	
Mean 6/7 12:30 - 7/7 09:30:	4.22	3.63	3.03	2.30	1.50	0.60	x	~110	~40	64.1	78	14.0	13.9	13.7	14.2	13.8	13.7
Max. 6/7 12:30 - 7/7 09:30:	6.00	5.18	4.38	3.35	2.19	1.10				312.0	96	16.8	17.0	16.9	19.5	16.2	18.8
Min. 6/7 12:30 - 7/7 09:30:	2.44	1.97	1.51	1.10	0.61	0.16				0.0	60	12.4	12.1	11.9	11.8	12.5	11.8
	[3] No signal from sensor							[*] not used									
Soil depos. _per.1[1]:																	
Mean 4/7 10:30 - 5/7 12:00:	3.34	3.07	2.60	2.01	1.35	0.76	x	~20	~50	249.6	73	15.5	15.2	15.2	17.1	15.2	18.3
Max. 4/7 10:30 - 5/7 12:00:	5.79	5.87	5.05	4.02	2.94	1.74				797.2	95	22.4	22.0	23.6	27.9	21.1	33.4
Min. 4/7 10:30 - 5/7 12:00:	0.95	0.89	0.81	0.65	0.33	0.14				0.0	51	6.5	6.5	6.0	6.7	8.6	7.9
[1] Depos. sampling finished at 13:00 but no signal from wind speed sensors after 12:00																	
Soil depos. _per.2[2]:																	
Mean 5/7 14:00 - 6/7 11:30:	NOS[3]	NOS	NOS	NOS	NOS	NOS	x	NOS	NOS	191.6	73	12.9	12.7	12.6	14.0	13.0	14.0
Max. 5/7 14:00 - 6/7 11:30:	NOS	NOS	NOS	NOS	NOS	NOS		NOS	NOS	631.3	95	18.2	18.0	18.1	20.9	16.7	21.2
Min. 5/7 14:00 - 6/7 11:30:	NOS	NOS	NOS	NOS	NOS	NOS		NOS	NOS	0.0	47	7.2	6.8	6.7	7.0	8.6	8.3
[2] Deposition sampling finished at 11:20																	

***Note*:** All values given here (mean, max. and min.) from the experimental site at Lövsta are based on primary *30-min. mean valus,* delivered as output "raw" data by the Campbell CR1000 logger system, regarding the July data (as it is also for *all* 2008 and 2010 data), but on *2-min. means* when it comes to the September 2009 data.

Appendix 1b, continued:

July 2009	**Precip. sum [mm]**	**Ri_B (16-0.15m) mean for whole period**	**mean for daytime hrs**	**mean for nightfall and night time hrs**	**Ri_B (2 m-surf.) [4] mean for whole period**	**mean for daytime hrs**	**mean for nightfall and night time hrs**
***Per.1* air sampling July -09:**							
Mean value 4/7 10:30 - 14:30:	0.0	-0.150			-0.189		
Max. 4/7 10:30 - 14:30:	0.0						
Min. 4/7 10:30 - 14:30:	0.0						
***Per.2* air sampling July -09:**							
Mean value 4/7 14:30 - 17:30:	0.0	-0.039			-0.073		
Max. 4/7 14:30 - 17:30:	0.0						
Min. 4/7 14:30 - 17:30:	0.0						
***Per.3* air sampling July -09:**							
Mean value 4/7 17:30 - 11:30 5/7:	0.0	0.035	-0.075	0.092	-0.058	-0.117	-0.027
Max. 4/7 17:30 - 11:30 5/7:	0.0		(6 hrs)	(12 hrs)		(6 hrs)	(12 hrs)
Min. 4/7 17:30 - 11:30 5/7:	0.0						
***Per.4* air sampling July -09:**							
Mean value 5/7 12:00 - 6/7 11:00:	0.0	0.197	-0.042	0.481	-0.041	-0.047	-0.033
Max. 5/7 12:00 - 6/7 11:00:	0.0		(12.5 hrs)	(10.5 hrs)		(12.5 hrs)	(10.5 hrs)
Min. 5/7 12:00 - 6/7 11:00:	0.0						
***Per.5* air sampling July -09:**							
Mean value 6/7 12:30 - 7/7 09:30:	0.0	0.013	-0.00024	0.019	-0.0036	-0.013	0.00065
Max. 6/7 12:30 - 7/7 09:30:	0.0		(6.5 hrs)	(14.5 hrs)		(6.5 hrs)	(14.5 hrs)
Min. 6/7 12:30 - 7/7 09:30:	0.0						
Soil depos. per.1[1]:							
Mean value 4/7 10:30 - 5/7 12:00:	0.0	-0.0059	-0.087	0.106	-0.081	-0.136	-0.0054
Max. 4/7 10:30 - 5/7 12:00:	0.0		(14.5 hrs)	(11 hrs)		(14.5 hrs)	(11 hrs)
Min. 4/7 10:30 - 5/7 12:00:	0.0						
Soil depos. per.2[2]:							
Mean value 5/7 14:00 - 6/7 11:30:	0.0	0.211	-0.046	0.481	-0.043	-0.052	-0.033
Max. 5/7 14:00 - 6/7 11:30:	0.0		(10.0 hrs)	(10.5 hrs)		(10.0 hrs)	(10.5 hrs)
Min. 5/7 14:00 - 6/7 11:30:	0.0						

[4] **"surf" = 0.65 m for June and July periods**

[1] **Depos. sampling finished at 13:00 but no signal from wind speed sensors after 12:00**

[2] **Deposition sampl. finished at 11:20**

Appendix 1c:

Sept. 2009

	Wind Sp. ū(16m) [m/s]	Wind Sp. ū(8m) [m/s]	Wind Sp. ū(4m) [m/s]	Wind Sp. ū(2m) [m/s]	Wind Sp. ū(1.0m) [m/s]	Wind Sp. ū(0.65m) [m/s]	Wind Sp. ū(0.35m) [m/s]	Wind Dir. mean [0-360]	Wind Dir. std dev. [0-360]	Solar rad. R_{sol} [W/m2]	Rel.Hum. 2 m [%]	Air_Temp. Rotr.(2m) [deg.C]	Temp(2m) ("T_2m") [deg.C]	Temp(0.15m) ("T_0m") [deg.C]	Temp. Surf. ("T_surf.") [deg.C]	Temp(15.5m) ("T_16m") [deg.C]	T_{soil}(-5cm) "Tsoil" [deg.C]
Per.1 **_air sampling_Sept. -09:**																	
Mean 18/9 11:40- 15:12:	4.34	4.14	3.87	3.57	3.23	2.83	2.34	240	8.9	297.9	55.9	15.6	16.2	17.2	17.8	15.5	20.8
Max. 18/9 11:40- 15:12:	6.57	6.10	5.67	5.36	4.89	4.32	3.57	276	43.5	561.2	59.7	17.1	17.2	18.4	18.9	17.0	25.7
Min. 18/9 11:40- 15:12:	2.85	2.72	2.25	1.99	1.77	1.42	1.20	185	1.4	128.8	42.9	15.5	15.2	16.4	17.2	14.5	17.7
Per.2 **_air sampling_Sept.-09:**																	
Mean 18/9 15:40- 18:34:	2.34	2.15	2.00	1.82	1.63	1.41	1.18	260	5.3	105.9	60.4	16.6	16.4	16.4	17.0	16.2	16.8
Max. 18/9 15:40- 18:34:	4.04	3.83	3.62	3.34	2.91	2.55	2.14	280	14.4	166.0	68.0	17.4	17.1	17.3	17.9	16.8	18.9
Min. 18/9 15:40- 18:34:	0.50	0.28	0.29	0.20	0.07	0.02	0.02	241	0.0	17.3	57.8	15.3	14.9	13.6	15.2	15.0	12.4
Per.3 **_air sampling_Sept.-09:**																	
Mean 18/9 19:00 - 19/9 12:00:	1.39	1.11	1.00	0.91	0.75	0.56	0.50	~220*)	2.9	83.7	90.6	8.4	8.0	7.3	8.5	10.6	8.9
Max. 18/9 19:00 - 19/9 12:00:	5.59	5.36	5.00	4.58	4.21	3.76	3.05	351	62.0	469.5	99.1	17.9	17.9	19.3	19.5	17.1	26.4
Min. 18/9 19:00 - 19/9 12:00:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0	0.0	-1.2	62.0	2.8	2.3	2.1	2.9	6.7	2.6
Per.4 **_air sampling_Sept.-09:**																	
Mean 19/9 12:40 - 20/9 12:06:	3.46	3.34	3.10	2.75	2.31	1.92	1.54	~220*)	4.6	133.3	77.0	12.8	12.6	12.2	12.9	13.4	13.1
Max. 19/9 12:40 - 20/9 12:06:	8.64	8.30	7.63	6.96	6.24	5.51	4.46	248	20.4	485.5	97.7	20.3	20.4	21.4	21.5	19.5	28.0
Min. 19/9 12:40 - 20/9 12:06:	0.56	0.53	0.44	0.26	0.20	0.07	0.13	79	0.0	-1.2	46.0	6.0	5.6	4.7	6.1	8.1	5.5
Per.5 **_air sampling_Sept.-09:**																	
Mean 20/9 12:58 - 22/9 11:52:	4.65	4.24	3.82	3.38	2.96	2.58	2.04	228	6.4	83.3	81.3	13.8	13.8	13.7	13.9	13.9	14.0
Max. 20/9 12:58 - 22/9 11:52:	10.60	9.77	9.00	8.04	7.09	6.26	5.06	359	47.5	654.2	98.3	19.9	19.9	20.8	20.9	19.0	26.8
Min. 20/9 12:58 - 22/9 11:52:	0.06	0.14	0.03	0.07	0.00	0.00	0.00	7	0.0	-1.2	52.1	11.4	11.2	10.5	10.9	11.4	9.3
Per.6 **_air sampling_Sept.-09:**																	
Mean 22/9 12:26 - 26/9 12:20:	6.00	5.47	4.93	4.34	3.76	3.32	2.68	236	6.1	94.4	77.9	12.0	11.9	11.6	11.9	12.4	11.9
Max. 22/9 12:26 - 26/9 12:20:	13.30	12.34	11.43	10.15	8.81	8.07	6.53	356	30.9	516.8	98.7	18.4	18.6	19.5	19.2	17.8	27.2
Min. 22/9 12:26 - 26/9 12:20:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0	0.0	-1.2	40.2	-0.3	-0.8	-1.3	-0.3	3.2	-2.0
								*) uncertain value due to frequent calms									
Per.1 **_soil deposition_Sept.-09**																	
Mean 18/9 12:00 - 19/9 12:05:	1.98	1.71	1.57	1.44	1.24	1.01	0.87	~235*)	4.1	113.1	81.4	10.7	10.4	10.1	11.0	12.1	11.6
Max. 18/9 12:00 - 19/9 12:05:	6.57	6.10	5.67	5.36	4.89	4.32	3.57	351	62.0	534.6	99.1	18.0	18.0	19.5	19.5	17.1	26.4
Min. 18/9 12:00 - 19/9 12:05:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0	0.0	-1.2	53.1	2.8	2.3	2.1	2.9	6.7	2.6
								*) uncertain value due to frequent calms									
Per.2 **_soil deposition_Sept.-09**																	
Mean 19/9 12:15 - 20/9 11:55:	3.46	3.34	3.10	2.75	2.32	1.93	1.54	~225*)	4.6	136.8	76.8	12.9	12.6	12.3	13.0	13.5	13.3
Max. 19/9 12:15 - 20/9 11:55:	8.64	8.30	7.63	6.96	6.24	5.51	4.46	248	20.4	486.1	97.7	20.3	20.4	21.4	21.5	19.5	28.0
Min. 19/9 12:15 - 20/9 11:55:	0.56	0.53	0.44	0.26	0.20	0.07	0.13	79	0.0	-1.2	46.0	6.0	5.6	4.7	6.1	8.1	5.5
Per.3 **_soil deposition_Sept.-09**																	
Mean 20/9 12:00 - 22/9 12:00:	4.72	4.32	3.89	3.45	3.02	2.63	2.09	228	6.4	89.4	80.8	13.9	13.9	13.8	14.0	13.9	14.2
Max. 20/9 12:00 - 22/9 12:00:	10.60	9.77	9.00	8.04	7.09	6.26	5.06	359	47.5	654.2	98.3	19.9	19.9	20.8	20.9	19.0	26.8
Min. 20/9 12:00 - 22/9 12:00:	0.06	0.14	0.03	0.07	0.00	0.00	0.00	7	0.0	-1.2	52.1	11.4	11.2	10.5	10.9	11.4	9.3

Appendix 1c, cont.:

Sept. 2009	**Precip. sum [mm]**	**Ri_B (16-0.15m) mean for whole period**	**mean for daytime hrs**	**mean for nightfall and night time hrs**	**Ri_B (2 m-surf.) [4] mean for whole period**	**mean for daytime hrs**	**mean for nightfall and night time hrs**
Per.1_air sampling_Sept. -09:							
Mean value **18/9 11:40- 15:12:**	0.0	-0.049			-0.01		
Max. 18/9 11:40- 15:12:	0.0						
Min. 18/9 11:40- 15:12:	0.0						
Per.2_air sampling:							
Mean value **18/9 15:40- 18:34:**	0.0	0.188	-0.039	0.946	-0.0071	-0.011	0.0070
Max. 18/9 15:40- 18:34:	0.0	(2.9 hrs)	(134 min.;	(40 min.;	(2.9 hrs)	(134 min.;	(40 min.;
Min. 18/9 15:40- 18:34:	0.0		15:40-17:54)	17:54-18:34)		15:40-17:54)	17:54-18:34)
Per.3_air sampling:							
Mean value **18/9 19:00 - 19/9 12:00:**	0.0	2.20	-0.129	2.4	0.031	-0.063	0.059
Max. 18/9 19:00 - 19/9 12:00:	0.0	(13.1 hrs;	(4 hrs)	(9.2 hrs;	(14.2 hrs;	(4 hrs)	(10.2 hrs;
Min. 18/9 19:00 - 19/9 12:00:	0.0	4.1 hrs excl.)[3]		4 hrs excl.)[3]	3.0 hrs excl.)[3]		3.0 hrs excl.)[3]
Per.4_air sampling:							
Mean value **19/9 12:40 - 20/9 12:06:**	0.0	0.281	-0.025	0.509	0.0030	-0.0071	0.010
Max. 19/9 12:40 - 20/9 12:06:	0.0	(23.2 hrs;	(9.9 hrs)	(13.3 hrs;	(23.4 hrs)	(9.9 hrs)	(13.5 hrs)
Min. 19/9 12:40 - 20/9 12:06:	0.0	10 min. excl.)[3]		10 min. excl.)			
Per.5_air sampling:							
Mean value **20/9 12:58 - 22/9 11:52:**	8.0	0.042	-0.030	0.084	0.0034	-0.012	0.012
Max. 20/9 12:58 - 22/9 11:52:		(46.6 hrs;	(17.3 hrs)	(29.3 hrs;	(46.5 hrs;	(17.3 hrs)	(29.2 hrs;
Min. 20/9 12:58 - 22/9 11:52:	0.0	18 min. excl.)[3]		18 min. excl.)	24 min. excl.)[3]		24 min. excl.)
Per.6_air sampling:							
Mean value **22/9 12:26 - 26/9 12:20:**	0[1]	0.087	-0.0079	0.152	0.0033	-0.0024	0.0071
Max. 22/9 12:26 - 26/9 12:20:	0.0	(92.6 hrs;	(37.6 hrs)	(55.0 hrs;	(94.4 hrs;	(37.6 hrs)	(56.8 hrs;
Min. 22/9 12:26 - 26/9 12:20:	0.0	3.3 hrs excl.)[3]		3.3 hrs excl.)	1.5 hrs excl.)[3]		1.5 hrs excl.)
***Per.1* _soil deposition_Sept.-09**							
Mean value **18/9 12:00 - 19/9 12:05:**	0.0	1.7	-0.010	2.4	0.020	-0.0078	0.059
Max. 18/9 12:00 - 19/9 12:05:	0.0	(20 hrs;	(10.6 hrs)	(9.4 hrs;	(21 hrs;	(10.4 hrs;	(10.5 hrs;
Min. 18/9 12:00 - 19/9 12:05:	0.0	4 hrs excl.)[3]		4 hrs excl.)	3.1 hrs excl)[3]	10 min. excl.)	3 hrs excl.)
***Per.2* _soil deposition_Sept.-09**							
Mean value **19/9 12:15 - 20/9 11:55:**	0.0	0.281	-0.025	0.509	0.0030	-0.0071	0.010
Max. 19/9 12:15 - 20/9 11:55:	0.0	(23.2 hrs;	(9.9 hrs)	(13.3 hrs;	(23.4 hrs)	(9.9 hrs)	(13.5 hrs)
Min. 19/9 12:15 - 20/9 11:55:	0.0	10 min. excl.)		10 min. excl.)			
***Per.3* _soil deposition_Sept.-09**							
Mean value **20/9 12:00 - 22/9 12:00:**	8.0	0.042	-0.030	0.084	0.0034	-0.012	0.012
Max. 20/9 12:00 - 22/9 12:00:		(46.6 hrs;	(17.3 hrs)	(29.3 hrs;	(46.5 hrs;	(17.3 hrs)	(29.2 hrs;
Min. 20/9 12:00 - 22/9 12:00:	0.0	18 min. excl.)[3]		18 min. excl.)	24 min. excl.)[3]		24 min. excl.)

[4] "surf" = 0.0 m for the September periods

[1] Four single ´ticks´ (each 0.2mm) disregarded (judged as spurious signals from sensor)

[3] Excessively large underlying 2-min. values excluded (mostly connected with calm or very low wind speeds)

Appendix 1d: **July 2010**	**Wind Sp. ū(0,35 m) [m/s]**	**Wind Sp. ū(0,65 m) [m/s]**	**Wind Sp. ū(1,0m) [m/s]**	**Wind Sp. ū(2m) [m/s]**	**Wind Sp. ū(4m) [m/s]**	**Wind Sp. ū(8m) [m/s]**	**Wind Sp. ū(16m) [m/s]**	**Wind Dir. mean [0-360]**	**Wind Dir. std dev [0-360]**	**Solar rad. R_{sol} (2m) $[W/m^2]$**	**Rel. Hum. (2m) [%]**	**Air Temp. Rotr.(2m) [deg.C]**	**Temp(2m) ("T_2m") [deg.C]**	**Temp(0.15m) ("T_0.15m") [deg.C]**
Per.1 **air sampl. July -10**														
Mean value 3/7 11:30-14:30:	x	1.24	2.08	2.94	3.83	4.64	5.23	206	21	690.9	48	27.9	28.2	28.4
Max. 3/7 11:30 - 14:30:	x	1.36	2.29	3.30	4.28	5.21	5.84	232	26	775.9	49	28.5	28.8	28.9
Min. 3/7 11:30 - 14:30:	x	1.10	1.89	2.65	3.42	4.18	4.67	185	18	584.7	48	26.9	27.3	27.5
Per.2 **air sampl. July -10**														
Mean value 3/7 14:30-17:00:	x	1.44	2.53	3.56	4.56	5.55	6.31	193	20	608.6	49	28.0	28.5	28.3
Max. 3/7 14:30 - 17:00:	x	1.56	2.72	3.85	4.91	6.00	6.86	199	22	679.3	50	28.3	28.7	28.8
Min. 3/7 14:30 - 17:00:	x	1.29	2.21	3.14	4.05	4.93	5.52	188	18	517.4	47	27.5	28.2	27.8
Per.3 **air sampl. July -10**														
Mean value 3/7 17:00-4/7 12:00:	x	0.58	1.07	1.65	2.34	3.01	3.57	166	16	201.2	63	21.0	20.9	20.5
Max. 3/7 17:00-4/7 12:00:	x	1.32	2.36	3.33	4.48	5.45	6.38	198	34	725.9	80	27.9	28.2	28.4
Min. 3/7 17:00-4/7 12:00:	x	0.19	0.46	0.73	1.14	1.36	1.30	93	5	0.0	46	15.1	14.7	14.0
Per.4 **air sampl. July -10**														
Mean value 4/7 12:00-5/7 11:30:	x	0.75	1.37	2.10	2.83	3.58	4.32	188	15	247.5	63	20.6	20.7	20.3
Max. 4/7 12:00-5/7 11:30:	x	1.61	3.09	4.49	5.78	7.06	8.27	268	23	756.6	93	28.7	29.2	29.2
Min. 4/7 12:00-5/7 11:30:	x	0.17	0.23	0.54	0.79	0.93	1.31	121	4	0.0	22	13.5	13.0	12.4
Per.5 **air sampl. July -10**														
Mean value 5/7 11:30-7/7 11:00:	x	0.36	0.64	1.06	1.47	1.85	2.17	228	16	193.8	74	18.2	17.9	17.6
Max. 5/7 11:30-7/7 11:00:	x	1.39	2.20	3.09	4.00	4.86	5.42	338	67	831.0	97	25.3	25.9	25.6
Min. 5/7 11:30-7/7 11:00:	x	0.00	0.03	0.12	0.15	0.17	0.29	30	0	0.0	37	10.0	9.6	8.7
Per.6 **air sampl. July -10**														
Mean value 7/7 11:30-9/7 11:30:	x	0.62	1.10	1.81	2.41	2.98	3.51	237	19	282.4	64	20.4	20.1	19.8
Max. 7/7 11:30-9/7 11:30:	x	1.43	2.37	3.45	4.40	5.35	6.19	359	55	813.0	85	26.4	26.7	26.1
Min. 7/7 11:30-9/7 11:30:	x	0.02	0.06	0.20	0.36	0.44	0.48	10	1	0.0	37	11.5	11.4	9.4
Per.7 **air sampl. July -10**														
Mean value 9/7 11:30-11/7 22:30:	x	0.71	1.27	2.03	2.70	3.33	3.85	188	19	307.0	60	22.7	22.5	21.9
Max. 9/7 11:30-11/7 22:30:	x	1.78	3.05	4.65	5.96	7.38	8.73	360	67	797.5	95	32.0	32.4	32.2
Min. 9/7 11:30-11/7 22:30:	x	0.00	0.02	0.18	0.29	0.27	0.55	16	0	0.0	39	11.3	10.6	9.3

***Note* :** All values given here (mean, max. and min.) from the experimental site at Lövsta
are based on 30-min. mean values delivered as the output "raw" data by the Campbell CR1000 logger.
Thus, max. and min. values in the table means the *highest and lowest 30-min. average* value, respectively

Appendix 1d, cont.: ***July 2010***	**Temp Surf. ("T_surf.") [deg.C]**	**Temp(15.5m) ("T_16m") [deg.C]**	**T_{soil}(-5 cm) "Tsoil(-5 cm)" [deg.C]**	**Precip. sum [mm]**	**Ri_B (16-0.15m) mean for whole period**	**mean for daytime hrs**	**mean for nightfall and night time hrs**	**Ri_B (2m-surf.)$^{1)}$ mean for whole period**	**mean for daytime hrs**	**mean for nightfall and night time hrs**
Per.1 **air sampl. July -10**										
Mean value 3/7 11:30-14:30:	30.6	26.9	32.5	0.0	-0.027			-0.038		
Max. 3/7 11:30 - 14:30:	31.0	27.6	33.6	0.0						
Min. 3/7 11:30 - 14:30:	30.2	25.9	30.7	0.0						
Per.2 **air sampl. July -10**										
Mean value 3/7 14:30-17:00:	31.3	27.3	33.8	0.0	-0.012			-0.028		
Max. 3/7 14:30 - 17:00:	31.6	27.6	35.6	0.0						
Min. 3/7 14:30 - 17:00:	30.8	27.1	32.7	0.0						
Per.3 **air sampl. July -10**										
Mean value 3/7 17:00-4/7 12:00:	22.4	21.6	22.0	0.0	0.094	-0.056	0.131	-0.064	-0.159	-0.018
Max. 3/7 17:00-4/7 12:00:	32.7	27.0	34.8	0.0		(6.0 hrs)	(12.5 hrs)		(6.0 hrs)	(12.5 hrs)
Min. 3/7 17:00-4/7 12:00:	14.5	17.2	14.7	0.0						
Per.4 **air sampl. July -10**										
Mean value 4/7 12:00-5/7 11:30:	22.0	20.9	22.6	0.0	0.065	-0.021	0.167	-0.046	-0.055	-0.035
Max. 4/7 12:00-5/7 11:30:	32.4	27.8	36.5	0.0		(13 hrs)	(10.5 hrs)		(13 hrs)	(10.5 hrs)
Min. 4/7 12:00-5/7 11:30:	13.0	15.3	13.0	0.0						
Per.5 **air sampl. July -10**										
Mean value 5/7 11:30-7/7 11:00:	19.3	18.5	19.6	0.2	0.759	-0.020	1.59	-0.087	-0.133	0.0053
Max. 5/7 11:30-7/7 11:00:	29.1	24.3	34.5	0.2		(24.5 hrs)	(23 hrs)		(22.0 hrs;	(20.5 hrs;
Min. 5/7 11:30-7/7 11:00:	9.4	12.0	9.8	0.0					*2.5 hrs excl.* $^{2)}$)	*2.5 hrs excl.* $^{2)}$)
Per.6 **air sampl. July -10**										
Mean value 7/7 11:30-9/7 11:30:	21.8	20.4	21.9	0.0	0.317	-0.033	0.690	-0.053	-0.077	-0.027
Max. 7/7 11:30-9/7 11:30:	30.5	24.9	31.7	0.0	*(1.5 hrs excl.* $^{2)}$)	(24 hrs)	(22.5 hrs;	*(1.5 hrs excl.* $^{2)}$)	(24 hrs)	(22.5 hrs;
Min. 7/7 11:30-9/7 11:30:	10.7	13.6	10.5	0.0			*(1.5 hrs excl.* $^{2)}$)			*(1.5 hrs excl.* $^{2)}$)
Per.7 **air sampl. July -10**										
Mean value 9/7 11:30-11/7 22:30:	24.3	23.2	24.0	0.0	0.401	-0.055	1.02	-0.186	-0.273	-0.079
Max. 9/7 11:30-11/7 22:30:	34.7	31.0	35.4	0.0	*(3.5 hrs excl.* $^{2)}$)	(32 hrs)	(23.5 hrs;	(1 hr excl.$^{2)}$)	(32 hrs)	(26 hrs;
Min. 9/7 11:30-11/7 22:30:	10.5	14.1	10.9	0.0			*(3.5 hrs excl.* $^{2)}$)			*1hr excl.*)

[1] **"surf" = 0.65 m for June and July periods (just below top of canopy)**

[2] Excessively large underlying half-hour means excluded from total mean (mostly connected with calm or very low wind speeds)

Appendix 1e: **Sept. 2010**	Wind Sp. ū(0.35m) [m/s]	Wind Sp. ū(0.65m) [m/s]	Wind Sp. ū(1.0m) [m/s]	Wind Sp. ū(2m) [m/s]	Wind Sp. ū(4m) [m/s]	Wind Sp. ū(8m) [m/s]	Wind Sp. ū(16m) [m/s]	Wind Dir. mean [0-360]	Wind Dir. std. dev [0-360]	Solar rad. R_{sol} (2m) [W/m^2]	Rel. Hum. (2m) [%]	Air Temp. Rotr.(2m) [deg.C]	Temp(2m) ("T_2m") [deg.C]	Temp(0.15m) ("T_0.15m") [deg.C]
***Per.1* _air sampl. Sept. -10**														
Mean value 8/9 12:30 -15:30:	1.34	1.58	1.72	2.03	2.27	2.43	2.66	112	18	219.4	63	17.6	18.6	17.9
Max. 8/9 12:30 -15:30:	1.71	2.10	2.26	2.65	2.89	3.09	3.27	136	28	571.5	70	18.6	19.9	19.3
Min. 8/9 12:30 -15:30:	0.73	0.75	0.92	1.12	1.51	1.59	1.96	83	12	64.9	59	16.8	17.4	16.6
***Per.2* _air sampl. Sept. -10**														
Mean 8/9 15:30 -18:00:	1.06	1.21	1.38	1.67	1.94	2.13	2.53	95	14	103.5	68	16.8	17.8	16.6
Max. 8/9 15:30 -18:00:	1.54	1.83	2.00	2.35	2.56	2.80	3.18	105	22	179.8	70	17.3	18.7	17.4
Min. 8/9 15:30 -18:00:	0.60	0.58	0.84	1.13	1.55	1.69	2.17	81	11	40.6	66	16.3	17.0	16.0
***Per.3* _air sampl. Sept. -10**														
Mean 8/9 18:00 -9/9 12:00:	1.09	1.30	1.42	1.69	1.88	2.11	2.48	141	16	79.8	89	12.2	11.9	11.5
Max. 8/9 18:00 -9/9 12:00:	3.04	3.60	3.75	4.25	4.56	4.90	5.29	345	41	487.0	99	16.6	18.1	17.4
Min. 8/9 18:00 -9/9 12:00:	0.13	0.13	0.18	0.26	0.31	0.35	0.27	9	3	0	67	7.3	7.2	5.1
***Per.4* _air sampl. Sept. -10**														
Mean 9/9 12:30 -10/9 12:30:	1.43	1.66	1.81	2.15	2.38	2.59	2.94	163	15	128.5	82	12.3	12.4	11.8
Max. 9/9 12:00 -10/9 12:30:	3.10	3.68	3.83	4.35	4.78	5.19	5.56	321	72	433.2	100	17.3	18.2	17.9
Min. 9/9 12:00 -10/9 12:30:	0.10	0.09	0.12	0.27	0.34	0.11	0.18	82	0	0	56	5.7	5.3	4.0
***Per.5* _air sampl. Sept. -10**														
Mean 10/9 13:00 -11/9 11:30:	1.36	1.51	1.66	1.86	2.25	2.51	2.83	90	11	63.2	87	13.7	13.7	13.5
Max. 10/9 13:00 -11/9 11:30:	3.53	4.08	4.28	4.93	5.40	5.90	6.42	129	31	315.3	98	17.4	18.0	17.9
Min. 10/9 13:00 -11/9 11:30:	0.11	0.12	0.14	0.18	0.21	0.24	0.39	54	0	0	61	12.0	11.9	11.6
***Per.6* _air sampl. Sept. -10**														
Mean 11/9 12:00 -13/9 12:00:	1.39	1.72	1.84	2.16	2.45	2.85	3.32	189	11	54.4	91	15.3	15.4	15.2
Max. 11/9 12:00 -13/9 12:00:	2.81	3.43	3.74	4.27	4.67	5.26	5.71	240	40	297.1	99	20.0	20.7	20.3
Min. 11/9 12:00 -13/9 12:00:	0.37	0.52	0.55	0.76	0.89	1.09	1.44	125	0	0	74	11.2	10.7	10.1
***Per.7* _air sampl. Sept. -10**														
Mean 13/9 12:30 -18/9 05:00:	1.95	2.39	2.55	2.95	3.34	3.83	4.40	181	12	90.0	88	11.8	11.8	11.6
Max. 13/9 12:30 -18/9 05:00:	4.65	5.70	6.08	6.84	7.58	8.44	9.30	281	34	582.5	99	16.7	17.0	17.3
Min. 13/9 12:30 -18/9 05:00:	0.19	0.26	0.30	0.46	0.69	0.91	1.36	120	2	0	58	6.0	5.4	5.1

***Note*:** All values given here (mean, max. and min.) from the experimental site at Lövsta are based on 30-min. mean values delivered as the output "raw" data by the Campbell CR1000 logger. Thus, max. and min. values in the table means the *highest and lowest 30-min. average* value, respectively

Appendix 1e, cont.: ***Sept. 2010***	**Temp Surf. ("T_surf.") [deg.C]**	**Temp(15.5m) ("T_16m") [deg.C]**	**T_{soil}(-5 cm) "Tsoil(-5 cm)" [deg.C]**	**Precip. sum [mm]**	**Ri_B (16-0.15m) mean for whole period**	**mean for daytime hrs**	**mean for nightfall and night time hrs**	**Ri_B (2m-surf.)3) mean for whole period**	**mean for daytime hrs**	**mean for nightfall and night time hrs**
***Per.1* air sampl. Sept. -10**										
Mean value 8/9 12:30 -15:30:	18.8	17.0	18.1	0.0	-0.056			0.0005		
Max. 8/9 12:30 -15:30:	20.2	17.5	19.8	0.0						
Min. 8/9 12:30 -15:30:	17.2	16.4	16.4	0.0						
***Per.2* air sampl. Sept. -10**										
Mean 8/9 15:30 -18:00:	17.4	16.4	15.7	0.0	-0.010			0.012		
Max. 8/9 15:30 -18:00:	18.5	16.8	16.3	0.0						
Min. 8/9 15:30 -18:00:	16.8	16.1	14.6	0.0						
***Per.3* air sampl. Sept. -10**										
Mean 8/9 18:00 -9/9 12:00:	12.2	12.8	11.2	0.0	0.697 (18 hrs)	-0.019 (5.0 hrs)	1.0 (11.5 hrs; *1.5 hrs excl.*)2)	0.01 (18 hrs)	-0.011 (5.0 hrs)	0.018 (12.5 hrs; *0.5 hrs excl.*)2)
Max. 8/9 18:00 -9/9 12:00:	18.9	16.1	18.1	0.0						
Min. 8/9 18:00 -9/9 12:00:	6.9	10.3	7.0	0.0						
***Per.4* air sampl. Sept. -10**										
Mean 9/9 12:30 -10/9 12:30:	12.6	12.9	12.0	0.0	0.804 (21.5 hrs; *3 hrs excl.*)2)	-0.019 (11 hrs)	1.670 (10.5 hrs; *3 hrs excl.*)2)	0.021 (23.5 hrs; *1 hr excl.*)2)	-0.0039 (11 hrs)	0.042 (12.5 hrs; *1 hr excl.*)2)
Max. 9/9 12:00 -10/9 12:30:	18.7	16.7	18.4	0.0						
Min. 9/9 12:00 -10/9 12:30:	4.8	8.7	6.0	0.0						
***Per.5* air sampl. Sept. -10**										
Mean 10/9 13:00 -11/9 11:30:	13.8	13.5	13.7	**0.2**	-0.0052 (22.5 hrs)	-0.096 (10.5 hrs)	0.074 (12 hrs)	-0.0056 (22.0 hrs)	-0.016 (10.5 hrs)	0.0036 (11.5 hrs; *0.5 hrs excl.*)2)
Max. 10/9 13:00 -11/9 11:30:	18.5	16.8	18.5	**0.2**						
Min. 10/9 13:00 -11/9 11:30:	11.7	12.0	11.2	0.0						
***Per.6* air sampl. Sept. -10**										
Mean 11/9 12:00 -13/9 12:00:	15.6	15.4	15.1	**1.4**	0.024 (48 hrs)	-0.031 (20.5 hrs)	0.064 (27.5 hrs)	-0.0041 (48 hrs)	-0.0097 (20.5 hrs)	0.00014 (27.5 hrs)
Max. 11/9 12:00 -13/9 12:00:	21.3	19.4	20.5	**1.0**						
Min. 11/9 12:00 -13/9 12:00:	10.8	12.2	10.3	0.0						
***Per.7* air sampl. Sept. -10**										
Mean 13/9 12:30 -18/9 05:00:	12.1	11.9	11.6	**19.0**	0.041 (112.5 hrs)	-0.0072 (47.5 hrs)	0.077 (65 hrs)	-0.0009 (112.5 hrs)	-0.0027 (47.5 hrs)	0.00049 (65 hrs)
Max. 13/9 12:30 -18/9 05:00:	18.2	16.3	16.8	**2.8**						
Min. 13/9 12:30 -18/9 05:00:	5.7	7.6	5.4	0.0						

3) **"surf" = 0.0 m for the September periods**

2) Excessively large underlying half-hour means excluded from total mean (mostly connected with calm or very low wind speeds)

Appendix 2

Table 1a. Concentration of pesticides in PUFs and air - June 2008 (three sampling periods)

The column "µg/PUF" gives the total recovery of the respective pesticide from the PUFs for each sampling period, and "air conc." means the respective *average concentration* in air during the same sampling period.

Sample number	**Period 1** time [hrs]	Height above ground [m]	Sampled air volume [m^3]	***Pendimethalin***		***Prosulfocarb***		***Pirimicarb***		***Fenpropimorph***	
				µg in PUF [µg]	air conc.. [ng/m3]	µg in PUF [µg]	air conc.. [ng/m3]	µg in PUF [µg]	air conc.. [ng/m3]	µg in PUF [µg]	air conc.. [ng/m3]
M 8:1	0-4	background	30.220	0.059	1.94	0.075	2.47	0.010	0.32	0.029	0.95
M 8:20	0-4	0.25	37.430	3.955	105.65	36.562	976.81	1.157	30.90	3.017	80.59
M 8:17	0-4	0.6	39.600	4.576	115.54	42.984	1085.44	1.419	35.82	3.623	91.49
M 8:15	0-4	1	39.314	5.286	134.46	49.029	1247.10	1.659	42.19	4.384	111.51
M 8:13	0-4	2	33.080	5.420	163.85	48.411	1463.44	1.821	55.06	4.729	142.95
M 8:10	0-4	4	39.213	2.960	75.49	22.629	577.07	0.994	25.35	2.977	75.91
M 8:7	0-4	8	38.787	2.335	60.19	10.435	269.02	0.516	13.30	1.406	36.25
M 8:4	0-4	16	39.250	0.023	0.59	0.132	3.37	0.009	0.24	0.018	0.45

Red figures: close to detection limit

Sample number	**Period 2** time [hrs]	Height above ground [m]	Sampled air volume [m^3]	***Pendimethalin***		***Prosulfocarb***		***Pirimicarb***		***Fenpropimorph***	
				µg in PUF [µg]	air conc.. [ng/m3]	µg in PUF [µg]	air conc.. [ng/m3]	µg in PUF [µg]	air conc.. [ng/m3]	µg in PUF [µg]	air conc.. [ng/m3]
M 8:2	4-16	background	119.040	0.006	0.05	0.163	1.37	0.002	0.02	0.032	0.27
M 8:21	4-16	0.25	138.282	51.600	373.15	278.400	2013.28	5.360	38.76	3.140	22.71
M 8:18	4-16	0.6	143.013	10.459	73.13	78.785	550.89	1.425	9.96	1.032	7.22
M 8:16	4-16	1	147.786	55.200	373.51	327.400	2215.37	5.900	39.92	3.560	24.09
M 8:14	4-16	2	144.162	41.200	285.79	241.600	1675.89	4.680	32.46	2.420	16.79
M 8:11	4-16	4	141.960	5.499	38.73	33.449	235.62	0.886	6.24	0.580	4.09
M 8:8	4-16	8	153.180	6.056	39.54	18.927	123.56	0.591	3.86	0.525	3.43
M 8:5	4-16	16	141.696	0.138	0.97	0.707	4.99	0.027	0.19	0.026	0.18

Sample number	**Period 3** time [hrs]	Height above ground [m]	Sampled air volume [m^3]	***Pendimethalin***		***Prosulfocarb***		***Pirimicarb***		***Fenpropimorph***	
				µg in PUF [µg]	air conc.. [ng/m3]	µg in PUF [µg]	air conc.. [ng/m3]	µg in PUF [µg]	air conc.. [ng/m3]	µg in PUF [µg]	air conc.. [ng/m3]
M 8:3	16-24	background	60.530	<0,01	0.00	<0,01	0.00	<0,01	0.00	<0,01	0.00
M 118:10	16-24	0.25	75.310	280.000	3717.97	370.000	4913.03	3.200	42.49	1.700	22.57
M 8:19	16-24	0.6	68.620	54.600	795.69	162.400	2366.66	1.510	22.01	0.620	9.04
M 118:7	16-24	1	83.780	270.000	3222.73	360.000	4296.97	2.900	34.61	1.400	16.71
M 118:4	16-24	2	61.620	200.000	3245.70	270.000	4381.69	2.300	37.33	1.300	21.10
M 8:12	16-24	4	71.770	33.000	459.80	98.200	1368.26	0.720	10.03	0.580	8.08
M 8:9	16-24	8	77.470	9.120	117.72	24.840	320.64	0.010	0.13	0.050	0.65
M 8:6	16-24	16	81.140	1.780	21.94	4.460	54.97	0.015	0.19	0.010	0.12

Appendix 2, cont.

Table 1b. Concentration of pesticides in PUFs and air - September 2008 (two sampling periods)

The column "µg/PUF" gives the total recovery of the respective pesticide from the PUFs for each sampling period, and "Air conc." means the respective *average concentration* in air during the same sampling period.

Sample number	**Period 1** time [hrs]	Height above ground [m]	Sampled air volume [m^3]	***Pirimicarb***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
				[µg/PUF]	Air conc. [ng /m^3]	[µg/PUF]	Air conc. [ng /m^3]	[µg/PUF]	Air conc. [ng /m^3]	[µg/PUF]	Air conc. [ng /m^3]
M41:2	0-17.5	Background	79.76	<LOD		3.25		<LOD		0.838	
M41:4	0-17.5	0.25	108.1	1.529	13.88	413	3820.54	20.21	185.01	88	814.06
M41:6	0-17.5	0.6	96.26	1.919	19.74	479	4976.11	24.48	249.32	81	841.47
M41:8	0-17.5	1	104.86	1.292	12.40	261	2489.03	15.48	143.05	47	448.22
M41:10	0-17.5	2	93.99	1.908	20.21	292	3106.71	21.31	223.43	43	457.50
M41:12	0-17.5	4	99.12	<LOD	0.10	45	454.00	4.17	42.37	7.83	78.69
M41:14	0-17.5	8	93.67	<LOD	0.00	5.66	60.85	<LOD	0.11	1.365	14.95
M41:16	0-17.5	16	102.17	<LOD	0.00	1.41	13.70	<LOD	0.01	0.298	2.94

<LOD: *below detection limit*

Sample number	**Period 2** time [hrs]	Height above ground [m]	Sampled air volume [m^3]	***Pirimicarb***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
				[µg/PUF]	Air conc. [ng /m^3]	[µg/PUF]	Air conc. [ng /m^3]	[µg/PUF]	Air conc. [ng /m^3]	[µg/PUF]	Air conc. [ng /m^3]
M41:3	18.5-28	Background	36.98	<LOD		3.10		<LOD		0.84	
M41:5	18.5-28	0.25	49.8	0.315	6.02	83	1666.67	3.83	76.31	27	542.17
M41:7	18.5-28	0.6	43.69	0.408	9.16	163	3730.83	6.53	148.78	42	961.32
M41:9	18.5-28	1	57.56	0.268	5.21	156	2710.22	6.08	105.98	36	625.43
M41:11	18.5-28	2	48.86	<LOD	0.20	80	1637.33	3.8	77.77	18	368.40
M41:13	18.5-28	4	47.79	<LOD	0.00	32	669.60	<LOD	0.21	7.38	154.84
M41:15	18.5-28	8	46.54	<LOD	0.00	5.72	122.48	<LOD	0.00	1.30	27.93
M41:17	18.5-28	16	49.86	<LOD	0.00	1.69	34.10	<LOD	0.00	0.47	10.03

<LOD: *below detection limit*

Appendix 2 (cont.)

Table 2a. Concentration of pesticides in PUFs and air - July 2009

Sample number	*Period time [hrs]*	*Height above gr. [m]*	*Sampled air volume [m3]*	**HCH-gamma**		**Pirimicarb**		**Tolclofos-met.**		**Prosulfocarb**		**Fenpropimorph**		**Pendimethalin**	
				µg in PUF [µg]	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*
Period 1															
M109 :1/09	0-3.5	*Field blank*		0.030		0.010		0.022		0.119		0.028		0.048	
M109 :2/09	0-3.5	0.25	25.424	7.722	303.72	2.516	98.96	8.667	340.92	92.672	3645.14	10.135	398.66	18.597	731.49
M109 :3/09	0-3.5	0.6	23.168	10.094	435.67	3.320	143.30	11.715	505.67	128.268	5536.50	13.072	564.22	25.079	1082.48
M109 :4/09	0-3.5	1	20.675	10.497	507.74	3.182	153.88	12.654	612.05	144.875	7007.31	12.314	595.60	26.987	1305.30
M109 :5/09	0-3.5	2	26.981	13.114	486.07	4.706	174.43	15.791	585.27	198.236	7347.28	18.752	695.03	33.312	1234.66
M109 :6/09	0-3.5	4	26.087	13.600	521.32	5.098	195.41	17.561	673.17	287.472	11019.69	19.318	740.51	44.151	1692.45
M109 :7/09	0-3.5	8	24.535	3.423	139.50	1.140	46.45	3.802	154.95	53.681	2187.94	4.080	166.30	7.630	310.99
M109 :8/09	0-3.5	16	24.865	0.821	33.02	0.279	11.20	0.822	33.06	8.886	357.37	1.046	42.07	1.379	55.47
Period 2															
M109 :9/09	3.5-7	0.25	43.368	8.050	185.62	3.934	90.71	19.093	440.24	243.083	5605.13	8.293	191.21	61.119	1409.30
M109 :10/09	3.5-7	0.6	43.399	5.331	122.84	2.873	66.20	12.879	296.75	161.036	3710.59	6.596	151.99	40.848	941.21
M109 :11/09	3.5-7	1	43.361	10.342	238.52	3.208	73.98	25.581	589.95	313.038	7219.35	2.827	65.20	80.361	1853.29
M109 :12/09	3.5-7	2	43.378	9.169	211.39	4.574	105.45	23.089	532.28	280.139	6458.08	7.821	180.31	75.050	1730.13
M109 :13/09	3.5-7	4	38.879	3.593	92.42	1.790	46.04	9.012	231.80	137.443	3535.15	2.365	60.84	35.431	911.31
M109 :14/09	3.5-7	8	36.850	1.231	33.42	0.749	20.33	2.919	79.22	38.983	1057.89	1.696	46.03	9.846	267.20
M109 :15/09	3.5-7	16	43.403	0.299	6.88	0.167	3.86	0.743	17.11	8.802	202.80	0.405	9.34	2.444	56.31
Period 3															
M109 :16/09	7-25	0.25	212.223	18.925	89.18	7.906	37.25	58.446	275.40	746.276	3516.47	11.779	55.50	265.579	1251.42
M109 :17/09	7-25	0.6	229.912	13.450	58.50	6.075	26.43	46.613	202.74	772.573	3360.30	8.315	36.17	370.493	1611.45
M109 :18/09	7-25	1	232.846	19.062	81.86	8.711	37.41	64.638	277.60	1034.810	4444.18	13.649	58.62	625.850	2687.83
M109 :19/09	7-25	2	225.705	12.646	56.03	6.108	27.06	40.654	180.12	651.554	2886.75	9.305	41.23	348.948	1546.04
M109 :20/09	7-25	4	265.568	5.369	20.22	2.801	10.55	17.551	66.09	283.275	1066.68	4.158	15.66	113.670	428.03
M109 :21/09	7-25	8	265.440	1.412	5.32	0.782	2.95	4.317	16.26	65.965	248.51	1.104	4.16	23.257	87.62
M109 :22/09	7-25	16	265.313	0.735	2.77	0.201	0.76	1.194	4.50	15.842	59.71	0.392	1.48	6.123	23.08
Period 4															
M109 :23/09	25-48	0.25	241.108	9.748	40.43	2.419	10.03	36.763	152.48	556.400	2307.68	3.755	15.57	484.452	2009.27
M109 :24/09	25-48	0.6	304.457	6.068	19.93	1.591	5.23	21.426	70.38	344.646	1132.00	3.023	9.93	274.009	899.99
M109 :25/09	25-48	1	289.501	9.840	33.99	2.890	9.98	39.185	135.35	629.547	2174.59	5.169	17.85	580.562	2005.39
M109 :26/09	25-48	2	282.213	5.131	18.18	1.614	5.72	19.829	70.26	310.153	1099.00	2.332	8.26	276.145	978.50
M109 :27/09	25-48	4	340.717	1.955	5.74	0.700	2.05	7.292	21.40	116.653	342.38	1.042	3.06	81.494	239.18
M109 :28/09	25-48	8	339.928	0.717	2.11	0.298	0.88	3.017	8.87	43.058	126.67	0.382	1.12	23.983	70.55
M109 :29/09	25-48	16	340.428	0.158	0.46	0.054	0.16	0.486	1.43	6.667	19.58	0.089	0.26	3.118	9.16

(table 2a cont. on next page)

Table 2a. continued: Concentration of pesticides in PUFs and air - July 2009

Sample number	*Period time [hrs]*	*Height above gr. [m]*	*Sampled air volume [m3]*	***HCH-gamma***		***Pirimicarb***		***Tolclofos-met.***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
				µg in PUF [µg]	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*
Period 5															
M109 :30/09	49-71	0.25	227.976	2.918	12.80	1.101	4.83	9.387	41.18	148.765	652.55	1.118	4.90	103.694	454.85
M109 :31/09	49-71	0.6	280.765	3.104	11.06	1.316	4.69	9.832	35.02	162.922	580.28	1.127	4.01	109.730	390.83
M109 :32/09	49-71	1	260.248	4.327	16.62	2.188	8.41	15.904	61.11	266.034	1022.23	1.887	7.25	207.286	796.49
M109 :33/09	49-71	2	256.714	3.104	12.09	1.832	7.14	10.798	42.06	176.726	688.42	1.288	5.02	129.290	503.64
M109 :34/09	49-71	4	314.327	0.873	2.78	0.899	2.86	2.387	7.59	37.535	119.41	0.411	1.31	23.893	76.01
M109 :36/09	49-71	8	313.319	0.259	0.83	0.850	2.71	0.352	1.12	4.777	15.21	0.116	0.37	2.884	9.18
M109 :35/09	49-71	16	314.038	0.096	0.31	0.675	2.15	0.057	0.18	0.808	2.58	0.054	0.17	0.176	0.56

Close to or below "detection limit"

Appendix 2 (cont.)

Table 2b. Concentration of pesticides in PUFs and air - September 2009

Sample number	*Period time [hrs]*	*Height above gr. [m]*	*Sampled air volume [m3]*	***HCH-gamma*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Pirimicarb*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Tolclofos-met.*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Prosulfocarb*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Fenpropimorph*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Pendimethalin*** *µg in PUF [µg]*	*Air conc. [ng/m3]*
Period 1															
M163 :1/09	0-3.5	0.25	44.52	11.407	256.22	1.244	27.94	6.394	143.62	2.968	66.66	0.357	8.02	3.559	79.95
M163 :2/09	0-3.5	0.6	43.77	3.823	87.33	0.767	17.52	4.236	96.78	1.950	44.55	0.157	3.60	0.994	22.70
M163 :3/09	0-3.5	1	43.43	3.771	86.83	0.586	13.49	3.759	86.55	1.055	24.28	0.227	5.23	0.774	17.83
M163 :4/09	0-3.5	2	52.62	4.199	79.81	1.740	33.06	4.551	86.49	2.419	45.97	0.244	4.64	1.080	20.53
M163 :5/09	0-3.5	4	52.66	1.121	21.29	0.189	3.58	1.067	20.26	0.666	12.64	0.048	0.91	0.338	6.42
M163 :6/09	0-3.5	8	51.88	0.174	3.35	0.039	0.75	0.146	2.82	0.128	2.47	0.034	0.66	0.038	0.74
M163 :7/09	0-3.5	16	42.13	0.025	0.59	0.002	0.05	0.025	0.60	0.060	1.42	0.010	0.23	0.056	1.32
Period 2															
M163 :8/09	4-7	0.25	37.14	6.914	186.19	0.658	17.72	5.282	142.24	3.066	82.56	0.030	0.81	1.471	39.62
M163 :9/09	4-7	0.6	37.44	4.326	115.54	0.373	9.96	3.020	80.65	1.560	41.67	0.060	1.61	0.782	20.89
M163 :10/09	4-7	1	36.19	2.128	58.80	0.120	3.31	1.515	41.87	0.279	7.70	0.034	0.95	0.279	7.71
M163 :11/09	4-7	2	43.65	2.073	47.50	0.138	3.17	1.517	34.75	0.799	18.31	0.012	0.27	0.434	9.94
M163 :12/09	4-7	4	42.94	0.459	10.69	0.021	0.49	0.309	7.19	0.149	7.56	0.012	0.28	0.080	1.87
M163 :13/09	4-7	8	38.64	0.075	1.95	0.004	0.10	0.051	1.31	0.224	5.80	0.004	0.11	0.022	0.58
M163 :14/09	4-7	16	42.01	0.031	0.73	0.005	0.11	0.030	0.72	0.317	3.47	0.003	0.08	0.030	0.71
Period 3															
M163 :15/09	7-24	0.25	158.31	29.230	184.64	0.878	5.55	17.889	113.00	4.153	26.23	0.534	3.37	1.021	6.45
M163 :16/09	7-24	0.6	172.87	15.246	88.19	0.397	2.29	9.850	56.98	2.025	11.71	0.126	0.73	0.570	3.30
M163 :17/09	7-24	1	149.58	10.961	73.28	0.231	1.55	7.156	47.84	1.379	9.22	0.081	0.54	0.425	2.84
M163 :18/09	7-24	2	179.39	3.525	19.65	0.061	0.34	2.057	11.47	0.421	2.35	0.016	0.09	0.152	0.85
M163 :19/09	7-24	4	226.76	1.341	5.91	0.040	0.18	0.817	3.60	0.446	1.96	0.020	0.09	0.084	0.37
M163 :20/09	7-24	8	188.53	0.307	1.63	0.010	0.05	0.188	1.00	0.256	1.36	0.004	0.02	0.059	0.31
M163 :21/09	7-24	16	197.39	0.044	0.22	0.003	0.02	0.026	0.13	0.014	0.07	0.002	0.01	0.004	0.02
Period 4															
M163 :22/09	25-48	0.25	241.97	7.934	32.79	0.106	0.44	6.471	26.74	1.470	6.08	0.141	0.58	0.465	1.92
M163 :23/09	25-48	0.6	224.55	5.607	24.97	0.074	0.33	4.246	18.91	0.779	3.47	0.118	0.53	0.342	1.52
M163 :24/09	25-48	1	222.27	5.336	24.01	0.090	0.40	4.368	19.65	0.864	3.89	0.194	0.87	0.356	1.60
M163 :25/09	25-48	2	284.31	1.948	6.85	0.038	0.14	1.575	5.54	0.405	1.43	0.076	0.27	0.169	0.60
M163 :26/09	25-48	4	254.56	0.226	0.89	0.009	0.03	0.153	0.60	0.026	0.10	0.012	0.05	0.017	0.07
M163 :27/09	25-48	8	256.18	0.026	0.10	0.003	0.01	0.016	0.06	0.012	0.05	0.008	0.03	0.003	0.01
M163 :28/09	25-48	16	262.22	0.017	0.06	0.003	0.01	0.023	0.09	0.216	0.83	0.003	0.01	0.031	0.12

Red figures: original order of heights has been reversed

Close to or below "detection limit"

Red figures: questionable original order of heights (***not changed here***)

(table 2b cont. on next page)

Table 2b. continued: Concentration of pesticides in PUFs and air - September 2009

Sample number	*Period time [hrs]*	*Height above gr. [m]*	*Sampled air volume [m3]*	**HCH-gamma**		**Pirimicarb**		**Tolclofos-met.**		**Prosulfocarb**		**Fenpropimorph**		**Pendimethalin**	
				µg in PUF [µg]	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*
Period 5															
M163 :29/09	49-96	0.25	424.80	15.338	36.11	0.247	0.58	26.440	62.24	7.377	17.37	2.017	4.75	9.313	21.92
M163 :30/09	49-96	0.6	449.39	10.475	23.31	0.166	0.37	17.379	38.67	5.038	11.21	1.520	3.38	5.606	12.48
M163 :31/09	49-96	1	431.13	10.047	23.30	0.182	0.42	18.514	42.94	5.172	12.00	1.544	3.58	5.752	13.34
M163 :32/09	49-96	2	511.93	10.527	20.56	0.223	0.44	19.100	37.31	5.813	11.35	2.205	4.31	7.635	14.91
M163 :33/09	49-96	4	562.24	12.411	22.07	0.219	0.39	22.216	39.51	5.149	9.16	0.815	1.45	9.720	17.29
M163 :34/09	49-96	8	481.58	1.652	3.43	0.041	0.08	2.983	6.19	0.896	1.86	0.395	0.82	0.990	2.06
M163 :35/09	49-96	16	521.65	0.042	0.08	0.006	0.01	0.064	0.12	0.196	0.38	0.018	0.03	0.052	0.10

Red figures: original order of heights (4 and 8m) has been reversed

Sample number	*Period time [hrs]*	*Height above gr. [m]*	*Sampled air volume [m3]*	**HCH-gamma**		**Pirimicarb**		**Tolclofos-met.**		**Prosulfocarb**		**Fenpropimorph**		**Pendimethalin**	
				µg in PUF [µg]	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*
Period 6															
M163 :36/09	96-193	0.25	1154.39	0.189	0.16	0.009	0.01	0.302	0.26	0.280	0.24	0.049	0.04	0.172	0.15
M163 :37/09	96-193	0.6	866.71	6.819	7.87	0.121	0.14	12.393	14.30	3.333	3.85	0.440	0.51	4.066	4.69
M163 :38/09	96-193	1	922.1	4.692	5.09	0.075	0.08	7.842	8.50	2.594	2.81	0.265	0.29	2.529	2.74
M163 :39/09	96-193	2	877.07	3.088	3.52	0.064	0.07	5.892	6.72	2.416	2.75	0.218	0.25	1.844	2.10
M163 :40/09	96-193	4	977.76	0.517	0.53	0.018	0.02	0.997	1.02	1.595	1.63	0.058	0.06	0.438	0.45
M163 :41/09	96-193	8	1007.92	0.039	0.04	0.005	0.00	0.111	0.11	1.092	1.08	0.013	0.01	0.209	0.21
M163 :42/09	96-193	16	1054.77	0.010	0.01	0.006	0.01	0.036	0.03	1.109	1.05	0.007	0.01	0.381	0.36

Appendix 2 (cont.)

Table 3a. Concentrations of pesticides in PUFs and air - July 2010

The column "µg in PUF" gives the total recovery of the respective pesticide from the PUFs for each sampling period, and "Air conc." means the respective *average concentration* in air during the same period.

Sample number	*Period time [hrs]*	*Height above gr. [m]*	*Sampled air volume [m3]*	***HCH-gamma***		***Pirimicarb***		***Tolclofos-met.***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
				µg in PUF [µg]	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*
Period 1															
M 99:		*Field blank*		<LOD		0.038		0.08		0.071		0.14		<LOD	
1	0-3	0.4	38.7	42	1085.27	41	1059.43	120	3100.78	94	2428.94	190	4909.56	64	1653.75
2	0-3	1	31.7	41	1293.38	46	1451.10	130	4100.95	120	3785.49	260	8201.89	80	2523.66
3	0-3	2	32.8	31	945.12	18	548.78	97	2957.32	57	1737.80	97	2957.32	45	1371.95
4	0-3	4	34	16	470.59	16	470.59	43	1264.71	26	764.71	64	1882.35	19	558.82
5	0-3	8	33.2	2.7	81.33	2.9	87.35	7.8	234.94	4.4	132.53	14	421.69	3.4	102.41
6	0-3	16	40.3	0.2	4.96	0.18	4.47	0.47	11.66	0.35	8.68	0.95	23.57	0.20	4.96
Period 2															
7	3-6	0.4	33.5	2.0	59.70	1.7	50.75	10	298.51	6.2	185.07	10	298.51	12	358.21
8	3-6	1	29	2.4	82.76	2	68.97	13	448.28	6.7	231.03	11	379.31	14	482.76
9	3-6	2	34.6	1.6	46.24	1.6	46.24	9.5	274.57	5.3	153.18	8.8	254.34	10	289.02
10	3-6	4	33.3	0.53	15.92	0.72	21.62	3.6	108.11	2.0	60.06	3.6	108.11	3.8	114.11
12	3-6	8	32.3	<LOD		0.13	4.02	0.60	18.58	0.65	20.12	0.60	18.58	0.81	25.08
13	3-6	16	36.2	<LOD		<LOD		0.068	1.88	0.040	1.10	0.041	1.13	<LOD	
Period 3															
14	6-24	0.4	240.9	8.6	35.70	4.4	18.26	26	107.93	16	66.42	13	52.72	15	62.27
15	6-24	1	194.8	9.6	49.28	5.0	25.67	29	148.87	17	87.27	13	66.74	17	87.27
16	6-24	2	221.9	5.6	25.24	3.2	14.42	16	72.10	9.6	43.26	8.5	38.31	10	45.07
17	6-24	4	240.1	1.4	5.83	1.0	4.16	5.4	22.49	3.0	12.49	3.3	13.74	4.0	16.66
18	6-24	8	246.7	0.3	1.22	0.15	0.61	0.84	3.40	0.69	2.80	0.66	2.68	0.73	2.96
19	6-24	16	251.7	<LOD		<LOD		0.062	0.25	0.043	0.17	0.046	0.18	<LOD	
Period 4															
20	24.5-48	0.4	287.1	3.2	11.15	0.93	3.24	6.9	24.03	3.2	11.15	6.3	21.94	4.4	15.33
21	24.5-48	1	235.3	4.2	17.85	1.3	5.52	9.6	40.80	5.2	22.10	8.7	36.97	6.5	27.62
22	24.5-48	2	264.6	2.5	9.45	0.84	3.17	5.4	20.41	3.1	11.72	4.9	18.52	4.3	16.25
23	24.5-48	4	292.8	0.79	2.70	0.42	1.43	2.3	7.86	1.6	5.46	2.4	8.20	2.0	6.83
24	24.5-48	8	318	<LOD		0.087	0.27	0.46	1.45	0.26	0.82	0.53	1.67	0.34	1.07
25	24.5-48	16	315	<LOD		<LOD		0.059	0.19	0.61	1.94	0.051	0.16	<LOD	
Period 5															
26	48-96	0.4	638.7	6.0	9.39	1.6	2.51	11	17.22	4.7	7.36	12	18.79	6.8	10.65
27	48-96	1	496.3	6.9	13.82	1.7	3.49	13	25.59	6.1	12.25	11	22.57	9.5	19.22
28	48-96	2	605.5	3.7	6.09	1.1	1.73	6.8	11.26	3.5	5.73	7.2	11.86	4.1	6.77
29	48-96	4	610.5	1.4	2.28	0.40	0.66	2.5	4.08	1.5	2.49	2.8	4.54	1.8	2.96
30	48-96	8	565.4	0.4	0.71	0.11	0.19	0.67	1.19	0.35	0.62	0.87	1.54	0.55	0.97
31	48-96	16	614.7	<LOD		<LOD		0.12	0.20	0.10	0.16	0.12	0.20	<LOD	

<LOD: below level of detection

(table 3a cont. on next page)

Table 3a, cont. Concentrations of pesticides in PUFs and air - July 2010 (periods 6-7)

Sample number	*Period time [hrs]*	*Height above gr. [m]*	*Sampled air volume [m3]*	***HCH-gamma***		***Pirimicarb***		***Tolclofos-met.***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
				µg in PUF [µg]	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*
Period 6															
32	96-144	0.4	611.6	1.8	2.94	0.37	0.60	2.7	4.41	1.3	2.13	3.6	5.89	1.5	2.45
33	96-144	1	493.7	2.0	4.05	0.41	0.83	2.9	5.87	1.5	3.04	3.3	6.68	2.0	4.05
34	96-144	2	569.2	1.8	3.16	0.28	0.49	1.8	3.16	1.1	1.93	2.6	4.57	1.5	2.64
35	96-144	4	605.5	<LOD		0.04	0.07	0.27	0.45	0.49	0.81	0.39	0.64	0.38	0.63
36	96-144	8	593.4	0.5	0.84	0.14	0.24	0.72	1.21	0.98	1.65	1.5	2.49	0.44	0.74
37	96-144	16	563.8	<LOD		<LOD		0.11	0.20	1.2	2.11	0.12	0.21	0.18	0.32
Period 7															
38	144-203	0.4	734.7	1.1	1.50	0.27	0.37	1.9	2.59	1.2	1.63	2.8	3.81	1.0	1.36
39	144-203	1	569.8	1.2	2.02	0.33	0.58	2.1	3.67	0.76	1.33	3.3	5.76	1.1	1.93
40	144-203	2	644.5	1.2	1.92	0.16	0.25	1.1	1.69	0.77	1.19	1.7	2.58	0.85	1.32
41	144-203	4	697.8	0.3	0.43	0.085	0.12	0.48	0.69	0.19	0.27	1.0	1.43	0.27	0.39
42	144-203	8	701.6	<LOD		0.03	0.04	0.14	0.20	0.095	0.14	0.36	0.51	<LOD	
43	144-203	16	701	<LOD		<LOD		0.059	0.08	0.30	0.43	0.076	0.11	<LOD	
	Period	**Background [µg/PUF]**													
44	I			trace(0.4)		<LOD		<LOD		<LOD		<LOD		<LOD	
45	II			<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
46	III			<LOD		<0.03		<LOD		<LOD		<LOD		trace(<0.2)	
47	IV			<LOD		<LOD		<LOD		<LOD		<0.03		<LOD	
48	V			<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
49	VI			<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
			Detection limit: [µg/PUF]	**0.2**		**0.02**		**0.01**		**0.01**		**0.01**		**0.05**	

<LOD: *below level of detection*

Appendix 2 (cont.)

Table 3b. Concentrations of pesticides in PUFs and air - September 2010

The column "µg in PUF" gives the total recovery of the respective pesticide from the PUFs for each sampling period, and "Air conc." means the respective *average concentration in air* during the same period.

Sample number	Period time [hrs]	Height above gr. [m]	Sampled air volume [m3]	***HCH-gamma*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Pirimicarb*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Tolclofos-met.*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Prosulfocarb*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Fenpropimorph*** *µg in PUF [µg]*	*Air conc. [ng/m3]*	***Pendimethalin*** *µg in PUF [µg]*	*Air conc. [ng/m3]*
Period 1															
M 163:															
1		***Field blank***		<LOD		<LOD		trace(0,008)		0.066		trace(0,02)		trace(0,02)	
2	0-3	0.4	43.37	11	253.62	6.6	152.17	12	276.68	6.4	145.95	9.9	228.26	4.8	110.67
3	0-3	1	43.12	10	231.91	7.3	169.29	11	255.10	5.6	128.24	10	231.91	4.3	99.72
4	0-3	2	43.32	7.4	170.83	5.3	122.35	8.9	205.45	4.5	102.26	8.7	200.84	3.3	76.18
5	0-3	4	43.46	3.1	71.33	2.7	62.13	3.8	87.44	1.8	39.90	5.5	126.56	1.3	29.91
6	0-3	8	43.41	1.1	25.34	0.96	22.11	1.5	34.55	0.74	15.53	1.2	27.64	0.73	16.82
7	0-3	16	39.45	0.34	8.62	0.24	6.08	0.39	9.89	0.20	3.40	0.53	13.44	0.15	3.80
Period 2															
8	3-5.5	0.4	32.62	7.7	236.06	4.1	125.69	9.2	282.04	3.9	119.56	5.9	180.88	3.3	101.17
9	3-5.5	1	35.89	5.0	139.31	3.1	86.38	6.6	183.90	2.9	80.80	4.3	119.81	2.2	61.30
10	3-5.5	2	36.86	3.2	86.81	2.2	59.68	4.2	113.94	1.9	51.54	4.0	108.51	1.5	40.69
12*	3-5.5	4	36.99	0.72	19.47	0.54	14.60	0.82	22.17	0.37	10.00	0.80	21.63	0.36	9.73
13*	3-5.5	8	36.94	trace(0,2)	5.41	0.17	4.60	0.27	7.31	0.12	3.25	0.25	6.77	0.090	2.44
11*	3-5.5	16	35.97	<LOD		trace(0,03)	0.83	0.11	3.06	0.13	3.61	0.13	3.61	trace(0,06)	1.67
	12, 13. 11*: order of heights (sample numbers) has been reversed (probable mistake in sample numbering)														
Period 3															
14	6-24	0.4	267.02	38	142.31	9.2	34.45	63	235.94	31	116.10	27	101.12	23	86.14
15	6-24	1	226.18	20	88.43	4.9	21.66	31	137.06	13	57.48	13	57.48	8.4	37.14
16	6-24	2	266.63	11	41.26	3.4	12.75	17	63.76	8.0	30.00	8.7	32.63	6.9	25.88
17	6-24	4	267.70	1.9	5.23	0.52	1.94	3.2	11.95	1.4	5.23	1.5	5.60	0.98	3.66
18	6-24	8	267.07	0.36	1.35	0.064	0.24	0.50	1.87	0.29	1.09	0.23	0.86	0.24	0.90
19	6-24	16	250.81	<LOD		<LOD		0.077	0.31	0.12	0.48	trace(0,03)	0.12	trace(0,05)	0.20
Period 4															
20	24-48	0.4	362.31	20	55.20	1.7	4.69	26	71.76	8.1	22.36	5.3	14.63	8.6	23.74
21	24-48	1	305.74	7.7	25.18	0.79	2.58	10	32.71	3.4	11.12	2.7	6.21	3.0	9.81
22	24-48	2	361.77	5.1	14.10	0.62	1.71	7.5	20.73	2.4	6.63	1.9	5.25	2.2	6.08
23	24-48	4	363.20	1.2	3.30	0.16	0.44	1.8	4.96	0.64	1.76	0.56	1.54	0.49	1.35
24	24-48	8	362.40	<LOD		trace(0,02)	≤0.06	0.26	0.72	0.33	0.91	0.22	0.61	0.17	0.47
25	24-48	16	324.54	trace(0,2)		trace(0,02)	≤0.06	0.24	0.74	0.21	0.65	0.084	0.26	0.12	0.37

(table 3b cont. on next page)

Table 3b, cont. Concentrations of pesticides in PUFs and air - September 2010 (periods 5-7)

Sample number	*Period time [hrs]*	*Height above gr. [m]*	*Sampled air volume [m3]*	***HCH-gamma***		***Pirimicarb***		***Tolclofos-met.***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
				µg in PUF [µg]	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*	*µg in PUF [µg]*	*Air conc. [ng/m3]*
Period 5															
M 163:															
26	48.5-71	0.4	330.51	12	36.31	1.6	4.84	17	51.44	6.1	18.46	3.3	9.98	5.9	17.85
27	48.5-71	1	268.65	6.6	24.57	0.99	3.69	10.0	37.22	3.8	14.14	2.4	8.93	4.0	14.89
28	48.5-71	2	338.12	2.7	7.99	0.43	1.27	4.1	12.13	1.6	4.73	1.1	3.25	1.7	5.03
29	48.5-71	4	339.42	1.8	5.30	0.30	0.88	2.9	8.54	1.1	3.24	0.91	2.68	1.1	3.24
30	48.5-71	8	338.66	0.56	1.65	0.085	0.25	0.92	2.72	0.43	1.27	0.32	0.94	0.40	1.18
31	48.5-71	16	293.12	<LOD	0.00	trace(0,03)	0.10	0.23	0.78	0.12	0.41	0.090	0.31	0.098	0.33
Period 6															
32	71.5-120	0.4	650.31	20	30.75	2.7	4.15	32	49.21	9.5	14.61	4.8	7.38	15	23.07
33	71.5-120	1	565.73	14	24.75	1.6	2.83	18	31.82	6.3	11.14	2.7	4.77	7.7	13.61
34	71.5-120	2	719.25	7.6	10.57	1.2	1.67	11	15.29	3.7	5.14	2.2	3.06	3.7	5.14
35	71.5-120	4	722.04	1.8	2.49	0.25	0.35	2.5	3.46	0.97	1.34	0.46	0.64	1.1	1.52
36	71.5-120	8	720.36	trace(0,2)	0.28	0.039	0.05	0.34	0.47	0.19	0.26	0.077	0.11	0.12	0.17
37	71.5-120	16	614.67	<LOD		<LOD		0.058	0.09	0.19	0.31	trace(0,03)	0.05	trace(0,02)	0.03
Period 7															
38	120-232	0.4	1661.03	15	9.03	0.80	0.48	28	16.86	9.3	5.60	3.6	2.17	13	7.83
39	120-232	1	1212.22	10.0	8.25	0.49	0.40	16.0	13.20	5.6	4.62	2.2	1.81	7.9	6.52
40	120-232	2	1681.10	6.5	3.87	0.40	0.24	12.0	7.14	4.1	2.44	1.7	1.01	5.7	3.39
41	120-232	4	1674.69	1.4	0.84	0.11	0.07	2.7	1.61	1.1	0.66	0.51	0.30	1.30	0.78
42	120-232	8	1563.02	trace(0,2)	0.13	trace(0,02)	0.01	0.27	0.17	0.29	0.19	0.10	0.06	0.10	0.06
43	120-232	16	1328.08	<LOD		<LOD		0.067	0.05	0.32	0.24	trace(0,03)	0.02	trace(0,04)	0.03
	detection limit [µg/PUF]:			**0.2**		**0.01**		**0.008**		**0.01**		**0.01**		**0.02**	

Appendix 3.

***The normalized source strengths** according to the two versions of the concentration equations, as described elsewhere in this report, for the six substances investigated; determined as averages for each of the specified sampling periods.*

a) June 2008

Normalized source strength [per mille of field dose/m^2 *per hour*] – June 2008													
		Lindane		***Pirimicarb***		***Tolclofos-methyl***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
Period	***Date/Time***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***
1	*24/6 17:00-21:00*	*not used in 2008*	*not used in 2008*	10.02	7.87	*not used in 2008*	*not used in 2008*	11.33	9.05	5.602	4.217	3.098	2.384
2	*24/6 21:30- 25/6 09:30*			2.424	2.355			4.941	4.793	0.320	0.315	1.867	1.828
3	*25/6 10:30-17:00*			3.352	1.820			20.25	20.06	0.332	0.325	21.08	21.80

b) September 2008

Normalized source strength [per mille of field dose/m^2 *per hour*] – September 2008													
		Lindane		***Pirimicarb***		***Tolclofos-methyl***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
Period	***Date/Time***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***
1	*21/9 14:00-22/9 07:30*	*not used in 2008*	*not used in 2008*	0.183	0.155	*not used in 2008*	*not used in 2008*	2.164	2.007	0.525	0.379	0.803	0.734
2	*22/9 8:30-18:00*			0.092	0.092			3.558	3.281	0.369	0.236	1.702	1.660

c) July 2009

Normalized source strength [per mille of field dose/m^2 *per hour*] – July 2009

		Lindane		*Pirimicarb*		*Tolclofos-methyl*		*Prosulfocarb*		*Fenpropimorph*		*Pendimethalin*	
Period	***Date/Time***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***
1	*4/7 10:30 – 14:30*	99.61	87.48	18.16	15.86	37.03	31.81	37.48	30.90	13.78	12.08	12.07	10.16
2	*4/7 14:30 – 17:30*	22.30	21.10	5.710	5.558	17.73	16.65	17.93	16.73	2.230	1.907	9.385	8.739
3	*4/7 17:30 – 5/7 11:30*	6.062	5.011	1.436	1.350	5.493	5.212	6.626	6.466	0.454	0.403	6.221	6.184
4	*5/7 12:00 – 6/7 11:00*	1.394	1.384	0.673	0.515	1.686	1.756	2.000	2.120	0.078	0.076	2.901	3.239
5	*6/7 12:00 – 7/7 09:30*	1.042	1.048	0.359	0.373	0.785	0.950	0.976	1.192	0.052	0.050	1.538	1.703

d) September 2009

Normalized source strength [per mille of field dose/m^2 *per hour*] – Sept. 2009

		Lindane		*Pirimicarb*		*Tolclofos-methyl*		*Prosulfocarb*		*Fenpropimorph*		*Pendimethalin*	
Period	***Date/Time***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***
1	*18/9 11:40-15:10*	12.63	11.40	0.245	0.134	3.654	2.437	3.079	2.465	0.099	0.092	2.755	1.812
2	*18/9 15:40-18:35*	4.311	4.011	0.036	0.030	1.068	0.874	1.456	1.856	0.0070	0.0101	0.476	0.477
3	*18/9 18:50-19/9 12:00*	1.167	1.730	0.0044	0.0050	0.231	0.341	0.096	0.174	0.0018	0.0021	0.026	0.046
4	*19/9 12:40-20/9 12:06*	1.050	0.730	0.0024	0.0027	0.264	0.194	0.092	0.077	0.0042	0.0043	0.037	0.029
5	*20/9 12:56-22/9 11:50*	3.489	3.994	0.0090	0.0098	1.941	2.232	1.193	1.267	0.0692	0.0678	1.132	1.326
6	*22/9 12:26-26/9 12:20*	0.615	0.595	0.0022	0.0015	0.348	0.348 1)	0.565	0.565 1)	0.0053	0.0049	0.256	0.220
5:4 2)	(Quotient)	3.3	5.5	3.75	3.6	7.4	11.5	13.0	16.5	16.5	15.8	30.6	45.7

1) The reoccurrence of the same value in both versions mostly depends on the lack of a reasonable alternative equation fit as "version 2"

2) The relation (as the quotient) between the source strengths in sampling periods 5 and 4, respectively, showing the marked increase in evaporation from period 4 to 5

e) July 2010

Normalized source strength [per mille of field dose/m^2 *per hour*] – July 2010													
		Lindane		***Pirimicarb***		***Tolclofos-methyl***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
Period	***Date/Time***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***
1	*3/7 11:30 – 14:30*	172.6	158.3	82.46	77.17	162.4	145.8	170.9	158.1	82.33	75.92	124.4	112.3
2	*3/7 14:30 – 17:00*	8.911	8.804	5.454	4.989	18.80	17.31	17.98	16.79	5.736	5.274	31.57	29.19
3	*3/7 17:00 – 4/7 12:00*	2.203	2.013	0.672	0.597	2.221	2.133	2.151	2.085	0.420	0.400	2.300	2.103
4	*4/7 12:00 – 5/7 11:30*	0.960	0.904	0.218	0.194	0.850	0.791	1.159	1.099	0.276	0.253	0.972	0.835
5	*5/7 11:30 – 7/7 11:00*	0.574	0.471	0.084	0.068	0.294	0.299	0.250	0.258	0.101	0.105	0.369	0.302
6	*7/7 11:30 – 9/7 11:30*	0.247	0.463	0.034	0.044	0.170	0.170	0.262	0.275	0.079	0.073	0.272	0.270
7	*9/7 11.30 – 11/7 22:30*	0.295	0.149	0.030	0.023	0.094	0.098	0.084	0.063	0.054	0.058	0.118	0.062

f) September 2010

Normalized source strength [per mille of field dose/m^2 *per hour*] – Sept. 2010													
		Lindane		***Pirimicarb***		***Tolclofos-methyl***		***Prosulfocarb***		***Fenpropimorph***		***Pendimethalin***	
Period	***Date/Time***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***	***Vers.1***	***Vers.2***
1	*8/9 12:30 – 15:30*	26.65	22.45	2.121	1.876	10.16	8.821	7.327	6.579	3.481	2.840	6.248	5.616
2	*8/9 15:30 – 18:00*	8.162	8.027	0.493	0.572	3.110	3.245	2.711	2.238	0.902	0.865	1.899	1.838
3	*8/9 18:00 – 9/9 12:00*	3.821	3.343	0.112	0.092	2.063	1.595	1.491	1.326	0.311	0.246	1.102	0.935
4	*9/9 12:00 – 10/9 12:30*	1.742	1.874	0.0199 1)	0.0215 1)	0.808	0.916	0.614	0.669	0.0817 1)	0.0927 1)	0.464	0.512
5	*10/9 13:00- 11/9 11:30*	1.708	1.693	0.0308 1)	0.0340 1)	0.882	1.001	0.586	0.633	0.0894 1)	0.0933 1)	0.554	0.615
6	*11/9 12:00- 13/9 12:00*	1.347	1.086	0.0200 1)	0.0167 1)	0.627	0.501	0.345	0.362	0.0358 1)	0.0313 1)	0.404	0.322
7	*13/9 12:30- 18/9 05:00*	0.626	0.842	0.0041	0.0050	0.356	0.309	0.219	0.267	0.0187	0.0180	0.261	0.268

1) All decimals given are certainly not significant, but shown here just to give an idea of the magnitude of the mostly small differences between vers. 1 and 2