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Pesticides in the atmosphere

Occurrence, distribution and behaviour of selected pesticides
in the vinicultural area of Trier, Germany

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Zusammenfassung

Die meisten Menschen sind über die Pestizidrückstände im Trinkwasser und in unseren Lebensmitteln sowie über die damit verbundenen gesundheitlichen Auswirkungen informiert und nehmen diese auch als Problem wahr. Dass Pflanzenschutzmittel aber auch im Regen und in der Luft vorhanden sind, ist vielen Menschen nicht bekannt.

Von allen Umweltkompartimenten – Luft, Wasser, Boden, Sediment und Biota – ist die Atmosphäre das größte und beweglichste Kompartiment, in das chemische Schadstoffe direkt emittiert oder langfristig eingetragen und transportiert werden können. Während und nach ihrer Anwendung gelangen Pflanzenschutzmittel in die Atmosphäre. Dies geschieht durch Evaporation und durch Winderosion der Partikel, an denen das Pestizid adsorbiert ist. Messungen an den Anwendungsorten haben gezeigt, dass sich manchmal mehr als die Hälfte der eingesetzten Pestizide innerhalb weniger Tage in der Atmosphäre verflüchtigt. Die Atmosphäre ist ein wichtiger Teil des hydrologischen Zyklus und kann Pestizide über weite Strecken transportieren, so dass es zu einem Eintrag dieser Pflanzenschutzmittel in emissionsferne aquatische und terrestrische Ökosysteme kommt.

In der Region Trier, einem der wichtigsten Zentren des Weinbaugebietes Mosel-Saar-Ruwer, kommen Pestizide umfassend zum Einsatz. Um Nutzpflanzen vor Schädlingen zu schützen und die Erträge im Weinbau zu erhöhen, werden von Anfang Mai bis Ende August durchschnittlich 6 bis 8 Pflanzenschutzmittelapplikationen durchgeführt. Aufgrund verbesserter Bodenbearbeitungsverfahren und der erfolgreichen Einführung biologischer Schädlingsbekämpfungsmittel konnte in den vergangenen Jahren ein Rückgang des *Herbizid-* und *Insektizideinsatzes* im Weinbau beobachtet werden. Auf der anderen Seite erfordert die große Anfälligkeit der Reben gegenüber Pilzkrankheiten nach wie vor den intensiven Einsatz von *Fungiziden* zur Bekämpfung von Rebenperonospora, Botrytis, Oidium und Roter Brenner. Während der Wachstumsphase werden in der Region zu unterschiedlichen Zeiten mehrere Mischungen von verschiedenen Fungiziden appliziert. Die Anwendung dieser drei Chemikalienklassen trägt zu der umfassenden Verteilung einer Vielfalt von Pestiziden in der Atmosphäre der Region bei. Die Auswirkungen dieser Applikationen auf die Luftbelastung der Region wurden bisher kaum untersucht.

Die vorliegende Arbeit hatte die Beschreibung und Bewertung der Präsenz verschiedener Pflanzenschutzmittel in der Atmosphäre der Region Trier sowie ihre zeitliche Variabilität, ihren Transport und ihre Deposition zum Ziel. Dazu wurden in den Jahren 2000, 2001 und 2002 während der Vegetationszeit wöchentlich Regenproben an acht Messstandorten gesammelt. In der Vegetationszeit 2002 wurden zusätzlich sieben Luftmesskampagnen an drei Messstellen durchgeführt. Es wurden Analysemethoden entwickelt, um Pestizide aus

verschiedenen chemischen Gruppen im Regenwasser und in Luftproben (Gas- und Partikelphase) zu bestimmen. Insgesamt wurden 24 Pestizide und 3 Pestizid-Metaboliten als repräsentative Substanzen mit dem Schwerpunkt auf Fungiziden ausgewählt.

24 von den 27 untersuchten Pestiziden konnten in den Regenproben, 17 in den Luftproben nachgewiesen werden. Die am häufigsten gefundenen Pestizide mit den höchsten Konzentrationen sowohl in den Regenproben als auch in den Luftproben sind Verbindungen, die zu der Gruppe der *Fungizide* gehören. Auch das *Insektizid* Parathion-methyl sowie die zwei *Herbizide* Atrazin (Anwendungsverbot in Deutschland seit 1991) und Simazin (Anwendungsverbot im Weinbau seit 1992) konnten in mehreren Regenproben nachgewiesen werden.

Bei den unterschiedlichen Pestizidklassen waren jahreszeitspezifische Trends zu beobachten, die mit den Hauptanwendungszeiten dieser Substanzen korreliert waren. Die Konzentrationen der verschiedenen Substanzen variierten während der Vegetationszeit, wobei die höchsten Werte zum Frühjahrsende und in den Sommermonaten gemessen wurden.

Die in den Regenproben gemessenen Konzentrationen bewegten sich im Allgemeinen im ng l^{-1} -Bereich. Zwar lagen die durchschnittlichen Konzentrationen für einzelne Substanzen bei unter 100 ng l^{-1} , die Gesamtkonzentration erreichte jedoch beträchtliche Werte und lag in einigen Fällen deutlich über der von der EU für Trinkwasser festgelegten Norm von 500 ng l^{-1} für Pflanzenschutzmittel insgesamt. Verglichen mit den für die Schädlingsbekämpfung eingesetzten Mengen erreichten die durch Regenwasser abgelagerten Mengen zwischen 0,004% und 0,10% der maximalen Aufwandmengen. Diese geringen, durch Niederschläge verursachten Pestizeinträge in Oberflächengewässer können in Weinbaugebieten vernachlässigt werden, zumal hier die Belastungen aus anderen Quellen wie Oberflächenabflüsse aus den behandelten Flächen oder infolge der Reinigung von Applikationsgeräten eine höhere Bedeutung haben. Jedoch, die potenziellen Auswirkungen des Pestizeintrag über die Luft auf Nutzpflanzen, die nicht Ziel der Anwendung sind wie zum Beispiel ökologisch angebaute Nutzpflanzen, oder auf empfindliche Ökosysteme sind noch nicht bekannt, da es kaum Informationen über die langfristigen ökotoxischen Auswirkungen von Pestiziden in geringen Konzentrationen gibt.

Die Konzentrationen in den Luftproben lagen an den Messstellen in der Nähe der mit Pestiziden behandelten Weinberge im ng m^{-3} -Bereich, während an Messstellen in weiterer Entfernung der behandelten Weinberge Werte im Bereich pg m^{-3} gemessen wurden. Die im Rahmen dieser Arbeit gemessenen Konzentrationen stellen für die menschliche Gesundheit keine Bedrohung dar. Inhalationstoxizitätsstudien haben gezeigt, dass ein akutes potenzielle Risiko nur bei Luftkonzentrationen im g m^{-3} -Bereich besteht.

Es muss abschließend darauf hingewiesen werden, dass für die vorliegende Arbeit nur eine geringe Anzahl von Pestiziden analysiert wurde, die in der untersuchten Region angewandt wurden. Um eine bessere Evaluierung der örtlichen Pestizidbelastung der Luft durchführen zu können, muss ein breiteres Spektrum der angewandten Substanzen (einschließlich der Metaboliten) untersucht werden.

Summary

Most people are aware of and concerned with the health effects of pesticide residues in the water they drink or the food they eat, but many are surprised to learn that pesticides are commonly found in air and rain.

Of the environmental compartments – air, water, soil, sediment and biota – the atmosphere represents the largest most mobile compartment into which a chemical contaminant might be directly released or subsequently move into, undergo transport, and, in some cases, accumulate. During and after application, pesticides enter the atmosphere by volatilisation and by wind erosion of particles on which the pesticide is sorbed. Measurements at application sites revealed that sometimes more than half of the amount applied is lost into the atmosphere within a few days. The atmosphere is an important part of the hydrologic cycle that can transport pesticides from their point of application and deposit them into aquatic and terrestrial ecosystems far from their point of use.

In the region of Trier, one of the main centres of the vinicultural area of the Moselle-Saar-Ruwer, pesticides are widely used. In order to protect crops from pests and increase crop yields in the viniculture, six to eight pesticide applications take place between May and August. Because of the improvement of tillage practices and of the successful introduction of biological control agents, a decline in herbicide and insecticide use in viniculture was observed in the past years. By contrast, the great liability of vines to pathogenic fungi still demands a high use of fungicide products against pests like *Peronospora*, *Botrytis*, *Oidium* and Roter Brenner. Several mixtures of fungicide active ingredients are sprayed in the region at different times during the growing season. Together, the use of these three classes of chemicals contribute to the widespread distribution of a great variety of pesticides in the atmosphere of the region. The impact that these applications have on the environmental pollution of the region is not yet well understood.

To address the lack of information on the presence of pesticides in the atmosphere of the area of Trier, the present study was developed to characterize the atmospheric presence, temporal patterns, transport and deposition of a variety of pesticides. To this purpose, rain samples were weekly collected at eight sites during the growing seasons 2000, 2001 and 2002, and seven air sampling campaigns were carried out at three locations during the growing season 2002. Multiresidue analysis methods were developed to determine multiple classes of pesticides in rain water, particle- and gas-phase samples. Altogether 24 active ingredients and 3 metabolites were chosen as representative substances, focussing mainly on fungicides.

Twenty-four of the 27 measured pesticides were detected in the rain samples; seventeen pesticides were detected in the air samples. The most frequently detected pesticides and at the highest concentrations, both in rain and air, were compounds belonging to the class of *fungicides*. The *insecticide* methyl parathion was also detected in several rain samples as well as two substances that are banned in Germany, such as the *herbicides* atrazine and simazine.

Characteristic seasonal trends were observed for the different classes of pesticides, mirroring the main application times of the substances. Concentration levels varied during the growing season with the highest concentrations being measured in the late spring and summer months, coinciding with application times and warmer months.

Concentration levels measured in the rain samples were, generally, in the order of ng l^{-1} . Though average concentrations for single substances were less than 100 ng l^{-1} , total concentrations were considerable and in some instances well above the EU drinking water quality standard of 500 ng l^{-1} for total pesticides. Compared to the amounts applied for pest control, the amounts deposited by rain resulted between 0,004% and 0,10% of the maximum application rates. These low pesticide inputs from precipitation to surface-water bodies is not of concern in vinicultural areas where the impact of other sources, such as superficial runoff inputs from the treated areas and cleaning of field crop sprayers, is more important. However, the potential impacts of these aerial pesticide inputs to non-target sites, such as organic crops, and sensitive ecosystems are as yet uncertain because of little available information on the long-term eco-toxicological effects of pesticides at low concentrations.

Concentration levels in the air samples were in the order of ng m^{-3} at sites close to the fields where pesticides were applied, while lower values, in the order of pg m^{-3} , were detected at the site located further away from fields where applications were performed. The measured air concentration levels found in this study do not represent a concern for human health in terms of acute risk. Inhalation toxicity studies have shown that an acute potential risk only arises at air concentrations in the range of g m^{-3} . However, no conclusions can be drawn on long-term effects of pesticides at low concentrations.

Finally, it must be kept in mind that only a small number of chemicals that were applied in the area were analysed in this study. In order to gain a better evaluation of the local atmospheric load of pesticides, a wider spectrum of substances (including metabolites) needs to be investigated.

For Jürgen, Giulia and Laura

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1 Introduction and study objectives

Most people are aware of and concerned with the health effects of pesticide residues in the water they drink or the food they eat, but many are surprised to learn that pesticides are commonly found in air and rain (MAJEWSKI & CAPEL 1995).

Of the environmental compartments – air, water, soil, sediment and biota – the atmosphere represents the largest most mobile compartment into which a chemical contaminant might be directly released or subsequently move into, undergo transport, and, in some cases, accumulate (MACKAY *et al.* 1997). During and after application, pesticides enter the atmosphere by drift, by volatilisation and by wind erosion of particles (soil, vegetation, formulation powders) on which the pesticide is sorbed. The extent to which pesticides enter the air compartment is dependent upon many factors: the properties of the substance, the amount used, the method of application, the formulation, the weather conditions, the nature of the crops and the soil characteristics (VAN DIJK & GUICHERIT 1999). Measurements at application sites revealed that sometimes more than half of the amount applied is lost into the atmosphere within a few days (VAN DEN BERG *et al.* 1999, KUBIAK 1999). The atmosphere is an important part of the hydrologic cycle that can transport pesticides from their point of application and deposit them into aquatic and terrestrial ecosystems far from their point of use. Pesticide deposition can be either wet, such as with rain or snow, or dry such as gaseous sorption and particle fallout (COUPE *et al.* 2000).

A variety of pesticides has been detected in the atmosphere throughout the world, but many of these studies have focussed on older generation organochlorine insecticides, most of which are banned in many countries (MAJEWSKI & CAPEL 1995). Several recent studies have focussed on current-use pesticides (MC CONNELL *et al.* 1998, VAN DIJK & GUICHERIT 1999). Nevertheless, reports of current-use pesticides in precipitation and, especially, in air are meager in comparison to studies in other matrices, in part because of low ambient air concentrations and a lack of regulatory focus on the atmosphere (FOREMAN *et al.* 2000). As a consequence, airborne transport and fate of pesticides represent an intriguing area of environmental sciences in need of further definition and study.

Deposition of airborne pesticides can have significant effects on water quality, but neither the nature of nor the magnitude of these effects can be determined with certainty on the basis of the type of data currently available (MAJEWSKI & CAPEL 1995). Risk estimation studies showed that the endangering of organisms by atmospheric input of pesticides cannot be excluded (GOTTSCCHILD 1996). Average annual concentrations of pesticides in air and rain are generally very low, although elevated concentrations may occur during periods of high use, usually in the spring and summer months. However, the effects of long-term

occurrences of low levels of pesticides in the atmosphere on quality and health of the environment and its inhabitants are not yet well understood and a risk assessment is still not possible (AKKAN 2003).

In the region of Trier, one of the main centres of the vinicultural area of the Moselle-Saar-Ruwer, pesticides are widely used. In order to protect crops from pests and increase crop yields in the viniculture, 6 to 8 pesticide applications take place between May and August. The decline in herbicide use in the viniculture observed in the past years is due, on the one hand, to the improvement of tillage practices (permanent greenery, mechanical soil treatment, specific vine treatment); on the other hand, only a few herbicides are allowed to be used in the viniculture as decided in the "Guidelines for the environmentally friendly controlled viniculture in Rheinland-Pfalz" (MWVLW 1997). The use of insecticides has also declined in the past years owing to the successful introduction of biological control agents like pheromones (BBA 1997a, PERMESANG 2000) or *Bacillus thuringiensis*-based products¹ (CHARUDATTAN & CHANDRAMOHAN 2002). By contrast, the great liability of vines to pathogenic fungi still demands a high use of fungicide products against pests like *Plasmopara viticola* (Peronospora), *Botrytis cinerea*, *Oidium tuckeri* and *Pseudopezicula tracheipila* (Roter Brenner). Several mixtures of fungicide active ingredients are sprayed in the region at different times during the growing season. The use of different substances is a strategic manoeuvre to avoid the development of pest populations which become resistant to a specific pesticide. Together, the use of these three classes of chemicals contribute to the widespread distribution of a great variety of pesticides in the atmosphere of the region.

The impact that these applications have on the environmental pollution of the region is not yet well understood. A research project on the input of pesticides used in the viniculture to surface- and groundwater bodies was carried out by the Department of Hydrology at the University of Trier in the past years (RÜBEL *et al.* 1998, RÜBEL 1999). A preliminary research study on the occurrence and concentrations of pesticides in precipitation was undertaken in 1999 by RIEFSTAHL (2000). Up to now, systematic studies on the presence of these pollutants in the atmosphere of the region are missing.

To address the lack of information on pesticides in the air, a 3-year study was conducted with the major goal to characterise the atmospheric presence of a variety of current-use pesticides in the region of Trier. In order to achieve this, the following questions needed to be answered:

- Which substances are detected in the region?
- When are these substances detected?

¹ Preparations of the bacterium *Bacillus thuringiensis* are applied as sprays to control insect pests on agricultural crops. The bacterium produces endotoxins that are highly toxic to insects. (WALKER 2001)

-
- What concentration levels are measured in the rain and in the air?
 - Is the local use the sole source responsible for the presence of airborne pesticides in the region?
 - Is the high use of fungicides a determining factor for the regional atmospheric pollution?
 - Do the estimated annual deposition rates represent a concern for the region?
 - What are the air concentration levels of the applied active ingredients after application and how long can the applied pesticides be detected in the air?

With these questions in mind, a sampling program was designed and rain samples were collected between 2000 and 2002 at different locations in the area of Trier. Furthermore, air sampling campaigns were carried out during the growing season in year 2002.

2 Pesticides in the atmosphere: a state of the art

In order to understand the occurrence and distribution of pesticides in the atmosphere it is necessary to consider pesticide sources, transport processes and mechanisms of degradation and removal from the atmosphere.

2.1 Sources

Much of the occurrence of pesticides in the atmosphere can be attributed to agricultural use. Other sources include manufacturing, formulation and disposal processes, waste effluents, urban sources, industrial sources, turf management of golf courses, parks, gardens and cemeteries (DÖRFLER & SCHEUNERT 1997). Because pesticides are primarily used in agriculture which involves large acreage, large quantities and most major types of pesticides (MAJEWSKI & CAPEL 1995, AKKAN 2003), this section focuses on agricultural sources and related processes.

Agricultural pesticides are released into the atmosphere by spray drift, post-application volatilisation and wind erosion of loaded soil particles. A great number of physical and chemical factors influence emissions by these different mechanisms: application methods, formulations, type of spray cloud, tillage practices, erosion conditions, meteorological conditions, soil moisture and temperature and physico-chemical properties of the substances (BIDLEMAN 1999, HARMAN-FETCHO *et al.* 2000, PECK & HORNBUCKLE 2005).

2.1.1 Spray drift

During the application a fraction of the dosage is lost to the atmosphere. The portion of this loss, in the form of droplets moving off-target (crossing the field border) through the air is referred to as *spray drift* (VAN DEN BERG *et al.* 1999). A portion of the spray drift usually is deposited quickly within a short distance from the application site. However, during aerial transport the diameter of the droplets can decrease through evaporation of the carrier formulation, and/or the pesticide, and when the diameter is sufficiently small, the droplets or particles can remain airborne. These particles have low depositional velocities and are likely to be transported over long distances by even a slight wind (MAJEWSKI & CAPEL 1995, RENNER 1997).

Many different factors combine to affect drift behaviour during the application processes and the rate of off-target deposition. They can be divided in three main categories: application methods, formulations and environmental conditions (wind, temperature, humidity, atmospheric stability) (VAN DEN BERG *et al.* 1999).

Application methods

MAYBANK *et al.* (1978) compared the amount of drift of aqueous solutions of a 2,4-D ester applied by ground-rig and aerial pesticide application systems. The drift during the ground-rig applications ranged from less than 0,5% to 8% of the nominal application and was dependent on the nozzle type, hydraulic pressure and wind speed. The drift from aircraft applications ranged from 1% to 31%. FROST & WARE (1970) compared the drift from several types of ground applications to aerial applications. They found that the ground-rig sprayer applications had 4 to 5 times less drift than aerial applications and 4 to 10 times less drift than ground mist-blower applications. Aerial application drift was up to 2 times less than that from ground mist-blower applications. In Germany, data on spray drift to adjacent watercourses for various techniques and crops have been collected by GANZELMEIER *et al.* (1995). The highest spray drifts were measured for those crops like hop-growing, orchard and vineyard where ground mist-blowers were used for applications. These radial and axial fan mist-blowers direct the spray up and away from the ground in an effort to cover the entire tree or crop canopy.

Formulation

Many different types of pesticide carrier formulations exist, as well as many different diluents. The use of any particular formulation and carrier is dependent on the required action and placement of the pesticide. An overview of the correlations between pesticide formulations and application drifts is given by MAJEWSKI & CAPEL (1995).

SEIBER *et al.* (1989) found a qualitative correlation between daily measured air concentrations and local use for methyl parathion, molinate and thiobencarb in a rice-growing area of northern California. This relation was strongest for methyl parathion. All three pesticides were applied by aircraft, but methyl parathion was applied as a water-based emulsifiable spray while the other two were applied as granular formulations. The closer correlation of air concentrations to use for methyl parathion was attributed to drift of the vapour and fine aerosol component of the liquid spray during application. There was very little measured drift associated with granular applications.

Environmental conditions

Environmental conditions are a determining factor which influences the behaviour of a spray cloud and as a consequence of the spray drift during applications. A drifting spray cloud can spread horizontally and vertically down- and cross-wind. The main parameters affecting its dispersion are wind speed and direction, ambient temperature and humidity, incoming solar radiation, and other micrometeorological parameters related to atmospheric stability, that is the degree of turbulent mixing (NORDBY & SKUTERUD 1975). BIRD *et al.* (1996) identified

increases in wind speed and intensification of stable conditions as important meteorological factors in increasing off-target drift and deposition from spray applications of pesticides. Long-range drift for all application systems can be reduced by spraying during calm (low wind speed), neutral atmospheric conditions. Cooler ambient temperatures during application will also reduce drift by minimising droplet evaporation (MAJEWSKI & CAPEL 1995).

In most cases drift measurements have been limited to the determination of the mass of pesticide deposited on the surface adjacent to the treated field and of droplets in the air close to the ground leaving the target area. Little is known about the total fraction of the dosage which does not reach the target area (VAN DEN BERG *et al.* 1999). In general, data from field experiment indicate that the emission during application can typically range from a few percent (GROVER *et al.* 1988, GLOTFELTY *et al.* 1990a, SIEBERS & GOTTSCHILD 1998) to 20-30% (BIRD *et al.* 1996). In some cases it may be as high as 50% or even more (VAN DEN BERG *et al.* 1999).

2.1.2 Post-application volatilisation

After the pesticide has been deposited on soil surface and/or plant surface, a fraction of this mass volatilise in the course of time. This is a continuous process and the resulting drift can be a significant source of pesticide input into the lower atmosphere. The dominant factors that affect volatilisation are the physico-chemical properties of the substance (e.g. vapour pressure, water solubility), its persistence in the soil, environmental conditions (soil and air temperature, soil water content and soil organic matter) (VAN DEN BERG *et al.* 1999) and tillage practices.

Potential volatility of a chemical is related to its inherent vapour pressure, but actual vaporisation rates will depend on environmental conditions and all factors that control the chemical at the soil-air-water interface (SPENCER & CLIATH 1990). Since pesticides, in general, have low vapour pressures, volatilisation has been regarded as being of little importance for a long time (SCHEUNERT 1992). However, research studies showed that more than 50% of the applied pesticide, in some cases as much as 80% to 90%, can volatilise within two days after application (SPENCER & CLIATH 1990, BOEHNCKE *et al.* 1990, TAYLOR & SPENCER 1990, MAJEWSKI *et al.* 1995). KUBIAK (1999) simulated field applications of methyl parathion and fenpropimorph in the volatilisation chambers and measured the volatilisation rates during the first 24 hours after application. Depending on the experimental conditions, volatilisation rates between 65% and 77% for methyl parathion and 6% and 11% for fenpropimorph were measured.

Studies have shown that pesticides with very high vapour pressures tend to volatilise from soil in large pulses immediately after application while those with lower vapour pressures volatilise more slowly and over longer period of time (ALEGRIA & SHAW 1999).

Volatilisation rates from soil surface resulted, in general, lower than those from plant surface, due to a higher adsorption capability of the soil and greater evaporating surfaces of the plants (AKKAN 2003). The nature of the soil surface also plays an important role in the volatilisation processes. Dry soils have been shown to effectively suppress pesticide release into the atmosphere, since further volatilisation is strongly dependent on additional moisture inputs. In this situation, volatilisation maxima occur with dew formation, usually in the early mornings and evenings, and with rain and irrigation (SPENCER & CLIATH 1990, MAJEWSKI & CAPEL 1995). A high soil organic matter content enhances pesticide adsorption and reduces the volatilisation rate (MAJEWSKI & CAPEL 1995).

Tillage practices can also affect pesticide transport into the lower atmosphere by volatilisation. A comparison of the effects that different practises have on pesticide volatilisation is reported by WHANG *et al.* (1993). The authors compared the volatilisation losses of fonofos, chlorpyrifos and atrazine from a conventional- and no-till field. The results showed that cumulative volatilisation losses from the no-till field for all substances were between 1,3 and 4,1 times greater than those from the conventionally tilled fields. They speculated that the no-till field volatility losses were greater because the mulch provided a greater surface area for contact between the pesticide residue and air. Furthermore, no-tillage practices can also be considered as higher concentrated emitting sources. In fact, these practices require frequently higher inputs of pesticides, since the mulch can intercept a portion of the sprayed pesticide and interfere with surface coverage (GHADIRI *et al.* 1984).

Volatilisation usually follows diurnal cycles and is very dependent on the solar energy input and the atmospheric stability. In general, the volatilisation rate is proportional to the solar energy input and to the atmospheric turbulence, both of which are typically maximised at noon and diminished at night (WHANG *et al.* 1993, MAJEWSKI & CAPEL 1995).

2.1.3 Wind erosion

Another emission pathway for pesticides into the atmosphere occurs when formulation dusts, small granules and pesticides sorbed to soil particles are released into the atmosphere on wind blown particles. This process, referred to as *wind erosion*, is generally considered to be less important than volatilisation. GLOTFELTY *et al.* (1989) found that the post-application volatilisation fluxes of a wettable powder formulation of atrazine and simazine exhibited wind erosion characteristics when measured over dry soil, but concluded that the amount of pesticide entering the atmosphere on wind-eroded wettable powder formulation particles was

small in comparison to the amount injected by true molecular volatilisation for those pesticides with appreciable vapour pressures.

According to FRITZ (1993), wind erosion of herbicides from arable land are more relevant than those of fungicides or insecticides. Fungicides and insecticides are usually applied on plants when the growing period has already started and the soil is normally covered with greenery. However, it is not yet clear if this is valid in viniculture. Although a permanent greenery in the vineyards is required between November and April, as established in the "Guidelines for the environmental friendly controlled viniculture in Rheinland-Pfalz" (MWVLW 1997), it is often the case that no vegetation grows under the vines, especially during the growing season. Fungicides and insecticides can, therefore, be deposited on the bare soil and undergo wind erosion processes. However, the typical vineyard cultivation can act as a wind barrier, therefore reducing the wind speed and the potential for wind erosion.

For those compounds that have long lifetimes in soil matrices, wind erosion represents an important mechanism of pesticide release into the atmosphere. Residues of organochlorine pesticides (OC) (DDTs, toxaphene, HCHs, chlordanes), that have been banned for years to decades in the U.S., Canada and European countries, are still routinely found in air and precipitation (BIDLEMAN 1999). Field measurements support the hypothesis that agricultural soils containing "old" OC residues are still capable of releasing them to the atmosphere (MEIJER *et al.* 2003). FINIZIO *et al.* (1998) found that concentrations of HCHs, chlordane and DDTs were highest in air samples collected 5 cm above a farm soil containing these residues, and decreased by a factor of 2-3 over a height of 140 cm. HAWTHORNE *et al.* (1996) measured vapour-phase and particulate-associated pesticides in air samples in North Dakota and concluded that blown soil might be a significant source for introducing pesticides into surface and ground waters.

The dimension of the particles to which the pesticide is bound is a decisive factor for the suspension in the atmosphere and the transport over long distances. Very large particles (500 μm to 1000 μm) tend to roll along the ground and, generally, do not become airborne, but they can break apart into smaller particles or dislodge small particles from the surface as they roll. Particles in the size range of 100 μm to 500 μm diameter move by saltation. Although large and saltating particles can move horizontally great distances, depending on the wind speed, their vertical movement is rarely above one meter and they are usually deposited near their source (MAJEWSKI & CAPEL 1995). The most important particle size range, with respect to atmospheric chemistry and physics is 0,002 μm to 10 μm (FINLAYSON-PITTS & PITTS 1986). These particles are not affected by rapid gravitational settling and those between 0,08 μm and 1-2 μm are only slowly removed by wet and dry deposition. They are, therefore, susceptible to long atmospheric lifetimes and have high potential for long-range atmospheric transport (BIDLEMAN 1988).

The contribution of pesticide-bound soil particles to the total atmospheric burden is still largely unknown, since the database provided by field studies that measured the pesticide content of windblown soil, dust and particulate matter from agricultural fields is still meagre (MAJEWSKI & CAPEL 1995, BIDDLEMAN 1999).

2.2 Fate of pesticides in the atmosphere

The atmosphere is an important component of the hydrologic cycle that acts to distribute and deposit pesticides in areas sometimes far removed from their application sites (Figure 1).

Assessing the fate of pesticides in the environment is complicated. Numerous mechanisms can deliver pesticides to the atmosphere. Once in the atmosphere, pesticides are distributed among the aqueous, particle and vapour phases. This distribution, along with transformation reactions, strongly affects the behaviour, transport and ultimate fate of airborne pesticides. Numerous mechanisms also deliver pesticides back to the surface of the earth. These include wet deposition, such as rain, snow and fog, and dry deposition of vapour-phase and particle-bound pesticides (MAJEWSKI & CAPEL 1995). These deposited residues can revolatilise, re-enter the atmosphere and be transported and redeposited downwind repeatedly until they are transformed or accumulate, usually in areas with cooler climates (WANIA & MACKAY 1996).

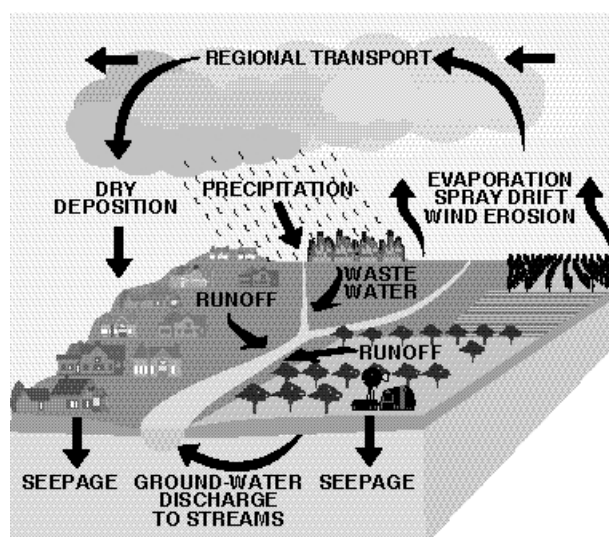


Figure 1: Pesticide movement in the hydrologic cycle (from MAJEWSKI & CAPEL 1995).

2.2.1 Physico-chemical properties and phase distribution

Pesticides represent a diverse group of chemicals of widely varying properties and use patterns. Once a pesticide gains entry to the environment it may enter one or more environmental compartments. The extent to which a substance is distributed among the different compartments is largely determined by its physico-chemical properties (SEIBER 2002). Regardless of the mechanism by which a pesticide enters the atmosphere, it will distribute among aqueous, particle and vapour phases as equilibrium conditions are approached (Figure 2). The equilibrium condition for a particular pesticide in the atmosphere is dependent on the properties of that chemical, including water solubility, Henry's law constant and vapour pressure and the characteristics of the atmosphere, including the

temperature (WANIA 1998), moisture content and nature and concentration of particulate matter (VAN DIJK & GUICHERIT 1999). The phase a pesticide is associated with strongly affects its removal potential from the atmosphere by degradation or wet and dry depositional processes (MAJEWSKI & CAPEL 1995, VAN PUL 1998), thus determining its atmospheric residence time (τ_a , see par. 2.2.3).

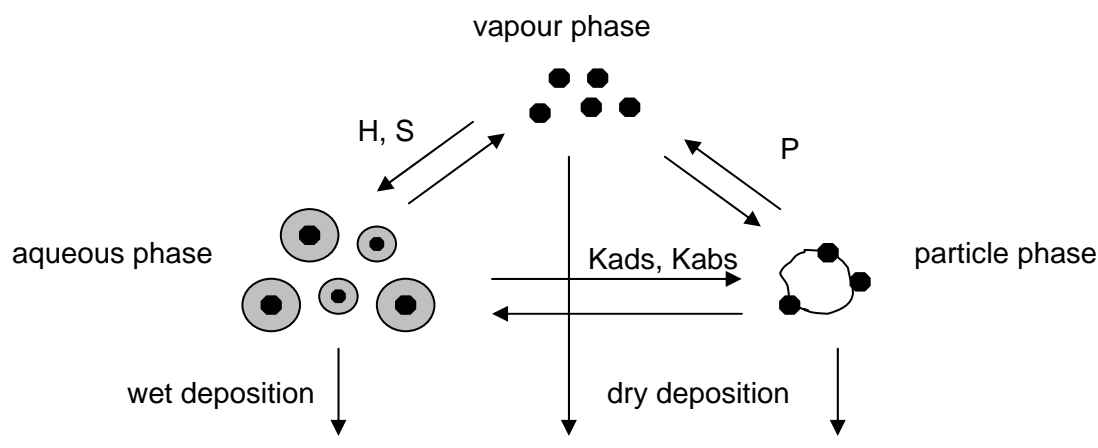


Figure 2: Distribution among aqueous, particle and vapour phase and depositional processes. H = Henry's law constant; S = saturated water solubility; P = vapour pressure, Kads = adsorption coefficient, Kabs = absorption coefficient.

Many pesticides have vapour pressure values between 10^{-3} Pa and 10^{-6} Pa and are therefore classified as semivolatile organic compounds (SOCs). Pesticides with low vapour pressures ($P < 10^{-4}$ Pa at 20 °C) will exist mainly in the particle phase (BOSSAN 1995) and be prone to removal from the atmosphere by dry deposition and rain scavenging of particles. Pesticides with high vapour pressures ($P > 10$ Pa) will primarily exist in the vapour phase, will be the least efficiently washed out by atmospheric droplets and will tend to accumulate in the atmosphere until they are removed or altered by transformation reactions (MAJEWSKI & CAPEL 1995).

Pesticides with high water solubilities (S) are the most efficiently removed from the atmosphere by wet depositional processes. In general, herbicides have higher water solubility values than insecticides and fungicides (AKKAN 2003).

The Henry's law constant (H) describes the solubility of a gas in the water phase. The higher the H value, the higher the potential for a substance to move from the water phase to the gas phase. Compounds with H values less than $2,65 \times 10^{-5}$ Pa m³ mol⁻¹ are essentially distributed in the water phase (AKKAN 2003). For pesticides with H values less than about 1 Pa m³ mol⁻¹, removal by vapour-water transfer into raindrops is an important control on their atmospheric concentration. As H increases, the importance of removal of chemicals by wet depositional processes diminishes (MAJEWSKI & CAPEL 1995).

VAN DIJK & GUICHERIT (1999) reported results of numerous studies on vapour- and particle phase partitioning of pesticides. Phase distributions varied during the season and considerably from year to year. Conflicting results were found among the different studies. For example, RAWN *et al.* (1998) found that the fraction of atrazine associated with the particle phase in 85 air samples varied from 0% to 100%, with an average value of 40%. By contrast, HERTERICH (1991) found that atrazine was almost completely bound to particulate matter in air above mountain forests in southern Germany. In comparing them with organochlorines, TURNBULL (1995) pointed out that modern pesticides showed a tendency towards particle phase partitioning, revealing their less volatile nature. However, all the monitoring data should be considered with caution as the phase distribution in the samples does not necessarily reflect ambient vapour-/particulate-phase distributions, since particulate-bound pesticides can be stripped during sampling and vapour-phase pesticides can be sorbed onto dust-containing filters (COTHAM & BIDDLEMAN 1992).

Interaction of airborne pesticides with atmospheric moisture is another area of much current interest (SEIBER 2002). Research on pesticides in fogwater pointed out the phenomenon of “enrichment” in fogwater, that is the pesticides were enriched in the suspended liquid fog droplets compared to equilibrium distributions expected from Henry's law coefficients for pure aqueous solutions (GLOTFELTY *et al.* 1987). SCHOMBURG *et al.* (1991) hypothesised that non-filterable dissolved organic carbon present in fogwater exists in a fine particle or colloidal form and has properties similar to activated carbon in being highly sorptive, thus causing the apparent pesticide enrichment. Alternatively, the enrichment may be caused by the presence of an organic film on the surface of the droplets (MAJEWSKI & CAPEL 1995), or the high surface area-to-volume ratio of fogwater, allowing the surface to act as a significant third phase (HOFF *et al.* 1993).

Generally, the distribution of pesticides among these three phases may be predicted from their physico-chemical properties. However, measurement data, necessary to validate the predictions, are scarce, especially for modern pesticides (DÖRFLER & SCHEUNERT 1997, BIDDLEMAN 1999).

2.2.2 Atmospheric transport

The temporal and spatial scales at which a component will be dispersed in the atmosphere and therewith the potential environmental risk of a substance, are largely determined by its atmospheric residence time (DE LEEUW 1993) (τ_a , see 2.2.3). Clearly, the longer a substance persists in the atmosphere, the further it can be transported.

Evidence for the long-range transport of substances with long atmospheric lifetimes such as DDTs, PCBs, toxaphene and HCHs has been widely reported (KURTZ 1990, WEBER &

MONTONE 1990, VOLDNER & SCHROEDER 1990, MAJEWSKI *et al.* 1991, FRITZ 1993, IWATA *et al.* 1993, CALAMARI *et al.* 1994, MAJEWSKI & CAPEL 1995, OEHME *et al.* 1996, WANIA & MACKAY 1996, KALLENBORN *et al.* 1998, BIDDLEMAN 1999, HARNER *et al.* 1999, WANIA 2003).

The lifetime of most current-use pesticides in the atmosphere is not known (VAN DIJK & GUICHERIT 1999). Their lower volatilities, higher water solubilities and lower chemical stabilities make them more prone to removal processes than the organochlorines and therefore shorter atmospheric lifetimes can be expected. The rate constant of the reaction of atrazine and terbuthylazine with OH radicals have been reported to be $1,4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for atrazine (KLÖPFER & KOHL 1990) and $1,1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for terbuthylazine (PALM *et al.* 1997). If this is the main degradation pathway, given an average OH radical concentration of $5\text{-}10 \times 10^5 \text{ cm}^{-3}$, the average lifetime of these compounds is approximately 1 day (PALM *et al.* 1997). With mean wind speeds of $3\text{-}5 \text{ m s}^{-1}$ (typical for northern Germany) these compounds may travel 250-500 km within a day before degradation (HÜSKES & LEVSEN 1997). The transport may also occur in aqueous phase (cloud droplet) leading to reduced degradation rates, longer lifetimes and thus possibly to longer transport distances (HÜSKES & LEVSEN 1997).

Several studies found that modern pesticides can travel over distances of tens to hundreds of kilometres (VAN DIJK & GUICHERIT 1999). The fact that certain pesticides are registered in some countries, whereas their use is prohibited in others, greatly enhances the possibility to study the atmospheric transport of these compounds, although illegal use can never be completely ruled out. Rainwater samples collected in 1992 along a transect across the southern part of Germany, from the border with France to the border with Austria revealed that atrazine concentrations were highest near the borders and lowest in the central part of Germany (OBERWALDER & HURLE 1993, cited by VAN DIJK & GUICHERIT 1999). Assuming that atrazine is not used illegally, the authors inferred that atrazine is transported through the atmosphere over at least 100-200 km. Atrazine and simazine in rainwater in the northern part of Germany, including the isle of Heligoland, originated probably from the Netherlands, some 100 km to the South-west (BESTER *et al.* 1995). MAJEWSKI *et al.* (2000) found that the three herbicides atrazine, CIAT and dachtal are relatively stable in the atmosphere and are subject to at least regional atmospheric transport (up to 1000 km).

Most of the pesticides currently used were specifically designed to have reduced environmental persistence as compared to the older organochlorine pesticides. Monitoring studies have, in fact, revealed a generally more localised and episodic contamination of the atmosphere with modern pesticides. Nevertheless, it is evident that they display, to some extent, the same phenomenon of atmospheric transport, if not at a global scale, then at least at a regional scale. Modelling studies of the fate of environmental chemicals have shown that

also moderately polar semivolatile organic compounds such as atrazine and methyl parathion have a potential for long-range transport (LAMMEL *et al.* 2001, LAMMEL *et al.* 2007).

Triazines, acetanilides, phenoxyacids, organophosphorus compounds and probably also many other pesticides are sufficiently stable, particularly in relatively unpolluted air, for atmospheric transport to occur over intermediate distances, typically 100-1000 km (VAN DIJK & GUICHERIT 1999). As a consequence, in small-scaled landscapes, like in many European countries, the distances between agricultural source areas and nature reserves are too small to prevent the latter from being contaminated by airborne pesticides.

2.2.3 Removal processes

Once in the atmosphere, the residence time (τ_a) of a substance depends on how rapidly the removal processes take place. In the atmospheric boundary layer (ABL), neglecting the exchange with the free troposphere, a chemical can be removed by (VAN PUL 1998):

- Photochemical reactions: chemical reactions with other atmospheric components and photolysis
- Wet deposition: uptake in cloud or rain droplets followed by droplet removal by precipitation
- Dry deposition: uptake at the earth's surface by water, soil and vegetation

According to VAN PUL (1998), these removal processes can be represented with pseudo first-order reaction rates and the atmospheric residence time τ_a , defined as the time period in which the mass of the pollutant in the atmospheric boundary layer is reduced by 50%, can then be formulated as:

$$\tau_a = \frac{\ln 2}{k_{\text{degr}} + k_{\text{wet}} + k_{\text{dry}}}$$

where: k_{degr} = photochemical degradation rate in air (s^{-1})

k_{wet} = wet deposition rate (s^{-1})

k_{dry} = dry deposition rate (s^{-1})

The effectiveness of the various removal processes depends on the physical and chemical properties of the compound and the phase distribution (Table 1), along with meteorological factors and the underlying depositional surface characteristics (MAJEWSKI & CAPEL 1995). Figure 3 shows a generalised schematic of the distribution and removal pathways.

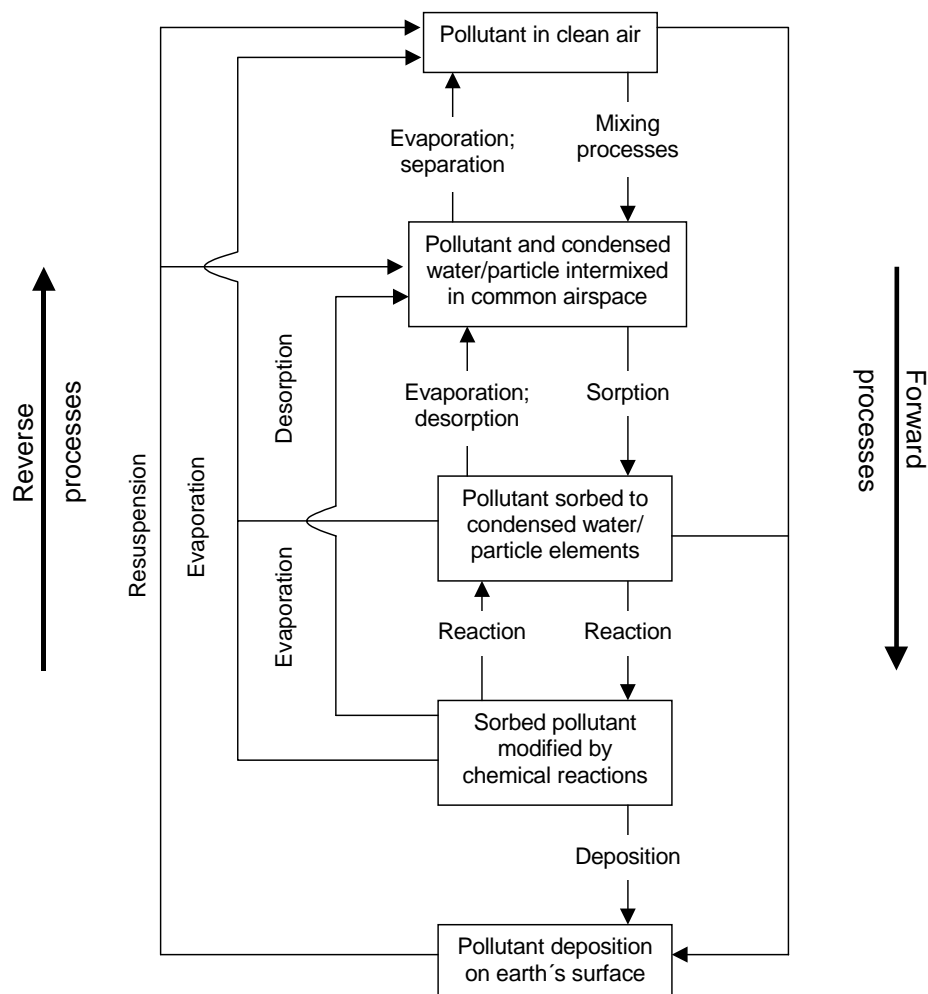


Figure 3: A simplified block diagram of gaseous and particulate pollution interconversion, and removal processes (from MAJEWSKI & CAPEL 1995).

Table 1: Removal and exchange characteristics of pesticides in gas and particle phase (from VAN JAARSVELD & VAN PUL 1999).

Process	Gas phase	Particle phase
Dry deposition	Depends on surface saturation, both deposition and re-emission possible	Depends on particle size ($V_d = 0,01-1 \text{ cm s}^{-1}$), pesticides distribute over particles according to particle surface area, therefore characteristic deposition velocity (V_d) in the order of $0,1 \text{ cm s}^{-1}$
Wet deposition	Depending on Henry's law constant	Depending on particle size, but very efficient
Chemical reaction in atmosphere	Usually estimated on the basis of chemical structure	Lower reaction rates for particles?

2.2.3.1 Photochemical reactions

The photochemical degradation of a substance occurs by photolysis and by reaction with the OH radical, the NO₃ radical and ozone (WINER & ATKINSON 1990, VAN PUL 1998). Photolysis by direct irradiation of sunlight and reaction with OH radicals are the main degradation pathways for pesticides in the atmosphere (DE LEEUW 1993). WINER & ATKINSON (1990) have shown that for organophosphorus pesticides in the gaseous phase lifetimes due to reactions with OH radicals may range from a few minutes to several hours, whereas reactions with NO₃ and ozone result in lifetimes of several days and at least 100 days, respectively. Photolysis is important only for compounds that absorb light above 290 nm (PALM *et al.* 1998). Many classes of pesticides possess no chromophore to absorb light above this wavelength, like triazines, ureas and many halogenated compounds. Therefore, degradation of the majority of these compounds is assumed to proceed mainly by reaction with OH radicals (PLIMMER & JOHNSON 1991, DE LEEUW 1993, PALM *et al.* 1998, ATKINSON *et al.* 1999). Reactions on aerosols and in the liquid phase (cloud water) are considered to be small (BRUBAKER & HITES 1997). Very few experimental data for atmospheric degradation of pesticides are available and most of them are related to gaseous phase transformations (BIDLEMAN 1999).

Photochemical reactions can lead to products that are themselves of concern because of their toxicity. Many organophosphorus pesticides are oxidised to their oxon analogs (ATKINSON *et al.* 1999), which are usually more potent acetylcholinesterase inhibitors (BIDLEMAN 1999). Dealkylation products of triazine herbicides are phytotoxic (VAN DIJK & GUICHERIT 1999). Most oxidative reaction products are more polar than the parent compound. This suggests that they also will be more water soluble and more readily removed by wet-depositional processes or by air-water exchange (MAJEWSKI & CAPEL 1995).

Transformation products of triazine herbicides are the most frequently reported in rainwater, particularly desethylatrazine (VAN DIJK & GUICHERIT 1999). Deisopropylatrazine has been found less often and usually in lower concentrations (GOOLSBY *et al.* 1997, BUCHELI *et al.* 1998). Reported values for the ratio of desethylatrazine to atrazine – often referred to as DAR – in rainwater are highly variable. BESTER *et al.* (1995) found that the parent compound was dominant in precipitation at sampling locations in northern Germany. However, the transformation product prevailed on the isle of Heligoland in the German Bight (BESTER *et al.* 1995). In rainwater samples collected near Hannover (Germany), the DAR varied between 0,4 and 2,0 (JAGER *et al.* 1998). GOOLSBY *et al.* (1997) reported an average DAR value in rainwater in the midwestern and northeastern USA of 0,5. Peak concentrations of desethylatrazine and desisopropylatrazine in rainwater are often observed with a delay of few weeks with respect to the parent compound (VAN DIJK & GUICHERIT 1999). Consequently, the DAR changes markedly over the season. BUCHELI *et al.* (1998)

reported an average value of 0,36 in the samples taken before June the 30th and of 0,70 in the samples collected after that date. In spite of the high variability, DAR values in precipitation are normally much higher than 0,1, a value commonly observed in surface run-off (GOOLSBY *et al.* 1997). It is therefore speculated that atrazine is desethylated in the atmosphere (GOOLSBY *et al.* 1997). Desethylatrazine has also been detected in air: MAJEWSKI *et al.* (1998) found desethylatrazine in 60% of the air samples taken along the Mississippi River in concentrations generally about 10 times less than atrazine.

Oxones, which result from the oxidation of sulphur containing organophosphorus insecticides, are also very frequently observed in air, rainwater and fog (VAN DIJK & GUICHERIT 1999). SCHOMBURG *et al.* (1991) found that the ratio of the oxones to their respective parent compounds, thions, in fog water collected near the California coast, were higher in non-agricultural areas than in agricultural areas.

In general, the importance of the transformation products relative to their parent compounds seems to increase with the remoteness of the receptor area (VAN DIJK & GUICHERIT 1999).

2.2.3.2 Depositional processes

Atmospheric depositional processes can be classified into two categories, those involving precipitation, called wet deposition, and those not involving precipitation, called dry deposition (BIDLEMAN 1988). Either category of processes involves both particle and gaseous transfer to the earth's surface (see Table 1). Removal involving fog, mist and dew lies somewhere between the wet and dry processes, but is more closely related to dry deposition (MAJEWSKI & CAPEL 1995).

In the dry deposition process of gaseous pesticides the interaction between pesticide and the surface, *i.e.* soil, vegetation and water, is very important (VAN JAARSVELD & VAN PUL 1999). Dry deposition of pesticides associated with particles includes gravitational setting and turbulent transfer to a surface followed by inertial impaction, interception or diffusion onto surfaces such as vegetation, soil and water (MAJEWSKI & CAPEL 1995). The deposition rate is strongly dependent on the size, surface area and mass of the particle and larger particle are greatly influenced by wind speed. Most of the pesticides may be concentrated on the smaller particles because of their higher surface area-to-volume ratio (BIDLEMAN & CHRISTENSEN 1979), thus remaining airborne for longer times. Deposited gaseous and particle-bound pesticides can be reintroduced to the atmosphere by revolatilisation, rebound, reentrainment or resuspension (AKKAN 2003).

Raindrops can act as a concentrating agent. They can concentrate cloud aerosols into droplets and scavenge vapour and particles as they fall through the atmosphere to the

ground. Two mechanisms are responsible for the wet removal of airborne compounds: rainout and washout (LIGOCKI *et al.* 1985a,b). Rainout is the process where cloud droplets acquire contaminants within the clouds. Washout is the process by which atmospheric contaminants are removed by rain below the clouds by the scavenging of particles and by the partitioning of organic vapours into the rain droplets or snowflakes as they fall to the earth's surface (MAJEWSKI & CAPEL 1995). The mechanisms of wet removal from the atmosphere are very different for particle-associated compounds and for gas phase compounds (LIGOCKI *et al.* 1985b).

The importance of wet versus dry deposition depends upon the frequency, intensity, duration of precipitation events as well as the concentration of pesticides in the air, the particle size distribution and concentration (MAJEWSKI & CAPEL 1995). By comparing the results of bulk and wet-only samplers, some authors (GLOTFELTY *et al.* 1990b, SIEBERS *et al.* 1994, DÖRFLER & SCHEUNERT 1997, BUCHELI *et al.* 1998) conclude that, in general, the contribution of dry deposition to total atmospheric pesticide fluxes is of minor importance. Dry deposition may gain relatively more importance after long dry periods (AKKAN 2003).

The washout dynamics of some pesticides during single rain events was investigated by BUCHELI *et al.* (1998). They found that compounds with low Henry's law constants like the triazines and phenoxy acids exhibit a so-called "first flush" effect, *i.e.* they are very effectively washed out at the onset of the rain event and decrease their concentrations by a factor of 10-20 within the first 2 mm of rain. The reason is that the initial part of a precipitation event tends to scavenge most of the pesticides from the atmosphere, especially those associated with particulate material and gaseous pesticide with high water solubility. Rainfall occurring later during the event dilutes the concentration of the pesticides that were deposited during the early part of the rainfall event (NATIONS & HALLBERG 1992, GOOLSBY *et al.* 1997).

2.3 Contribution to surface and ground water

The potential contribution of pesticides from the atmosphere to a surface-water body depends on pesticide levels in atmospheric deposition and on how much the water budget is derived from surface runoff and direct precipitation (MAJEWSKI & CAPEL 1995).

An atmospheric pesticide input of up to a few grammes per hectare per year constitutes normally far less than 1% of the recommended application rate (GLOTFELTY *et al.* 1990b, DÖRFLER & SCHEUNERT 1997). Nevertheless, in areas where no pesticides are used and that are not connected to use areas by surface or ground-waters, the total load can be attributed to atmospheric deposition and this input may be significant (VAN DIJK & GUICHERIT 1999).

2.4 Studies on current-use pesticides in the atmosphere

A comprehensive overview of all the local, state-wide, multistate and national monitoring studies within the United States and Canada was compiled by MAJEWSKI & CAPEL (1995). Since then, additional data from these countries have been presented by several authors (BAKER *et al.* 1996, HAWTHORNE *et al.* 1996, GOOLSBY *et al.* 1997, MAJEWSKI *et al.* 1998, MC CONNEL *et al.* 1998, RAWN *et al.* 1999, HARMAN-FETCHO *et al.* 2000, MILLER *et al.* 2000, THURMAN & CROMWELL 2000, COUPE *et al.* 2000, MAJEWSKI *et al.* 2000, FOREMAN *et al.* 2000). Extensive overviews of the results from European monitoring studies are given by DÖRFLER & SCHEUNERT (1997) and by VAN DIJK & GUICHERIT (1999). Additional data are presented by CHARIZOPOULOS & PAPADOPOULOU-MOURKIDOU (1999), POLKOWSKA *et al.* (2000), GRYNKIEWIEZ *et al.* (2001) AKKAN *et al.* (2003) and SIEBERS *et al.* (2003).

Concentration of modern pesticides in air often range from a few pg m^{-3} to many ng m^{-3} . In rain, concentrations have been measured from a few ng l^{-1} to several $\mu\text{g l}^{-1}$. In general, the occurrence of pesticides in air and rain shows a distinct seasonal variation, with peak concentrations occurring during application periods (SIEBERS & GOTTSCHILD 1998, VAN DIJK & GUICHERIT 1999, AKKAN 2003). The temporal variations also depend upon the pesticides' persistence in soil, water and air, as well as their volatility. Relatively volatile compounds with low persistence, such as alachlor and metolachlor, often exhibit high peak concentrations which are strictly limited to the application period. More persistent, less volatile pesticides, such as lindane, atrazine, simazine and 2,4-D, show lower peak concentrations, but remain in the air for a much longer time after they have been applied (GLOTFELTY *et al.* 1990b, GOOLSBY *et al.* 1997, BUCHELI *et al.* 1998). Several studies revealed the presence of these compounds in air and rainwater outside the application period. This may be the result of either medium- and long-range transport or the entrance into the atmosphere of old residues, either as vapours or adsorbed to soil dust or crop material, e.g. due to agricultural activities (VAN DIJK & GUICHERIT 1999).

Pesticides are predominantly found in air and precipitation in agricultural areas, but some investigations revealed high concentrations of some organophosphorus insecticides, such as chlorpyrifos, diazinon, malathion and methyl parathion, and the herbicide atrazine in air and precipitation in urban areas (NATIONS & HALLBERG 1992, CHEVREUIL & GARMOUMA 1993, MAJEWSKI *et al.* 1998, COUPE *et al.* 2000, FOREMAN *et al.* 2000, MAJEWSKI *et al.* 2000).

Estimated deposition of pesticides, based on the analysis of precipitation collected with bulk or wet-only samplers, is generally in the order of a few $\text{mg ha}^{-1} \text{y}^{-1}$ up to more than $1 \text{ g ha}^{-1} \text{y}^{-1}$

for individual pesticides (AKKAN 2003). In relation to the s-triazine input in agriculture the atmospheric immission is very low. Normally, the contribution of atmospheric atrazine input to the direct application in agriculture (about $1 \text{ kg atrazine ha}^{-1} \text{ y}^{-1}$) is in the promille range (DÖRFLER & SCHEUNERT 1997). In Switzerland, BUSER (1990) calculated a deposition rate of $0,2 \text{ g ha}^{-1} \text{ y}^{-1}$, corresponding to 0,02% of the application rate in agriculture. Considerable between-year variation, sometimes amounting to more than a factor of 10, may exist in the deposition of a certain pesticide at a specific sampling site (GLOTFELTY *et al.* 1990b, HATFIELD *et al.* 1996, MC CONNELL *et al.* 1998, RAWN *et al.* 1999). This may be explained by differences in application amounts and atmospheric conditions, including the timing of rainfall events relative to application (HATFIELD *et al.* 1996).

Apart from lindane, herbicides are the current-use pesticides most frequently looked for and detected in air and precipitation. This holds for both Europe and North America (VAN DIJK & GUICHERIT 1999). Most attention has been focused on the triazines, such as simazine, cyanazine, terbuthylazine and in particular atrazine (DÖRFLER & SCHEUNERT 1997), but also acetanilides (alachlor, metolachlor) and phenoxyherbicides (2,4-D, MCPA, dichlorprop, mecoprop) have been targeted frequently (VAN DIJK & GUICHERIT 1999). Among the insecticides, organophosphorus compounds (parathion, malathion, diazinon, chlorpyrifos) have been looked for most often. The occurrence of other groups of pesticides in air and rain has generally been poorly investigated (MAJEWSKI & CAPEL 1995).

The evidence from the literature shows that most of the pesticides that have been targeted for analysis have been detected in at least one atmospheric matrix. There are many more pesticides with similar physical and chemical properties as those detected, but that have not been found in the atmosphere. There are several reasons for this fact and these may include low use, short atmospheric residence time (considering deposition and transformation processes), the timing of use, the predominant atmospheric phase in which a pesticide will accumulate relative to the phase being sampled, or, perhaps most important, whether or not it has been included in the analysis program (MAJEWSKI & CAPEL 1995). In fact, only a small number of the pesticides which are currently on the market have been analysed (AKKAN 2003). As a consequence, the presence in the atmosphere of pesticides other than those detected cannot be excluded. Hence, during the main application times, rainwater may exhibit total pesticide concentrations that markedly exceed the EU drinking water standard of 500 ng l^{-1} (BUCHELI *et al.* 1998).

2.5 Summary

Sources

Pesticides are released into the atmosphere mainly during agricultural activities. Urban and industrial use can be considered as minor sources in comparison to the large use of these substances made in the agriculture. Together, these sources contribute to the widespread distribution of a great variety of pesticides in the atmosphere. Agricultural pesticide inputs to the atmosphere occur during the application process through evaporation and drift, and post-application through volatilisation and wind erosion. The degree of losses during and after application depends, in part, on the application method, pesticide formulation and local meteorology.

Phase distribution and atmospheric transport

Once a pesticide becomes airborne, it will distribute itself between the vapour, aqueous and particle phases in order to reach an equilibrium condition. The extent to which a substance is distributed among these phases is dependent on its physical and chemical properties, such as water solubility and vapour pressure, as well as environmental factors, such as temperature, moisture and the nature and concentration of suspended particulate matter. These factors also dictate the atmospheric residence time of the pesticide through their effects on the transformation reaction rates and depositional rates to the surface, thereby determining the potential for atmospheric transport. The longer a substance persists in the atmosphere, the further it can be transported. Several studies proved that modern pesticides can travel over distances of tens to hundreds of kilometres.

Airborne pesticides and their transformation products are continuously deposited on every surface of the earth as dry deposition and in rain, snow and fog. Atmospheric deposition, however, is not a one-way process and the deposited chemicals can be reintroduced into the atmosphere for further downwind dispersal. The airborne movement of pesticides in the environment has been described as a global gas chromatographic system where pesticide molecules move many times between the vapour-soil-water-vegetation phases in maintaining an equilibrium of chemical potential (fugacity) between the phases (MAJEWSKI & CAPEL 1995).

Concentration levels in air and rain	Concentration levels of pesticides detected in the air range from a few pg m^{-3} to many ng m^{-3} . In rain, concentrations range from ng l^{-1} to several $\mu\text{g l}^{-1}$. Temporal variations often show seasonal trends, with the highest concentrations corresponding to local use and growing seasons. Concentration levels are usually higher in agricultural areas, though high concentrations of some organophosphorus insecticides and atrazine were also detected in urban areas.
Pesticide load in the atmosphere	Not all the pesticides which are dispersed in the atmosphere have been analysed, many more other products are in use whose presence in the atmosphere cannot be excluded. As a consequence, during the application periods total loads of pesticides in the atmosphere are higher than those measured and rainwater may reach total pesticide concentrations that markedly exceed the drinking water standard of 500 ng l^{-1} . This atmospheric input, in areas where no pesticides are used, may significantly affect the aquatic ecosystems.
Need for further studies on fungicides	Research studies on current-use pesticides have been mainly focused on lindane, herbicides (mainly triazines) and organophosphorus insecticides. Much less attention has been paid to fungicides. Nevertheless, this class of substances is the most widely used in vinicultural areas. Further monitoring studies are needed in order to provide information on the variation in observed levels caused by such factors as distance from application areas, meteorological conditions and quantity and timing of applications, thereby increasing our understanding of the behaviour of these compounds in the atmosphere and their environmental impact on such areas.
Data needed for model calibration and validation	Monitoring provides the information necessary for the development and the calibration of emission, atmospheric transport and deposition models. It enables to validate predictions, thereby increasing the confidence in predictions regarding the atmospheric dispersal of new pesticides prior to registration.

3 Experimental section

3.1 Study area

3.1.1 Trier and the Moselle-Saar-Ruwer wine-growing area

The town of Trier, with about 99.500 inhabitants (LUFTREINHALTEPLAN TRIER-KONZ 1996), is located near the river Moselle, in south-western Germany, and is one of the main centres of the vinicultural area of the Moselle-Saar-Ruwer. The river Moselle flows through the area of Trier in a 3-km-wide valley, the so-called “Trierer Talweite”, in a southwest-northeast direction. As a result of lateral erosion, the altitude of the “Trierer Talweite” is about 300 meters below the elevation of the surrounding plateau. The rivers Saar and Ruwer flow into the Moselle respectively southwest and northeast of the town. The residential areas are located along the “Trierer Talweite” as well as on the plateau, in the sections of Mariahof, Trimmelter Hof, and Tarforst. The industrial areas are settled along the Moselle valley and are principally located in Zewen and Kenn. The profound loamy flat soils are used as arable land, while the slopes of this typical low mountain region are mainly used as grasslands, woodlands or vineyards.

The viniculture in the region of Trier has a long tradition. The landscape is characterised by vines grown on the steep slopes (in general with an inclination of about 30%) with south-easterly and westerly exposure. The widest vineyards of the area of Trier are located in the valleys of the rivers Ruwer, Aveler, and Olewiger. The size of wine-growing area per activity is mainly (about 95% of the activities) smaller than 5 ha, and one third of these activities has a cultivated area smaller than 1,5 ha (LUFTREINHALTEPLAN TRIER-KONZ 1996). The conventional viniculture is the most widespread form of cultivation, whereas the integrated-controlled (environmentally friendly) and the ecological viniculture are not yet very common.

The typical landscape and economic structure of the vinicultural area of Trier reflect those of the wine-growing area of the Moselle-Saar-Ruwer. This area extends along the river Moselle in northeast direction from the border with Luxembourg and France to Koblenz, where the river Moselle flows into the river Rhine. The statistical data summarised in Table 2 show how most vineyards are grown on slopes, and most activities have a wine-growing area smaller than 3 ha. In most cases, these particular conditions are not economically favourable and do not provide a sufficient income for a living; as a consequence, about 60% of the activities are extra-income activities.

Table 2: The Moselle-Saar-Ruwer wine-growing area (from RÜBEL 1999).

Moselle-Saar-Ruwer wine-growing area	12130 ha
Percentage of vineyards grown on steep slopes (>30% inclination)	50,4%
Percentage of vineyards grown on flat sites or slopes (0-30% inclination)	49,6%
Percentage of the wine-growing area in Germany	11,6%
Number of wine-growing activities	6643
Percentage of extra-income activities	60%
Number of ecological wine-growing activities	31
Percentage of the wine-growing area	0,55%
Activities with a wine-growing area of	
Less than 3 ha	52%
Between 3 ha and 5 ha	26%
More than 5 ha	22%

3.1.2 The climate

The climate in the region of Trier is mainly characterised by west-European-Atlantic conditions (humid-temperate climate) with temperate summers and mild winters.

Being a low mountain region, with elevations between 120 m and 480 m above sea level (asl), its climate is subjected to considerable meso-scale variations. In the valleys, warmer and slightly dryer conditions prevail in comparison to the surrounding countryside and continental draught conditions can occur. Stable atmospheric conditions frequently occur in the valley, usually at night and in the late summer and are responsible for the formation of stable atmospheric layers and the development of thermic inversion conditions at the earth surface. At night, after warm sunny days, cold air masses flow down-slope from the valleys Olewiger Tal, Aveler Tal, and Aulbachtal towards the town.

The annual average ambient temperatures measured at the DWD (Deutscher Wetterdienst) meteorological station Trier-Petrisberg (256 m asl) range between 9 °C and 10 °C, while annual average values measured at the LfUG (Landesamt für Umweltschutz und Gewerbeaufsicht) meteorological station Trier-Weberbach (140 m asl) range between 10 °C and 12 °C (LUFTREINHALTEPLAN TRIER-KONZ 1996). This difference of about 2 °C can be explained with the different elevation and anthropogenic influences which characterise the two meteorological stations.

Annual precipitation values range between 700 mm and 800 mm (l m⁻²). Precipitations are relatively evenly distributed during the year, with higher frequencies measured in the months of July/August and December/January (LUFTREINHALTEPLAN TRIER-KONZ 1996).

The solar radiation value of 1574 hours per year, being lower than values measured in other continental regions with a similar topography (Würzburg: 1730 h y⁻¹), reflects the frequent occurrence of cloudy conditions in the area of study.

Wind speed and wind direction are determining factors for the atmospheric transport and dispersion of pollutants. Furthermore, wind direction values provide important information about the possible location of emitting sources of pollutants to the atmosphere. Wind speed values measured at the station Trier-Petrisberg between 1982 and 1991 reveal that the highest wind speeds occur during the spring period (from March till the end of May, wind speed between 2,5 m s⁻¹ and 5,1 m s⁻¹), whereas the lowest values are measured in summer and autumn (from July till October, wind speed between 1,9 m s⁻¹ and 3,0 m s⁻¹) (LUFTREINHALTEPLAN TRIER-KONZ 1996).

The relief of the region is responsible for the canalisation of the air currents, *i.e.* wind directions close to the earth surface are strongly influenced by the regional topography. Thereby, easterly and westerly winds once canalised in the Moselle valley change their direction becoming, respectively, north-easterly and south-westerly winds. Wind direction measurements carried out at the station Trier-Petrisberg between 1982 and 1991 confirm this characteristic phenomenon as the north-easterly and south-westerly winds were the most frequently detected wind directions (LUFTREINHALTEPLAN TRIER-KONZ 1996).

The interaction of Atlantic and Mediterranean influences with the typical climate of the valley creates very favourable conditions for the viniculture.

3.1.3 Pesticide application

In Germany, about 35.000 t of active ingredients are sold every year (Table 3) (BVL 2003). It is expected that pesticides are released into the environment more or less in this order of magnitude. Figure 4 shows the percentage of the active ingredients sold between 1999 and 2003 divided by classes. Herbicides are the most frequently sold substances, followed by fungicides, insecticides, and other pesticides.

Table 3: Amount of active ingredients (t) sold in Germany between 1999 and 2003 (BVL 2003).

Class	1999	2000	2001	2002	2003
Herbicides	15.825	16.610	14.942	14.328	15.350
Fungicides	9.702	9.641	8.246	10.129	10.033
Insecticides, Acaricides	6.125	6.111	6.518	5.889	6.370
Other active ingredients	3.751	3.232	3.957	4.332	4.002
Total amount	35.403	35.594	33.663	34.678	35.755

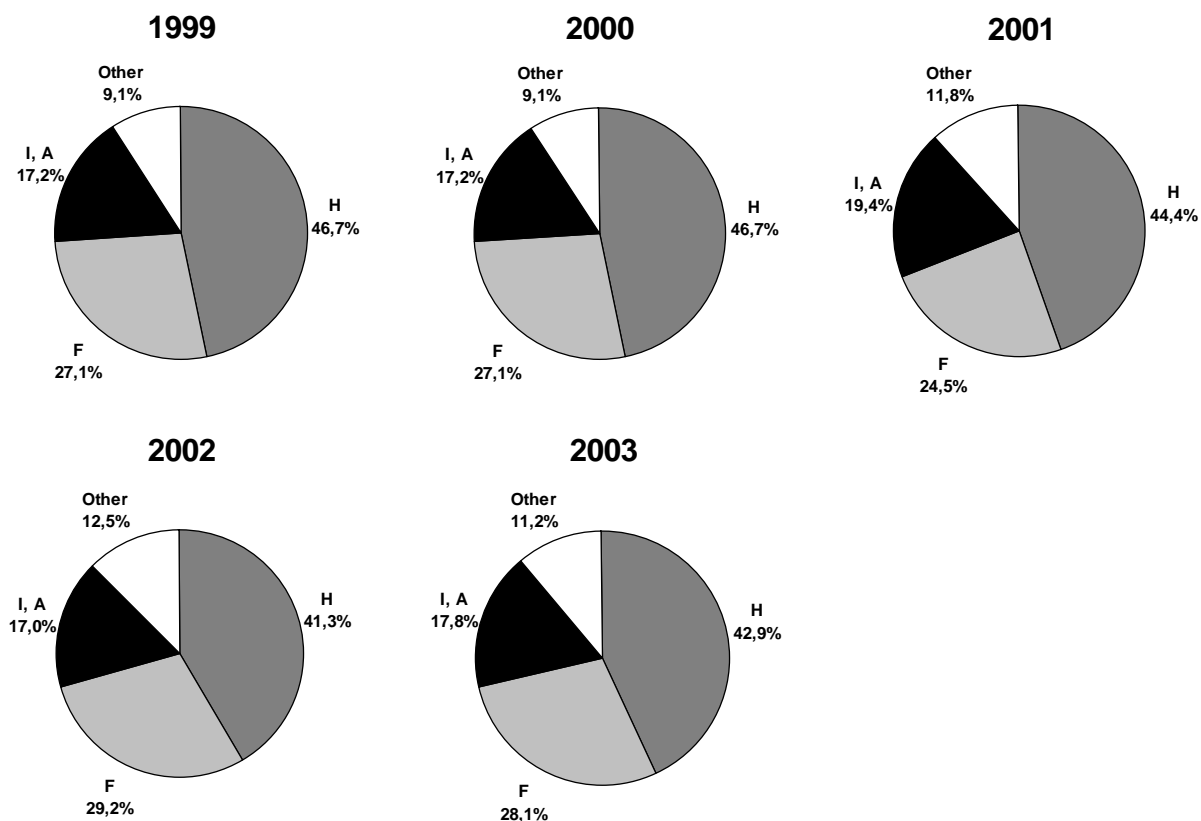


Figure 4: Percentage of active ingredients sold between 1999 and 2003 divided by classes: herbicides (H), fungicides (F), insecticides and acaricides (I, A) and other active ingredients. (Data from Table 3)

Though herbicides are the most used plant protection products in the country, specific local conditions, *i.e.* prevailing agricultural activities, usually dictate which pesticides will be used, as each pesticide is registered for use only on specific crops. As a consequence, a quite different picture on the use of pesticides may result when considering smaller areas.

In the viticulture, the use of only a restricted number of the registered active ingredients is permitted. In 1997, 261 active ingredients were officially registered in Germany, but only 51 of these substances were registered for use in the viticulture (BBA 1998). In 2003, the number of registered active ingredients dropped to 248, 63 of which were allowed to be used in the viticulture (BVL 2003). Table 4 shows the distribution of these substances in different classes. The importance of the use of fungicides in this specific agricultural activity is clearly represented by the high number of allowed active ingredients of this class.

Table 4: Number of active ingredients allowed in the viniculture in Germany in 1997 (BBA 1998) and 2003 (BVL 2003).

Class	1997	2003
Fungicides	26	35
Acaricides	8	7
Insecticides	10	13
Herbicides	7	8

Usually, herbicides in the viniculture are applied only once a year; only in particular cases multiple applications are allowed (BBA 2000). The decline in the use of herbicides in the viniculture in the past years is due, on the one hand, to the improvement of agricultural practices (permanent greenery, mechanical soil treatment, specific vine treatment); on the other hand, to the fact that only few herbicides are allowed to be used as decided in the “Guidelines for the environmentally friendly controlled viniculture in Rheinland-Pfalz” (MWVLW 1997). The use of insecticides has also declined in the past years owing to the successful introduction of biological control agents like pheromones (BBA 1997a, PERMESANG 2000) or *Bacillus thuringiensis*-based products (CHARUDATTAN & CHANDRAMOHAN 2002). By contrast, the great liability of vines to pathogenic fungi still demands a high use of fungicide products against pests like *Plasmopara viticola* (Peronospora), *Botrytis cinerea*, *Oidium tuckeri* and *Pseudopezicula tracheiphila* (Roter Brenner). The high number of permitted fungicides in the viniculture is an incentive for the farmer to use different products in order to avoid the development of pest populations which become resistant to a specific pesticide. The suggested strategy is to diversify mortality sources by managing resistance such as sequencing, rotating or alternating pesticides with different modes of action (MOTA-SANCHEZ *et al.* 2002). To this purpose, different mixtures of fungicide active ingredients are sprayed in the region at different times during the growing season.

Because of the particular topography of the region, different application methods are used. Fan mist-blowers (known also as air blast sprayers) are the most commonly used equipments for pesticide application (Figure 6); however, where the inclination of the slope is unsuitable for farm tractors, diluted liquid pesticides are applied by means of hand-held spray guns.

Aerial applications with helicopters are still carried out in some areas, although a reduction of about 60% of the areas treated with this method could be observed between 1985 and 2001 (Figure 5) (MADER 2002).

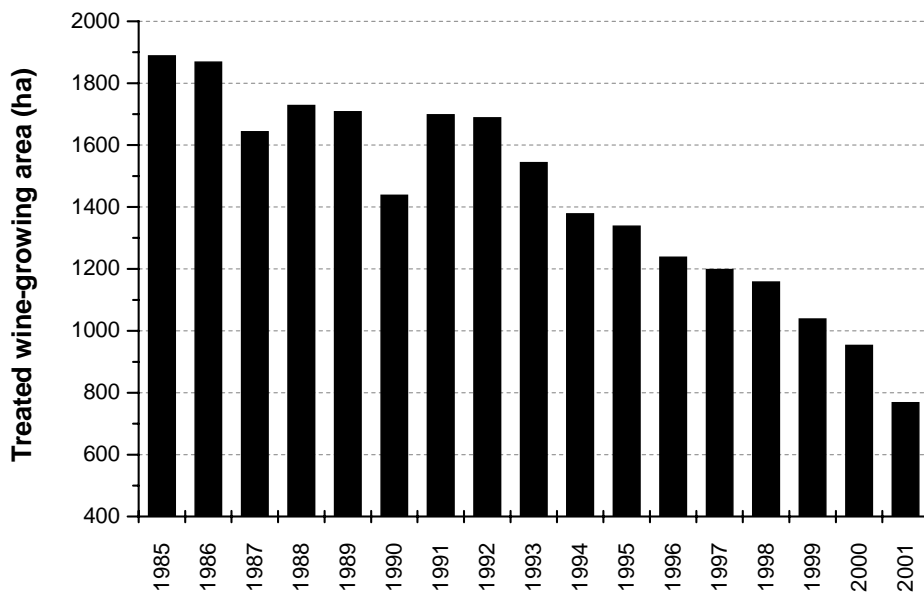


Figure 5: Wine-growing areas treated with pesticides by means of helicopter applications in the district of Trier-Saarbrug (MADER 2002).

Aerial applications are a convenient method for applying pesticides in areas characterized by steep slopes; furthermore, only registered substances and legally permitted quantities are applied, whereas a control of the products and quantities used by single winegrowers is nearly impossible. However, aerial applications are less effective than ground applications: pesticides deposit only on the surfaces of the leaves and do not reach lower parts of the vines. Targeted ground applications are, therefore, necessary at least in the final period of the growing season (LUFTREINHALTEPLAN TRIER-KONZ 1996).

Pesticide applications which are carried out in the area of study are very heterogeneous. In general, every single farmer or wine-growing activity has its own strategy. Detailed information on the usage of pesticides (type, frequency and amount of used substances) is very difficult to be obtained. General information on the data on pesticide applications which could be gathered during the period of study are reported in Table 5.

Table 5: Data on pesticide applications. Sources: (1) Mr. MADER, National Institute of Trier for Education and Research (Staatliches Lehr- und Versuchsanstalt Trier), (2) Mr. KIRCHEN, “Schloss Marienlay” winery, (3) Mr. PERMESANG, Trier/Mosel national wine-growing domain.

Area of application	Period	Application Method	Available data	Source	Details
Trier-Saarburg district	2000 – 2001	Helicopter	Time and place of application, type and amount of substances.	(1)	Appendix A Table A1
Kasel and Morscheid (Ruwer valley)	2000 – 2002	Fan mist-blower and hand-held spray gun	Time and place of application, type and amount of substances.	(2)	Appendix A Table A2-A3
Avelsbach wine-growing domain	2001 – 2002	Fan mist-blower	Time and place of application, type and amount of substances.	(3)	Appendix A Table A4



Figure 6: Pesticide application with a fan mist-blower in the steep vineyards of the study area.

3.2 Sampling strategy

3.2.1 Sampling sites

Eight monitoring sites were chosen in the area of study according to the following criteria:

- In order to investigate the atmospheric dispersion of pesticides, different types of sites had to be included: rural, industrial and urban sites.
- Sites had to be accessed at any time and be protected from vandalism.
- Air samplers could be installed only where power supply was available (except for the portable low volume air sampler, see par. 3.2.2.2).

An overview of the geographic position of the sampling sites is given in Figure 7, while the main characteristics of the stations are summarised in Tables 6 and 7.

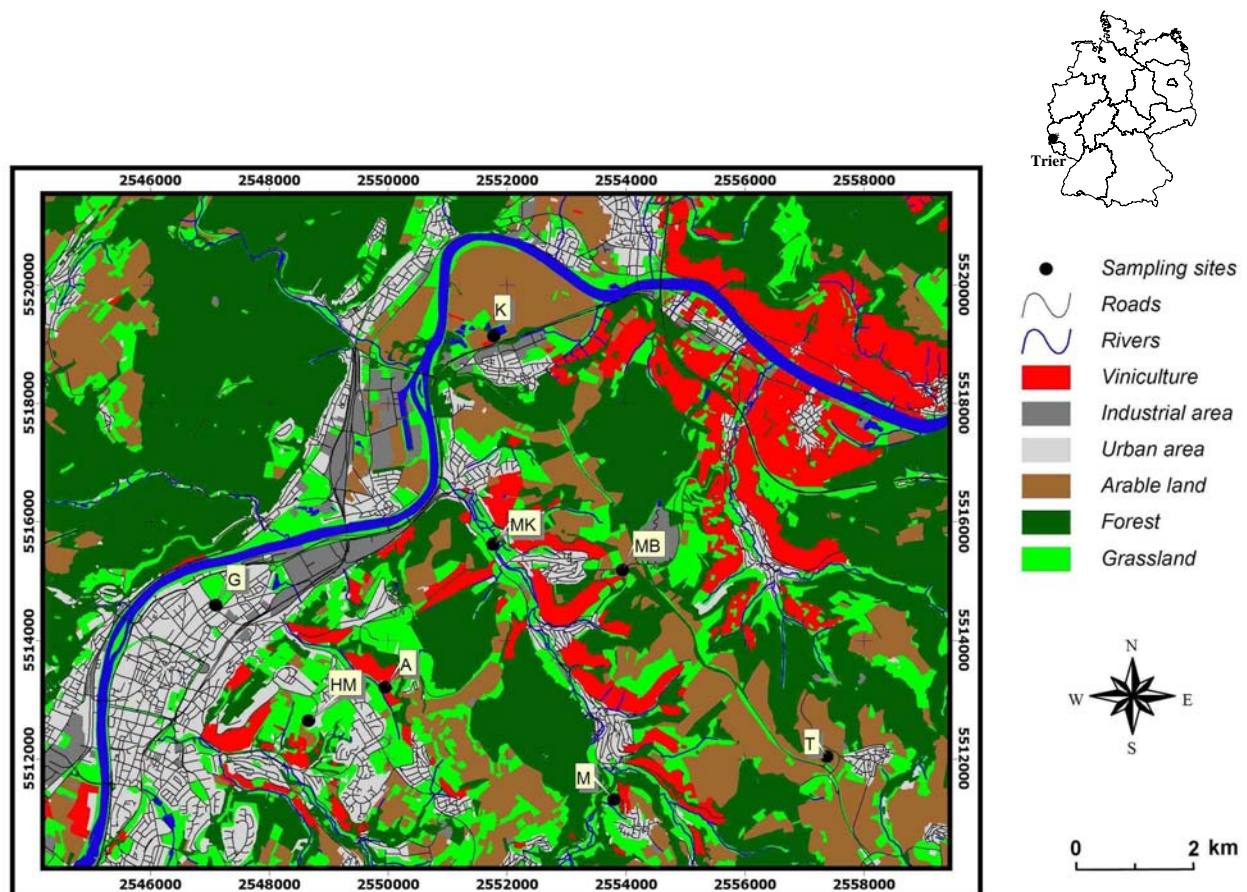


Figure 7: Area of study and sampling sites. Geospatial reference data (ATKIS - Basis - DLM; DGM) published with the permission of the Land Survey Office (Landesvermessungsamt) Rheinland-Pfalz, 06.10.2000 - Az.: 26 722-1.11; ESRI Data & Maps (2000).

A – Avelsbach

The station was located in the Avelsbach wine-growing domain, at an altitude between the Mosel valley and the plateaux. It was equipped with a rain sampler from May 2000 until September 2002. In order to avoid the direct contamination by drift during pesticide applications, the rain sampler was located ca. 250 m from the vineyards where pesticides were applied. From May until September 2002 the station was also equipped with two air samplers (portable low volume and PM₁₀ low volume, see 3.2.2.2). The portable low volume air sampler was located in the vineyards (sampling site: **W**) where pesticides were applied, the PM₁₀ low volume air sampler was installed at about 100 m from the edge of the closest vineyards where pesticide applications were performed (sampling site: **AA**). Pesticides were applied exclusively with fan mist-blowers. Data on type and amount of used pesticides and time of application performed in the area of the domain are reported in Appendix A, Table A4.

The site was also equipped with a meteorological station of the agro-meteorological measuring network of the Rheinland-Pfalz State (located ca. 50 m from the PM₁₀ low volume air sampler and ca. 150 m from the rain sampler) and, from April till September 2002, with a meteorological station installed next to the portable low volume air sampler (site W) in collaboration with the department of Climatology of the University of Trier (see Table 7).

G – Grünflächenamt (Office for Green Areas)

The station was located in the Northern part of the town, at the site of the Office for Green Areas. It was equipped with a rain sampler from May 2000 until September 2002 and it represented the atmospheric deposition of the urban area. No pesticide applications were carried out in the vicinity.

H – Geo-centre

The station was located nearby the department of geography at the University of Trier. No vineyards were in the vicinity of the sampling site, but west of the site was located the wine-growing area of the Olewiger valley. The station was equipped with a rain sampler from May 2000 until September 2002 and with an air sampler (high volume air sampler, see 3.2.2.2) from May until September 2002. The equipment with a high-volume air sampler was required because of the expected low air concentration levels of the analysed substances, especially in areas where no direct applications are performed (DFG 2000).

The site was also equipped with the meteorological station of the department of Climatology of the University of Trier (located ca. 10 m from the rain and air samplers) (see Table 7).

K – Kenn

The station was located in the “Trierer Talweite”, north-east of Trier, in the industrial area of Kenn. The rain sampler, installed from May 2000 until September 2002, was built up at ca. 800 m from the motorway A602 and at the border between a farmed area (major crop: maize) and a nature reserve. No information about pesticide applications performed on the farmed area could be obtained.

M – Morscheid

The sampling site was located in the area of the “Schloss Marienlay” winery, at Morscheid, in the Ruwer valley. The station was equipped with a rain sampler from June 2000 until September 2002. In order to avoid the direct contamination by drift during pesticide applications, the rain sampler was built up at ca. 0,5 km from the vineyards. Given the elevated inclination of the vineyards at this site, pesticide were applied only by means of hand-held spray guns. Type and amount of applied substances are reported in Appendix A, Table A3.

MB – Mertesdorf Berg

The station was located on the plateaux of the Ruwer valley, in the district of Mertesdorf. The area was used as grassland during the whole period of study. The station was equipped with a rain sampler from June 2000 until September 2002.

MK – Mertesdorf Kläranlage

The station was located in the area of the water treatment plant of Mertesdorf, in the Ruwer valley. No vineyards were in the vicinity of the station. The station was equipped with a rain sampler from June 2000 until September 2002.

From January 2001 until September 2002 the site was equipped with a precipitation counter in collaboration with the department of Soil Sciences of the University of Trier (see Table 7).

T – Thomm

The station was located on the plateaux of the Ruwer valley, in the district of Thomm. The area was used as grassland during the whole period of study. The rain sampler, installed at this site from June 2000 until September 2002, was located ca. 1 km from farmed fields (major crops: maize, wheat, cereals). No information about pesticide applications performed on the farmed area could be obtained.

Table 6: Summary of the characteristics of the sampling sites.

Sampling site	Elevation (m)	Description	Equipment
A – Avelsbach	227,8	Vineyard	Rain sampler, air sampler, meteorological station
G – Grünflächenamt	130,3	Urban area	Rain sampler
H – Geo-centre	261,3	Residential area	Rain sampler, air sampler, meteorological station
K – Kenn	136,7	Industrial area	Rain sampler
M – Morscheid	173,8	Vineyard	Rain sampler
MB – Mertesdorf Berg	329,8	Rural area	Rain sampler
MK – Mertesdorf Kläranlage	140,6	Rural area	Rain sampler, precipitation counter
T – Thomm	457,7	Rural area	Rain sampler

Table 7: Meteorological stations.

Location	Sampling site	Ownership	Measured Parameters
Geo-centre	H	Dep. of Climatology Univ. of Trier	Ambient temperature, relative humidity, precipitation, solar radiation, wind speed, wind direction
Avelsbach	A	Rheinland-Pfalz State	Ambient temperature, relative humidity, precipitation, solar radiation, wind speed
Avelsbach	W	Dep. of Climatology Univ. of Trier	Wind speed, wind direction
Mertesdorf	MK	Dep. of Soil Sciences, Univ. of Trier	Precipitation

3.2.2 Sampling equipment

3.2.2.1 Rain sampler

The rain samplers (Figure 8) were built by the locksmiths of the University of Trier. A stainless steel surface (LAWA 1998) of ca. 0,44 m², delimited by a 3-cm-high edge, was used as catch basin. The surface had a slight inclination towards one corner that allowed the rain to be collected, by means of a darkened Teflon tube, into a 4-litre brown glass bottle. The catch basin was at about 1,50 m from the ground. The Teflon tube was covered with dark tape to prevent the growing of algae and bacteria cultures. The brown glass bottle was inserted in a hard-foam isolating box in order to avoid photo-degradation of the substances, growing of algae and bacteria cultures and to reduce temperature variations of the sample. The opening on the cap for the connection with the Teflon tube was kept as small as possible to reduce any evaporation of the sample (DVWK 1984). The construction design of the sampler allowed the collection of bulk samples (no distinction could be made between wet and dry deposition). Furthermore, a precise determination of the fallen amount of rain (mm) could not be possible by means of these samplers because of the impossibility of taking into account the following losses:

- Losses due to evaporation occurred on the stainless steel surface (during days with elevated and prolonged solar radiation the temperature of the metal surface increased considerably).
- Losses due to splashes of rain drops over the edge (especially during heavy rain events).
- Losses due to the impossibility of collecting more than 4 litres of rainwater per sampling.

Data on precipitation amount (mm) were obtained from three meteorological stations available in the area (see Table 7).



Figure 8: Rain sampler in Thomm.

3.2.2.2 Air samplers

Air samples were collected using three different devices: portable low-volume, high-volume and PM₁₀ low-volume air sampler. The portable low-volume and the high-volume air samplers were designed and assembled at the University of Trier (as a result of the collaboration of the departments of hydrology and electronics with the electricians and locksmiths of the campus) in accordance with the design of the air samplers generally used by the scientific community (GLOTFELTY *et al.* 1990b, HAWTHORNE *et al.* 1996, CORTES *et al.* 1998, FOREMAN *et al.* 2000, KARLSSON *et al.* 2000, TSAI *et al.* 2002). The PM₁₀ low-volume sampler is the Partisol 2000 (R+P Co., Inc.) equipped with a PM-10 size-selective inlet designed to collect particles with an aerodynamic diameter less than 10 µm (PM₁₀). All samplers consisted of filters to collect airborne particles followed by polyurethane foam (PUF) plugs that were positioned in series to collect gas-phase pesticides. Polyurethane foam was selected as the sorbent material in this study because it allows the high sampling flows needed for a high-volume sampler and because its use for the collection of semivolatile pesticides has been well documented in the literature (BARRIE *et al.* 1993, BURGOYNE & HITES 1993, WHANG *et al.* 1993, ZABIK & SEIBER 1993, HAWTHORNE *et al.* 1996, KARLSSON *et al.* 2000). The sampling head was at about 1,80-2,00 m from the ground.

A general scheme of the air samplers is given in Figure 9.

Table 8 contains a summary of the technical details of each air sampler.

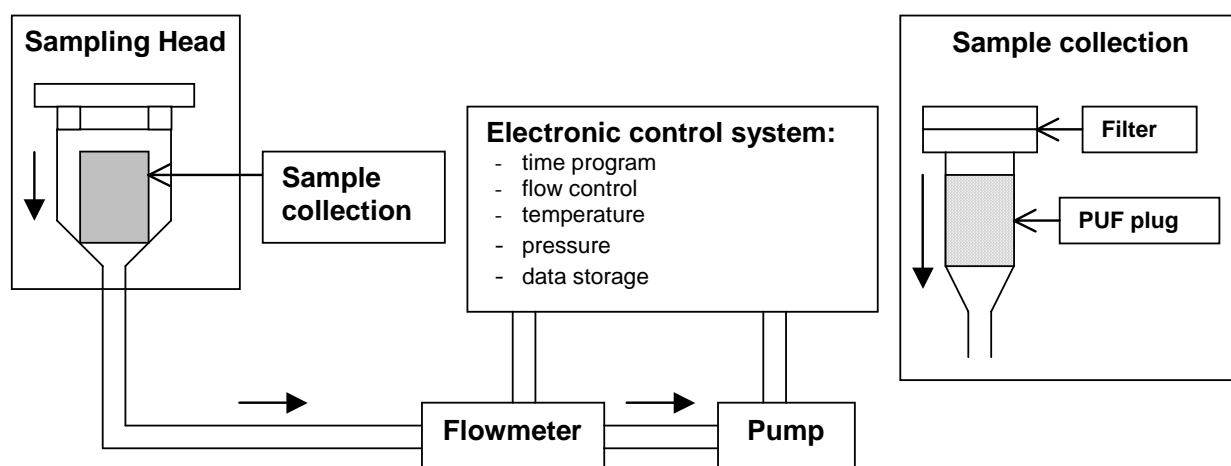


Figure 9: General scheme of the air samplers.

The electronic flow meters, installed on the portable low-volume sampler and on the Partisol 2000, converted automatically the value of the sampled volume into a standard volume value (V_{Std}). The V_{Std} is necessary to report mass concentration data referenced to standard cubic meters of air based on a standard temperature of 25 °C and standard pressure of 1 atmosphere (US-EPA standard conditions).

The high volume device was equipped with a rotary-piston gas meter and a standardisation of the volume of sampled air was manually calculated as follows:

$$V_{Std} = \frac{P_s \times V_s \times (273,15 + t_{Std})}{P_{Std} \times (273,15 + t_s)}$$

where: P_s = average pressure during sampling (atm) P_{Std} = standard pressure (1 atm)

V_s = volume of sampled air (m^3) V_{Std} = standard volume of sampled air (m^3)

t_s = average temperature during sampling ($^{\circ}C$) t_{Std} = standard temperature (25 $^{\circ}C$)

Table 8: Technical data of the air samplers.

	Portable low-volume	High-volume	Partisol 2000
Manufacturer	University of Trier		R+P Co., Inc.
Type of Sample	TSP ^(c) and gas-phase	TSP ^(c) and gas-phase	PM ₁₀ and gas-phase
Pump details:			
Nominal flow ^(a)	20 l min ⁻¹	40 m ³ h ⁻¹	---
Working flow ^(b)	15,5 l min ⁻¹	30 m ³ h ⁻¹	1 m ³ h ⁻¹
Flow meter	Thermic	Rotary-piston gas meter	?
Temperature-pressure volume correction	Yes	No	Yes
Filter	quartz filter	glass-fiber filter	glass-fiber filter
Filter diameter	27 mm	70 mm	47 mm
Pore size	ca. 0,6 μ m	ca. 0,6 μ m	ca. 0,6 μ m
PUF diameter	22 mm	70 mm	27 mm
PUF length	75 mm	50 mm	75 mm
Operation mode	Programmable by time and day	Programmable by time and day	Programmable by time and day
Power source	Battery and power supply network	Power supply network	Power supply network

^(a) Maximum operating flow without adsorbing media (filter and PUF) declared by the manufacturer.

^(b) Maximum operating flow with adsorbing media (filter and PUF).

^(c) Total Suspended Particles.

3.2.3 Sample collection

3.2.3.1 Rain samples

Rainfall was accumulated for a period of one week, and then the sampling bottles were removed, the catch basins were rinsed with distilled water and clean sampling bottles were connected to the samplers. Samples were collected from 2000 till 2002 during the following periods:

- May 2000 – November 2000
- Mid-April 2001 – October 2001
- Mid-April 2002 – September 2002

3.2.3.2 Air samples

Because of technical reasons air samples could be collected only as of May 2002. Seven air sampling campaigns were carried out between May and September 2002 at the sites Geo-centre (H) and Avelsbach (A and W). The campaigns started between 1 h and 24 h after pesticide applications performed in the wine-growing domain of Avelsbach. The duration of the sampling campaigns varied from three to five days depending upon weather conditions: the occurrence of a rain event during the campaign caused its termination. Sampling times varied from 1 h to 24 h according to the following strategy:

- Immediately after application: short sampling times (1-6 h) were chosen in order to investigate the temporal variations of air concentrations of the applied substances on a detailed basis.
- 24 h after application: longer sampling times (8-24 h) were chosen in order to allow for the detection of lower air concentrations resulting from the atmospheric dispersion of the applied substances.

3.3 Analytical methods

The analytical methods were designed to determine multiple classes of pesticides in rain water, particle- and gas-phase samples (in accordance with the DFG (2000)).

3.3.1 Analysed substances

The main goal of the study was the assessment of the level of atmospheric pollution of the area due to the use of pesticides. The final list of analysed substances was compiled on the grounds of the following considerations:

- Fungicide products are the most frequently used pesticides in vinicultural areas (see par. 3.1.3).
- Previous research studies (RÜBEL *et al.* 1998, RÜBEL 1999, RIEFSTHAL 2000) pointed out the occurrence of a variety of pesticides in the area of Trier which have been used in the past years.
- Data on pesticide applications carried out in 1999 and 2000 (Appendix A, Tables A1-A3) revealed the use of different/new products in comparison to the past years.
- The methodology for the extraction and analysis of the substances had to be practicable in the framework of the project, where a multiresidue analysis method for the routine analysis of a high number of samples was foreseen.

Altogether, 24 active ingredients and 3 metabolites were chosen as representative substances for this study (Table 9).

Although the fungicides dithianon, cymoxanil, metiram and mancozeb along with the herbicides glyphosate and glufosinate are commonly applied in the region, they were excluded from the monitoring program because of analytical reasons. The inorganic sulphur- and copper-compounds were also not considered for analysis. Other substances, whose use is not allowed in the viniculture (like the triazine herbicide terbuthylazine and the fungicide triadimefon) or which are banned in Germany (atrazine and simazine), were included in the study on the grounds of the results obtained by RÜBEL (1999) and RIEFSTAHL (2000) which pointed out the presence of these substances in runoff water, soil and rain water samples collected in the area of Trier. Furthermore, the use of pesticide products containing these substances is still allowed in the neighbouring countries like France, Luxembourg and Belgium and the hypothesis of an atmospheric transport from those areas cannot be ruled out.

The seven fungicides marked in light grey in Table 9 were added to the monitoring program in a second phase of the project, and samples were analysed for these substances as of year 2001.

The investigated substances belong to different chemical groups and their physico-chemical properties differ greatly from each other as shown in Table 10. The chemical structures are illustrated in Appendix B.

Table 9: Active ingredients and metabolites analysed in the framework of the project. (Classes: H = herbicide, M = metabolite, F = fungicide, I = insecticide, A = acaricide).

Active ingredient	Class	Abbreviation	Chemical group	Reference
Atrazine	H	ATR	Triazine	RÜBEL (1999), RIEFSTAHL (2000)
Cyprodinil	F	CYP	Anilinopyrimidine	PERMESANG (2000)
Desethylatrazine	M	DEA	Metabolite	RÜBEL (1999), RIEFSTAHL (2000)
Desethylterbuthylazine	M	DET	Metabolite	RÜBEL (1999), RIEFSTAHL (2000)
Desisopropylatrazine	M	DIA	Metabolite	RÜBEL (1999), RIEFSTAHL (2000)
Dichlofluanid	F	DIC	Sulphamide	RÜBEL (1999), RIEFSTAHL (2000)
Dichlorvos	I	DCV	Organophosphorus	RÜBEL (1999), RIEFSTAHL (2000)
Diethofencarb	F	DIE	N-phenyl carbamate	RÜBEL (1999), RIEFSTAHL (2000)
Ethyl parathion	I, A	PET	Organophosphorus	RÜBEL (1999), RIEFSTAHL (2000)
Fenarimol	F	FEN	Pyrimidine	MADER (2000), PERMESANG (2000)
Fludioxonil	F	FLO	Phenylpyrrole	PERMESANG (2000)
Fluquinconazole	F	FLU	Triazole	MADER (2000)
Folpet	F	FOL	Phthalimide	PERMESANG (2000)
Kresoxym-methyl	F	KRE	Strobilurin	MADER (2000), PERMESANG (2000)
Metalaxyl	F	MTX	Acylalanine	PERMESANG (2000)
Methidation	I	MET	Organophosphorus	RÜBEL (1999), RIEFSTAHL (2000)
Methyl parathion	I	PME	Organophosphorus	RÜBEL (1999), RIEFSTAHL (2000)
Penconazole	F	PEN	Triazole	RÜBEL (1999), RIEFSTAHL (2000)
Procymidone	F	PRO	Dicarboximide	RÜBEL (1999), RIEFSTAHL (2000)
Pyrifeno [*]	F	PYR	Pyridine	RÜBEL (1999), RIEFSTAHL (2000)
Quinoxifen	F	QUI	Quinoline	MADER (2000), PERMESANG (2000)
Simazine	H	SIM	Triazine	RÜBEL (1999), RIEFSTAHL (2000)
Tebuconazole	F	TEB	Triazole	RÜBEL (1999), RIEFSTAHL (2000)
Terbuthylazine	H	TER	Triazine	RÜBEL (1999), RIEFSTAHL (2000)
Triadimefon	F	TRF	Triazole	RÜBEL (1999), RIEFSTAHL (2000)
Triadimenol [*]	F	TRL	Triazole	RÜBEL (1999), RIEFSTAHL (2000)
Vinclozoline	F	VIN	Dicarboximide	RÜBEL (1999), RIEFSTAHL (2000)

^{*} Determined as sum of two isomers (pyrifeno^{*} I + II, triadimenol A + B)

Table 10: Physico-chemical properties of the investigated substances (TOMLIN 2000, IVA 2000).

Active ingredient	Molecular Weight	Vapour pressure (mPa, 25 °C)	Log Kow (25 °C)	Water solubility (mg l ⁻¹ , pH 7, 25 °C)	Henry's law constant (Pa m ³ mol ⁻¹)
Atrazine	215,7	$3,85 \times 10^{-2}$ $4,0 \times 10^{-2}$ (20 °C)	2,34	33 (20 °C)	$1,5 \times 10^{-4}$ (C)
Cyprodinil	225,3	$4,7\text{-}5,1 \times 10^{-1}$	3,9-4,0	13	$6,6\text{-}7,2 \times 10^{-3}$ (C)
Desethylatrazine	-	$1,23 \times 10^{-4}$	1,51	3200 (22 °C)	-
Desethylterbutylazine	-	-	-	-	-
Desisopropylatrazine	-	$2,78 \times 10^{-4}$	1,15	670 (22 °C)	-
Dichlofluanid	333,2	0,014 (20 °C)	3,7 (21 °C)	1,3 (20 °C)	$3,6 \times 10^{-3}$ (C)
Dichlorvos	221,0	$2,1 \times 10^3$	1,9	ca. 8800 (20 °C)	$2,58 \times 10^{-2}$ (E)
Diethofencarb	267,3	8,4 (20 °C)	3,02	26,6 (20 °C)	$8,44 \times 10^{-2}$ (C)
Ethyl parathion	291,3	0,89 (20 °C)	3,83	11 (20 °C)	0,0302
Fenarimol	331,2	$6,5 \times 10^{-2}$	3,69	13,7	$1,57 \times 10^{-3}$ (C)
Fludioxonil	248,2	$3,9 \times 10^{-4}$	4,12	1,8	$5,4 \times 10^{-5}$ (C)
Fluquinconazole	376,2	$6,4 \times 10^{-6}$ (20 °C)	3,24 (20 °C)	1,2 (pH 6,6, 20 °C)	$2,09 \times 10^{-6}$ (E)
Folpet	296,6	$2,1 \times 10^{-2}$	3,11	0,8	$7,8 \times 10^{-3}$ (C)
Kresoxym-methyl	313,4	$2,3 \times 10^{-3}$ (20 °C)	3,4	2 (20 °C)	$3,6 \times 10^{-4}$ (E)
Metalaxyl	279,3	0,75	1,75	7100 (20 °C)	$1,6 \times 10^{-5}$ (C)
Methidation	302,3	$2,5 \times 10^{-1}$ (20 °C)	2,2	200	$3,3 \times 10^{-4}$ (C)
Methyl parathion	263,2	0,41 0,2 (20 °C)	3,0	55 (20 °C)	$8,57 \times 10^{-3}$ (E)
Penconazole	284,2	0,37 0,17 (20 °C)	3,72	73 (20 °C)	$6,6 \times 10^{-4}$ (C)
Procymidone	284,1	18	3,14 (26 °C)	4,5	-
Pyrifenox	295,2	1,7	3,4-3,7	3,7	$5,8 \times 10^{-3}$ (C)
Quinoxifen	308,1	$2,0 \times 10^{-2}$ $1,2 \times 10^{-2}$ (20 °C)	4,66 (20 °C)	0,116 (pH 6,45, 20 °C)	$3,19 \times 10^{-2}$ (C)
Simazine	201,7	$2,94 \times 10^{-3}$	2,1	6,2 (20 °C)	$5,6 \times 10^{-5}$ (C)
Tebuconazole	307,8	$1,7 \times 10^{-3}$ (20 °C)	3,7 (20 °C)	36 (20 °C)	1×10^{-5} (E) (20 °C)
Terbutylazine	229,7	0,15	3,21	8,5 (20 °C)	$4,5 \times 10^{-3}$ (C)
Triadimefon	293,8	0,06 0,02 (20 °C)	3,11	64 (20 °C)	9×10^{-5} (E) (20 °C)
Triadimenol (A, B) Ratio A:B = 7:3	295,8	A: 6×10^{-4} (20 °C) B: 4×10^{-4} (20 °C)	A: 3,08 B: 3,28	A: 62 B: 33 (20 °C)	A: 3×10^{-6} (E) B: 4×10^{-6} (E) (20 °C)
Vinclozolin	286,1	0,13 (20 °C)	3	2,6 (20 °C)	-

(C) Calculated value, (E) Experimental value.

3.3.2 Sample storage, preparation and extraction

3.3.2.1 Rain matrix

After collection, all samples were brought to the laboratory and immediately prepared for extraction. According to the results obtained by several studies dry deposition contributes very little to the bulk pesticide deposition (ATLAS & GIAM 1988, GLOTFELTY *et al.* 1990b, NATIONS & HALLBERG 1992, SIEBERS *et al.* 1994, DÖRFLER & SCHEUNERT 1997, BUCHELI *et al.* 1998, MAGUHN *et al.* 2002). Therefore, while the sampling technique allowed wet and dry deposition to collect, precipitation samples were vacuum-filtered through glass-fiber filters GF-4 (MN, 1,4 µm nominal pore size) and only the aqueous phase was analysed. 500 ml of the filtrate were transferred to a 500-ml pre-cleaned brown-glass bottle and stored overnight at 4 °C in the dark for pesticide analysis. All samples were extracted within one day of collection. The filters were oven dried at 50 °C for 24 h and stored in a dry keeper box for mass determination of the collected particle deposition.

The method used for extraction of pesticides from the rain matrix was based on the solid-phase extraction (SPE) method used by RÜBEL (1999). The method was modified and optimised within the project. Various adsorbing materials with different properties were tested: HR-P (Chromabond MN and Baker), C18 ec (Baker), C18 polar plus (Baker), C18 Hydra (Chomabond MN) and ENV+ (Separtis AG). The material C18 Hydra (see technical details in the box on the right in Figure 10) revealed to be more suitable than the C18 ec (used by RÜBEL (1999)) for the analysis of slightly polar substances. It presented the highest recovery rates for most of the investigated substances, in particular for the fungicide compounds. Recovery experiments with laboratory spike blanks were carried out to validate the final method illustrated in Figure 10. The laboratory spike blanks were prepared by fortifying different amounts (50-200 ng) of standard solutions containing the 27 pesticides and 2 internal standards (d5-atrazine and sebuthylazine) into 500 ml of distilled water. Percentage recoveries determined for the investigated substances are shown in Table 11.

The low recovery obtained for quinoxifen can be explained with the low water solubility of this compound. Experiments carried out by spiking a standard solution directly into the solid phase extracting columns gave a recovery value for quinoxifen of 91% (std. dev. 7%). It can be assumed that the procedure by which the laboratory spike standards were prepared did not allowed a complete dissolution of this compound into the water matrix, therefore affecting the effectiveness of the extraction.

Folpet was never detected in the recovery experiments performed with the laboratory spike blanks, although the recovery rate obtained with the direct spike into the extracting columns was 80% (std. dev. 26%). Two major factors may have affected the recovery experiments for

this compound: low water solubility and low sensitivity of the analytical system for this specific compound (see limit of detection in Table 13).

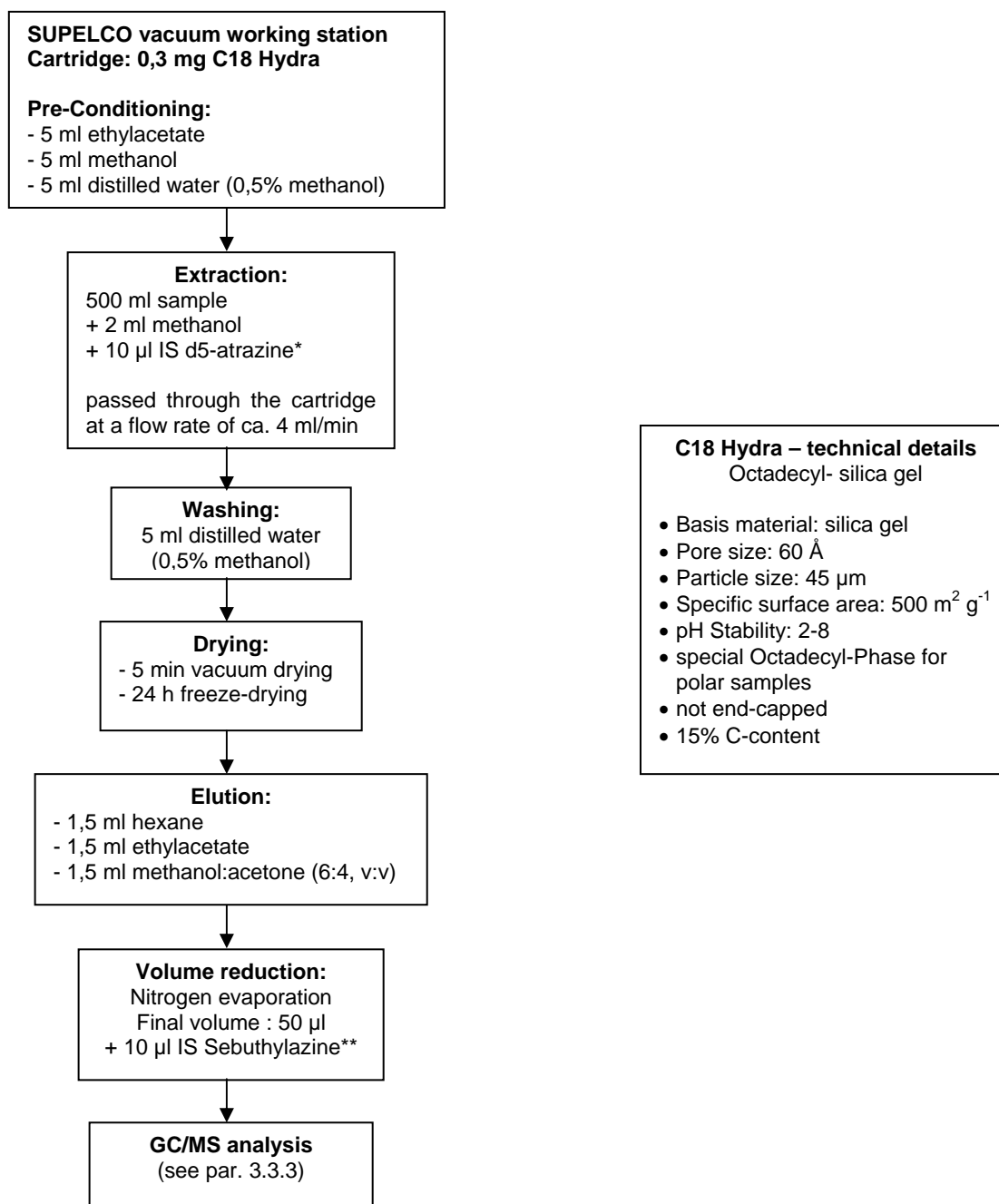


Figure 10: Analytical method for the extraction of pesticides from the rain matrix.

(*Internal standard d5-atrazine, 10 ng/µl; **internal standard Sebuthylazine, 10 ng/µl)

3.3.2.2 Particulate matter and gas phase

- Particulate matter: the filters used to trap particulate matter were pre-cleaned by heating at 500 °C for 4 h. They were equilibrated in a dry keeper box at constant temperature and humidity conditions (t: 22-25 °C and rel. hum.: 20-45%) for 24 h and then weighed before use. After sampling, filters were placed in petri dishes, protected from light by means of aluminium foil and immediately returned to the lab. They were equilibrated for 24 h at the above mentioned conditions and finally weighed. The net mass filter loading was determined by subtracting the initial filter weight from the final filter weight (US-EPA reference method for the gravimetric determination of particulate matter). The gravimetric determination was performed with a Sartorius balance (precision: 0,01 mg). Filters were then stored at 4 °C in petri dishes in the dark until extracted.
- Gas phase: the PUF plugs used for the adsorption of substances dispersed in the gas phase were pre-cleaned for 24 h with hexane:acetone (1:1, v:v) using a Soxhlet apparatus. The plugs were dried under clean air and stored in sealed glass jars before use. After sampling, PUF plugs were placed in pre-cleaned brown glass jars (15 ml), sealed with Teflon lids, immediately returned to the lab and stored at 4 °C in the dark until extracted.

All samples (filters and PUF plugs) were extracted within two weeks after collection.

The analytical method for extraction of pesticides from the particulate and gas phase was developed and validated within the project. Several recovery experiments were performed with laboratory spike blanks by using three extraction procedures: soxhlet extraction, microwave extraction and sonication. The laboratory spike blanks were prepared by fortifying different amounts (50-100 ng) of a standard containing the 27 investigated pesticides and 2 internal standards onto clean filters and PUF plugs. The best recovery results were obtained with the method based on sonication. Further recovery experiments with laboratory spike blanks were made to validate the final method; recoveries obtained with the final method for the extraction of the target substances from filters and PUF plugs are listed in Table 11.

Before extraction, filters and PUF plugs were spiked with 100 ng of sebuthylazine as internal standard. Each sample was extracted using hexane:acetone (1:1, v:v) and 90 minutes of sonication, in three steps of 30 minutes each. After each extracting step, the solvent was removed and fresh solvent was added to the sample for the following extraction step. All three fractions were collected together and reduced to ca. 2 ml using a rotary vacuum evaporator and finally to 100 µl under a gentle stream of clean nitrogen. The extracts were transferred to autosampler vial inserts and analysed by gas chromatography as described in par. 3.3.3.

Table 11: Percentage recovery for rain, particle- and gas-phase samples.

Compound	Rain		Particle phase		Gas phase	
	(n = 7)		(n = 7)		(n = 5)	
	(%)	SD	(%)	SD	(%)	SD
d5-atrazine (IS)	105	5	90	7	-	-
Sebuthylazine (IS)	108	4	98	8	86	5
Atrazine	104	4	98	9	86	5
Cyprodinil	84	5	96	1	90	2
Desethylatrazine	94	8	101	8	87	5
Desethylterbuthylazine	96	14	99	8	86	4
Desisopropylatrazine	59	11	119	12	110	7
Dichlofluanid	84	23	130	7	116	4
Dichlorvos	60	5	120	8	105	17
Diethofencarb	90	8	110	11	90	5
Ethyl parathion	51	6	72	4	70	3
Fenarimol	86	4	93	1	93	5
Fludioxonil	84	9	65	1	95	4
Fluquinconazole	86	16	112	5	105	3
Folpet	-	-	80	9	92	12
Kresoxym-methyl	60	4	90	2	90	4
Metalaxyl	95	7	96	5	74	6
Methidation	95	6	110	7	99	5
Methyl parathion	54	11	102	6	76	2
Penconazole	91	7	99	8	85	4
Procymidone	99	3	96	8	84	3
Pyrifenox	94	10	101	6	86	4
Pyrifenox II	91	5	101	6	88	3
Quinoxifen	38	4	88	1	84	5
Simazine	97	15	101	9	90	6
Tebuconazole	90	7	107	8	93	4
Terbuthylazine	106	4	98	9	86	5
Triadimefon	108	3	95	7	86	6
Triadimenole	98	17	81	10	-	-
Vinclozoline	100	4	94	9	84	3

3.3.3 GC/MS analysis

All pesticide extracts were analysed using a Hewlett-Packard model 5890 Series II GC equipped with a 5970B mass spectrometer detector (MSD) in the selected-ion-monitoring mode (SIM). Positive identification for each detected species was based on correct retention time (within 0,05 min) of each monitored ion compared with standards and on the correct ratios of the integrated peak areas (within 20% of the expected value) for each ion compared with those of the standard compounds. Analytes were quantified using external standard solutions and corrected for extraction losses and volume changes using the internal standard (IS) d5-atrazine for the rain samples and sebuthylazine for the air samples. Operating conditions used for GC/MS analysis are described in Table 12; limits of detection and limits of determination of the methods are summarised in Table 13.

Table 12: GC/MS operating conditions.

GC:	HP 5890 Series II
MSD:	HP 5970B
Capillary column:	DB-5 MS (30 m; 0,25 i.d.; 0,25 film thickness; J&W Scientific)
Oven temperatures:	90 °C (1 min); 6 °C min ⁻¹ to 220 °C (0 min); 10 °C min ⁻¹ to 250 °C (5 min)
Injector temperature:	250 °C
Interface temperature:	250 °C
Detector temperature:	250 °C
Carrier gas:	Helium (4.6); 1,2 ml min ⁻¹
Injection:	2 µl, 1 min splitless
Detector settings:	El-Mode(70EV); SIM; Dwell-Time: 70 ms/mass

3.3.4 Quality control

Several control measures were taken in order to guarantee the quality of the results.

Laboratory

- Pesticide-grade solvents only were used for extraction.
- Glassware cleaning: all glassware used for pesticide analysis was first washed with detergents and then organically cleaned by rinsing with distilled water, then sequentially with acetone and hexane. It was oven dried at 130 °C for 4 hours and capped with clean lids or covered with aluminium foil for storage.

Rain samples

- Sampling bottles were cleaned by washing with detergent and rinsing with distilled water.
- Parallel extraction of blanks: one blank sample, prepared by adding 500 ml of distilled water to a clean brown-glass bottle used for pesticide analysis, was extracted every two batches of samples (one batch of sample was defined by the eight samples weekly collected) to control laboratory contamination. Pesticide residues were detected in less than 3% of the laboratory blanks.
- Stability test: three rain samples and three blanks were spiked with pesticide standards and stored, at ambient temperature and in dark conditions, for one week before extraction to determine the stability of the analysed substances during sampling. Recoveries after one week of storage remained above 90% for all substances except vinclozoline (62%) and dichlofluanid (0%), in agreement with the results obtained by RÜBEL (1999).
- The internal standard sebuthylazine, added at the end of the volume reduction process, was used as control standard and a ratio d5-atrazine/sebuthylazine was calculated for each sample.

Air samples

- Parallel extraction of laboratory air blanks: one PUF blank sample and one filter blank sample were extracted for each sampling campaign to control laboratory contamination. PUF plugs used for laboratory blanks included reused cleaned PUF from previous field samples. No pesticide residues were detected in any of the laboratory blanks.
- Field air blanks: three field air blanks were obtained throughout the study (one at each sampling site) and consisted of a clean filter and a PUF plug that were briefly placed in the air sampler to simulate field handling. No pesticide residues were detected in any of the field air blanks.
- Potential break-through: two collection efficiency tests were performed to monitor the migration of pesticides through the PUF plug. One test was carried out in the laboratory by spiking 100 ng of the 27 target compounds onto a cleaned PUF plug, adding a second clean PUF plug behind the front plug as back-up and drawing ambient air through the sampler at $15,5 \text{ l min}^{-1}$ for 24 h. The other test was carried out in the field during one of the hottest days of sampling: a back-up PUF plug was placed behind the front PUF plug and sampling was performed for 24 h at $30 \text{ m}^3 \text{ h}^{-1}$. No pesticide residues were detected in any of the back-up plugs.

GC/MS analysis

- The presence of the pesticides detected was confirmed in several of the sample extracts by running the analysis in the full-scan mode and matching the mass spectra with those of standard compounds.
- Quantitation of individual pesticides was calculated by means of four-point standard calibration curves. All curves showed linearity with R^2 values $> 0,97$. The instrument was recalibrated every 30 sample injections.

Table 13: Target ions (m/z), qualifier ions (m/z), limits of detection and limits of determination of the methods.

	Target/ Qualifier	Detection Limit	Limit of Determination			
			Rain	Air		
Compound		ng	ng l ⁻¹	Low Volume ^a ng m ⁻³	High Volume ^b ng m ⁻³	Partisol 2000 ^c ng m ⁻³
<i>d5-atrazine (IS)</i>	205/220	-	-	-	-	-
<i>Sebuthylazine (IS)</i>	200/229	-	-	-	-	-
Atrazine	200/215	0,1	10	1,1	0,013	0,407
Cyprodinil	224/225	0,05	5	0,5	0,007	0,204
Desethylatrazine	172/187	0,1	10	1,1	0,013	0,407
Desethylterbuthylazine	186/201	0,1	10	1,1	0,013	0,407
Desisopropylatrazine	173/158	0,2	20	2,2	0,027	0,814
Dichlofluanid	224/123	0,1	10	1,1	0,013	0,407
Dichlorvos	109/185	0,1	10	1,1	0,013	0,407
Diethofencarb	267/225	0,1	10	1,1	0,013	0,407
Ethyl parathion	291/109	0,1	10	1,1	0,013	0,407
Fenarimol	139/219	0,1	10	1,1	0,013	0,407
Fludioxonil	248/127	0,1	10	1,1	0,013	0,407
Fluquinconazole	340/342	0,1	10	1,1	0,013	0,407
Folpet	260/130	0,2	20	2,2	0,027	0,814
Kresoxym-methyl	206/116	0,05	5	0,5	0,007	0,204
Metalaxyl	206/160	0,05	5	0,5	0,007	0,204
Methidation	145/85	0,2	20	2,2	0,027	0,814
Methyl parathion	263/109	0,1	10	1,1	0,013	0,407
Penconazole	248/159	0,1	10	1,1	0,013	0,407
Procymidone	283/96	0,1	10	1,1	0,013	0,407
PyrifenoX	262/187	0,1	10	1,1	0,013	0,407
PyrifenoX II	262/187	0,1	10	1,1	0,013	0,407
Quinoxifen	237/272	0,05	5	0,5	0,007	0,204
Simazine	201/186	0,1	10	1,1	0,013	0,407
Tebuconazole	250/125	0,1	10	1,1	0,013	0,407
Terbuthylazine	214/229	0,1	10	1,1	0,013	0,407
Triadimefon	208/57	0,1	10	1,1	0,013	0,407
Triadimenole	112/168	0,1	10	1,1	0,013	0,407
Vinclozoline	285/198	0,1	10	1,1	0,013	0,407

^a Limit based on 9 m³ sampling volume (10 h sampling time)^b Limit based on 750 m³ sampling volume (24 h sampling time)^c Limit based on 24 m³ sampling volume (24 h sampling time)

4 Results and discussion

This project was developed at the University of Trier to address the lack of information on the impact that local applications of pesticides have on the environmental conditions of the area of Trier. The very first study on pesticides dispersed in the atmosphere of the area was carried out by RIEFSTAHL (2000), who collected rain samples between July and December 1999. On the basis of those results, the project was developed as illustrated in the following flow chart (Figure 11):

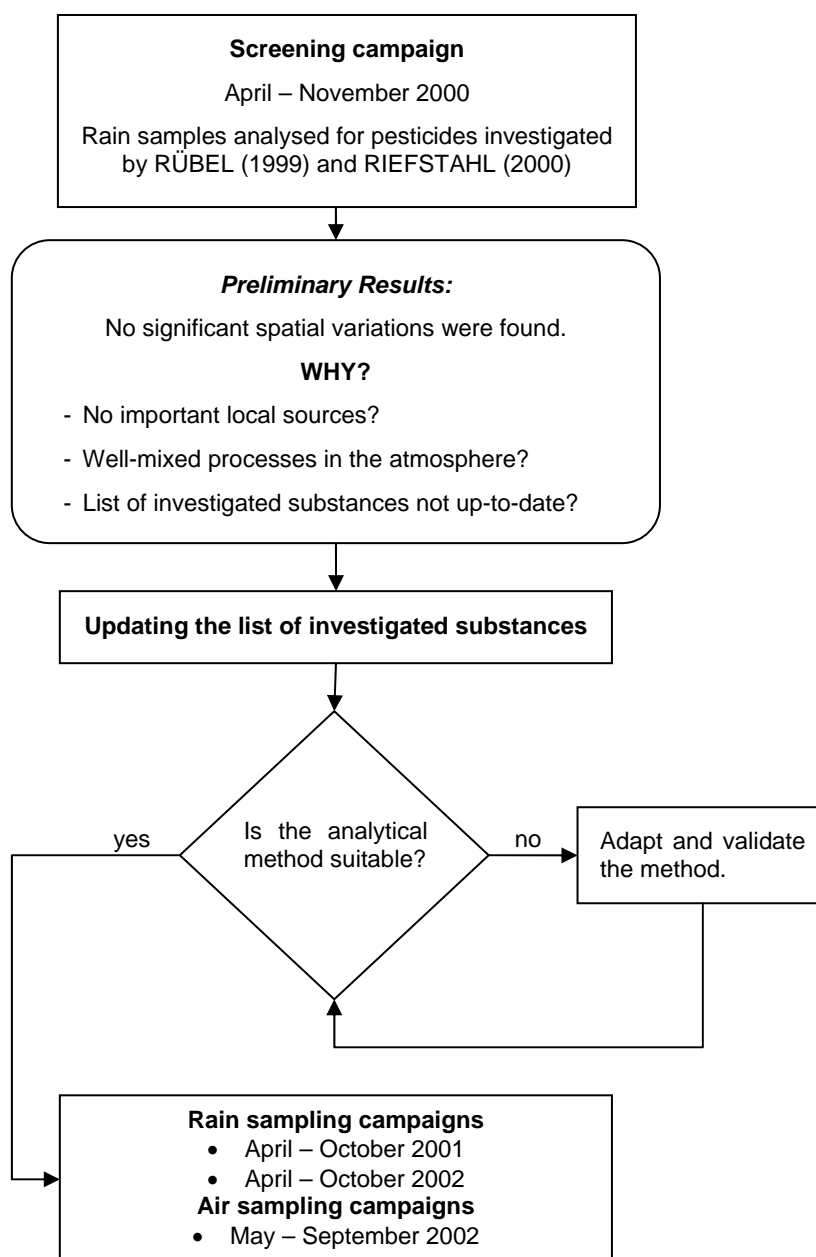


Figure 11: Flow chart of the development of the research project.

Since the study carried out by RIEFSTAHL (2000) started in the middle of the growing season (July 1999), the results obtained were not sufficient to gain information on the occurrence of pesticides in the atmosphere during the whole growing season. A screening sampling campaign was, therefore, the first necessary step of the present project. The screening campaign was carried out between May and November 2000 and rain samples were analysed for the pesticides investigated by RÜBEL (1999) and RIEFSTAHL (2000). The results (see par. 4.1) from this campaign were not in agreement with what is generally expected to be found in areas where emitting sources are present. The absence of significant spatial variations was the striking result of the campaign. The possible explanations for these findings were:

- There are no locally significant emitting sources.
- The locally emitted substances undergo a well-mixed process in the atmospheric boundary layer.
- The list of investigated substances is not up-to-date.

A comparison with the data on pesticide applications performed in the area of study in 2000 (see Appendix A) revealed the need of an updating of the list of the investigated substances. Seven fungicides were added to the list and the analytical methods were adapted and validated for the extraction and analysis of these compounds from rainwater and air samples. Rain sampling and air sampling campaigns were carried out in 2001 and 2002 and samples were analysed for the updated list of compounds (see par. 4.2 and par. 4.3).

In the next paragraphs, the results from these campaigns will be presented and discussed. Capital letters will be used to refer to the sampling sites (see Table 6).

4.1 Screening campaign

Rain samples were weekly collected from April through November 2000 and analysed for the pesticides investigated by RÜBEL (1999) and RIEFSTAHL (2000) (see Table 9, except the substances marked in light grey). Each rain sample was a composite of the precipitation events that occurred during the one-week collecting period. During the month of July, however, because of the occurrence of extremely prolonged rain events, samples were collected bi-weekly.

The results from the campaign are summarised in Table 14. Concentrations above limit of determination only ($> \text{LoD}$) were considered for calculation of the statistics given in the table. Substances which are not listed in the table were not detected in any of the samples. Sixteen of the 20 investigated pesticides were detected at least once in the 148 samples analysed. No average pesticide concentration exceeded 100 ng l^{-1} (the European Union drinking water

standard for single pesticide). Maxima also did not show extreme values and only atrazine and methyl parathion were measured at concentrations higher than 100 ng l⁻¹. The most frequently detected compounds were methyl parathion (58,1%), followed by the triazines atrazine (27,0%) and simazine (26,4%) and the metabolite desethylatrazine (25,0%).

Table 14: Statistics on pesticides detected in rainwater from May 2000 through October 2000 (ng l⁻¹, n = 148). Positive values only (> LoD) are considered.

Compound	mean	median	max	n > LoD	freq (%)
Herbicides					
Atrazine	82,1	69,5	228	40	27,0
Desethylatrazine	42,0	46,0	74	37	25,0
Desethylterbuthylazine	30,5	25,0	69	35	23,6
Simazine	29,8	31,0	42	39	26,4
Terbuthylazine	36,1	38,0	51	16	10,8
Insecticides					
Ethyl parathion	32,7	33,0	46	25	16,9
Methidation	-	-	11	1	0,7
Methyl parathion	45,4	45,0	131	86	58,1
Fungicides					
Dichlofluamid	34,2	28,4	72	17	11,5
Diethofencarb	25,9	20,5	64	14	9,5
Penconazole	20,9	21,0	36	19	12,8
Procymidone	24,9	30,8	37	15	10,1
Pyrifenox	-	-	73	2	1,4
Tebuconazole	44,5	46,5	76	40	21,6
Triadimefon	-	-	33	1	0,7
Vinclozoline	15,4	12,5	35	8	5,4

Overall, concentrations detected in 2000 were lower than those measured by Riefstahl in 1999, except for atrazine and desethylatrazine. At these latitudes, atrazine is generally applied as a maize herbicide during the spring months and its detection in rainwater is widely reported to be between mid April and July, with the highest concentrations measured in May and June (BUSER 1990, NATIONS & HALLBERG 1992, GEIßLER & SCHÖLER 1993, SIEBERS *et al.* 1994, BESTER *et al.* 1995, GOOLSBY *et al.* 1997, BUCHELI *et al.* 1998, SIEBERS & GOTTSCHILD 1998, MILLER *et al.* 2000, THURMAN & CROMWELL 2000). The fact that the sampling campaign in 1999 started in July accounts for the low concentrations found for atrazine and its metabolite. In 2000, atrazine and desethylatrazine maximum concentrations were detected in the months of May and June (Figure 12).

The detection of lower concentration levels than those measured by Riefstahl might find an explanation in the unusual weather conditions that occurred during the sampling campaign in 2000. Precipitation for July 2000 was reported as 229 mm compared to the average value of 70 mm measured in the area for that month. Approximately 3 times more precipitation fell in July 2000 than average, indicating that the measurements made at that time corresponded to a wetter than average period. Lower concentration levels might have been the direct consequence of a dilution effect occurred during the sampling of long rain events. By sequentially sampling single rain events, BUCHELI *et al.* (1998) found that the wash out of atrazine and other pesticides exhibited a so-called “first flush” effect and the concentration levels decreased by a factor of 10-20 within the first 2 mm of rain. As a consequence, rainfall occurring later during the event dilutes the concentration of the pesticides that were deposited during the early part of the event (NATIONS & HALLBERG 1992, GOOLSBY *et al.* 1997).

Concentrations of atrazine were similar to those detected in rainwater by BESTER *et al.* (1995) in northern Germany where no local sources could account for the presence of this compound in the atmosphere. The author suggested that the occurrence of atrazine was the result of atmospheric transport from countries where this compound was still applied like the Netherlands. By contrast, concentrations measured in Switzerland (BUCHELI *et al.* 1998), Greece (CHARIZOPOULUS & PAPADOPOULOU-MOURIKIDOU 1999) or in the USA (NATIONS & HALLBERG 1992, HATFIELD *et al.* 1996, GOOLSBY *et al.* 1997, MILLER *et al.* 2000), where atrazine was applied, showed maximum levels in the order of $\mu\text{g l}^{-1}$. Concentrations found for terbuthylazine in this study were similar to those found by BESTER *et al.* (1995) at the site where local use could be ruled out.

Concentrations of methyl parathion detected by RIEFSTAHL (2000) were higher than those measured in this study. The author reported a maximum concentration of $1,2 \mu\text{g l}^{-1}$ and median concentration of 105 ng l^{-1} . COUPE *et al.* (2000) reported median concentrations for methyl parathion in rainwater collected in urban areas (where methyl parathion is not registered for use) and agricultural areas (where the insecticide is heavily used) of Mississippi of 24 ng l^{-1} and 120 ng l^{-1} , respectively. Maximum concentrations were 300 ng l^{-1} at the urban sites and $22,9 \mu\text{g l}^{-1}$ at the agricultural site. CHARIZOPOULUS & PAPADOPOULOU-MOURIKIDOU (1999) found mean concentrations of methyl parathion of 250 ng l^{-1} in rain collected in the agricultural area of the Axios river basin where the insecticide is extensively used. The authors reported also a maximum concentration of $1,65 \mu\text{g l}^{-1}$, a value comparable to the findings of RIEFSTAHL (2000).

A comparison with available field measurements on fungicides from the literature is restricted to only a few substances as this class of compounds is not as widely investigated as herbicides and insecticides (see par. 2.5). A concentration range between 3 ng l^{-1} and

320 ng l⁻¹ and a mean of 100 ng l⁻¹ was reported for tebuconazole by HÜSKES & LEVSEN (1997) in the rain collected in Lower Saxony (Germany). SIEBERS *et al.* (1994) found mean concentrations for vinclozoline of 11 ng l⁻¹ and 16 ng l⁻¹ in Northern Germany.

Pesticides were detected from the beginning of sampling (mid-May) through the beginning of September showing a clear seasonal trend. They were rarely detected during October and then at very low concentrations. No pesticides were found in any samples collected in November. Concentrations had a very well defined temporal variation. Herbicides were detected from mid-May (the beginning of sampling) through the beginning of August, while fungicides and the insecticide methyl parathion were detected from mid-May through September. These trends show a strong concurrence with the pesticide application periods: herbicides are usually applied in spring, whereas fungicides and insecticides are applied from May through the growing season until the end of August, depending upon weather conditions. Figure 12 illustrates the time-series of the herbicides and metabolites (top graphic) and of some fungicides and the insecticide methyl parathion (bottom graphic) found at the site A. Similar trends were detected at all sampling sites.

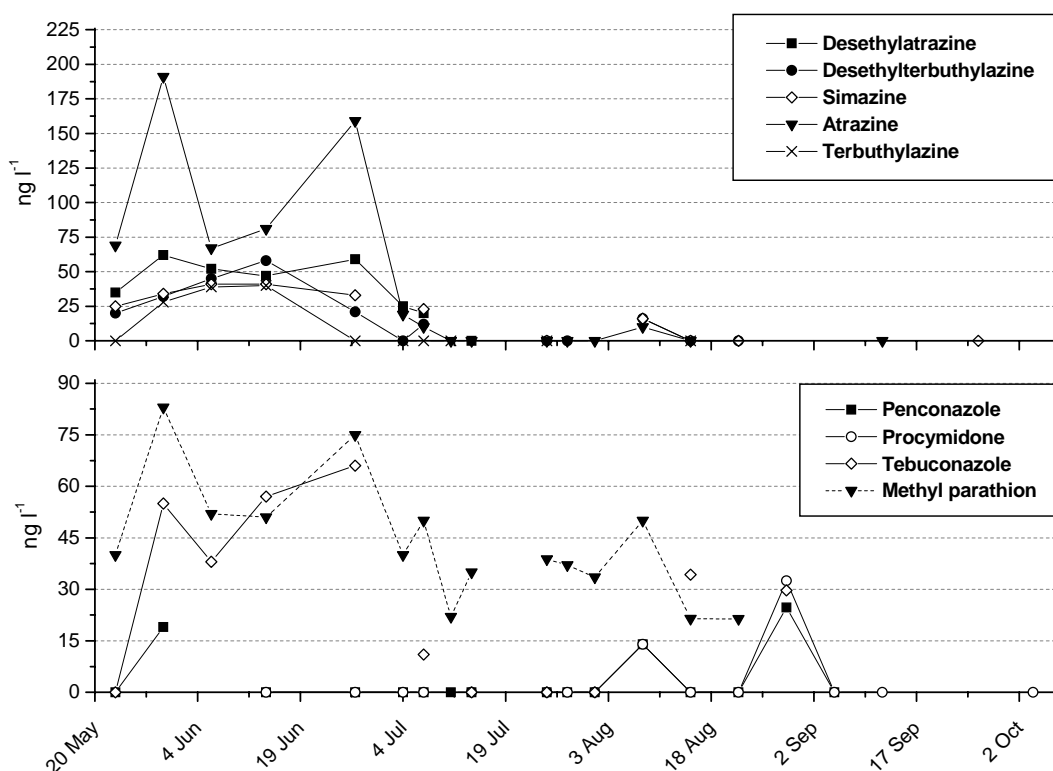


Figure 12: Time-series of herbicide and metabolite concentrations (top graphic), fungicide and methyl parathion concentrations (bottom graphic) in rainwater measured at the site A (vineyard). Zero values represent < LoD values.

No significant spatial variations could be observed for the investigated pesticides. Figure 13 depicts the time-series of the concentrations of three pesticides (atrazine, methyl parathion, tebuconazole) measured at all sampling sites over the whole sampling campaign. All triazines showed low differences from site to site, the highest differences were observed for atrazine on 27 June and 4 July (top graph). Methyl parathion (central graph) did not show evident spatial variations, though a more complicated pattern than atrazine could be observed. Tebuconazole (bottom graph) showed a similar pattern as atrazine during the first period of sampling (until the beginning of July), where low spatial variations could be observed, while as of mid July differences in concentrations from site to site seemed to gain significance.

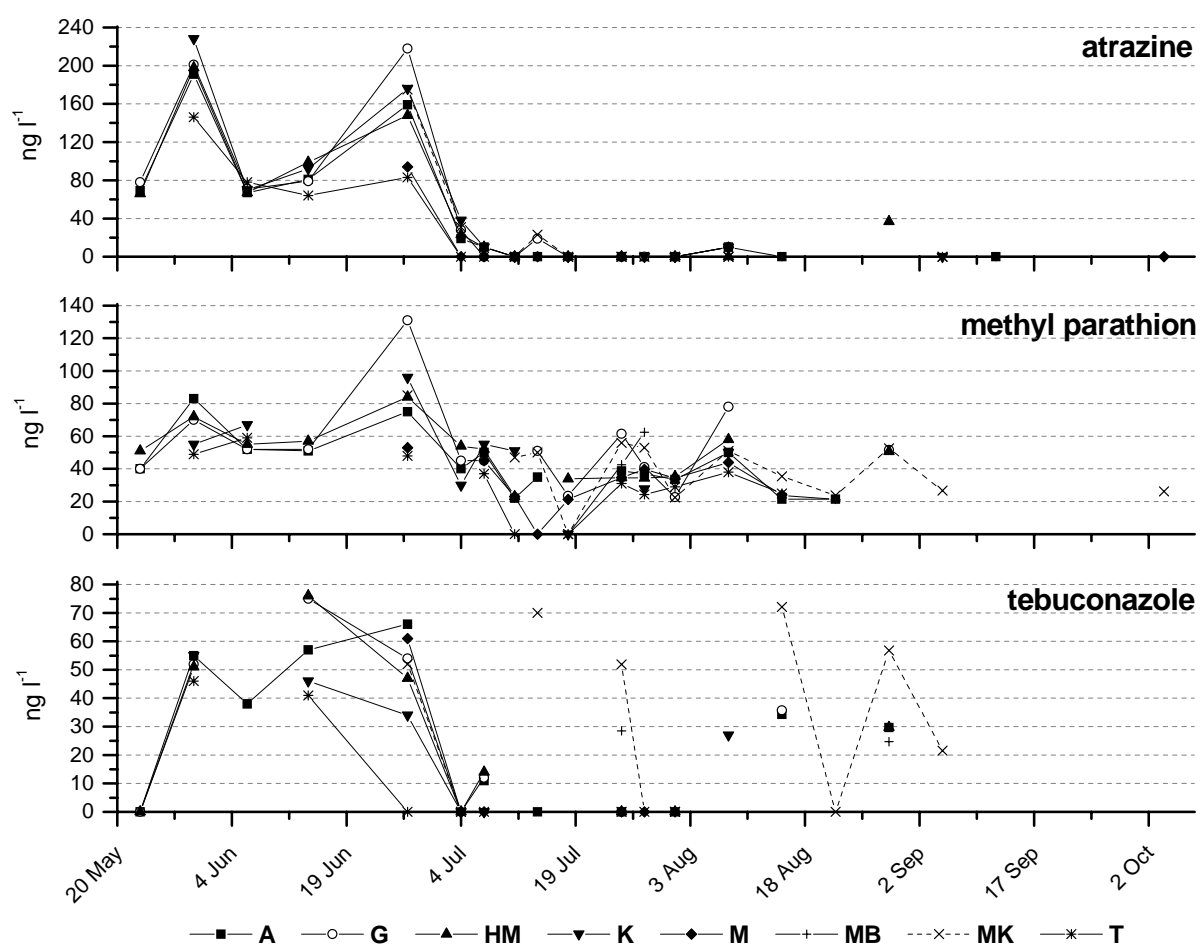


Figure 13: Spatial distribution of atrazine, methyl parathion and tebuconazole. Zero values represent < LoD values.

Overall, the triazines showed lower spatial variations than methyl parathion and tebuconazole. These results are in agreement with the fact that methyl parathion and tebuconazole are currently applied in the region, whereas atrazine, simazine and terbuthylazine are not expected to be used (atrazine has been banned in Germany since 1991 and simazine and terbuthylazine are not registered for use in the viniculture). However, though higher spatial variations could be observed for methyl parathion and tebuconazole, they were not very considerable since maximum concentration differences among the sampling sites were less than 150 ng l^{-1} . According to VAN DIJK & GUICHERIT (1999), if local sources dominate, a pesticide's concentration in air or precipitation may be highly variable, both in space and time. GEIßLER & SCHÖLER (1993) concluded, from precipitation analysis at four sampling sites near Cologne (Germany), that local sources must have been dominant, because input patterns differed greatly from site to site. COUPE *et al.* (2000) found that the total pesticide concentrations in rain were 5 to 10 times higher at the agricultural site than at the urban site.

A Kruskal-Wallis test (H-Test) was performed in order to evaluate the significance of the low spatial variations which were observed. The H-test is a nonparametric approach where no specific distributional model is assumed for the populations to be studied. By comparing the mean rank scores of k samples of sizes n_1, n_2, \dots, n_k , the Kruskal-Wallis statistic tests the null hypothesis of homogeneity, that is the k samples belong to the same population, against the alternative hypothesis that they are different. (KRISHNAIAH & SEN 1984)

The test was run on the pesticides which were more frequently detected during the sampling campaign, and the k samples were the 8 sampling sites. Positive values only were considered for calculation. The results of the Kruskal-Wallis test are given in Table 15. According to these results, the differences observed from site to site are statistically not striking enough to reject the hypothesis of homogeneity. It is noteworthy that the hypothesis was confirmed with a higher level of probability for atrazine and simazine than for methyl parathion and tebuconazole, being the asymptotic significance coefficients (light-grey-marked cells) for atrazine and simazine much higher than those calculated for methyl parathion and tebuconazole.

Table 15: Statistics from the Kruskal-Wallis Test.

	Atrazine	Simazine	Methyl parathion	Tebuconazole
Chi-Square	0,970	2,079	12,205	5,839
df	6	6	7	7
Asymptotic Significance	0,987	0,912	0,094	0,559

Level of significance $\alpha = 0,05$

Conclusions on the screening campaign

Pesticides detected in rainwater collected between May and November 2000 showed a marked temporal trend, but strikingly very low spatial variations. In areas where pesticides are applied, higher differences in concentrations than those found in this study are expected among urban, agricultural and industrial sites.

The variety of pesticides detected in this screening campaign was in agreement with the findings of RIEFSTAHL (2000) and RÜBEL (1999) and confirmed the use of different plant protection products in the region. However, the results obtained did not allow to draw conclusions on the impact of local use of pesticides on the atmosphere of the area. Evidences for local use could not be confirmed and the occurrence of most of the detected pesticides seemed rather to be the result of atmospheric transport processes.

In order to achieve the goals of the project, the list of investigated substances needed to be updated by taking into account the information on pesticide usage in the area available for the year 2000 (see Appendix A).

4.2 Rain sampling campaigns

Based upon the results from the screening sampling campaign, rain samples were weekly collected from mid April through November 2001 and from mid April through early October 2002, and analysed for all pesticides listed in Table 9. Each rain sample was a composite of the precipitation that occurred during the one-week collecting period.

4.2.1 Occurrence of pesticides

Figure 14 shows the frequencies of detection for pesticides measured during the two sampling campaigns, while the statistics on detected pesticides are listed in Table 16. Positive values only ($> \text{LoD}$) were considered for calculation. All the substances detected in the rain samples are listed in Table 16.

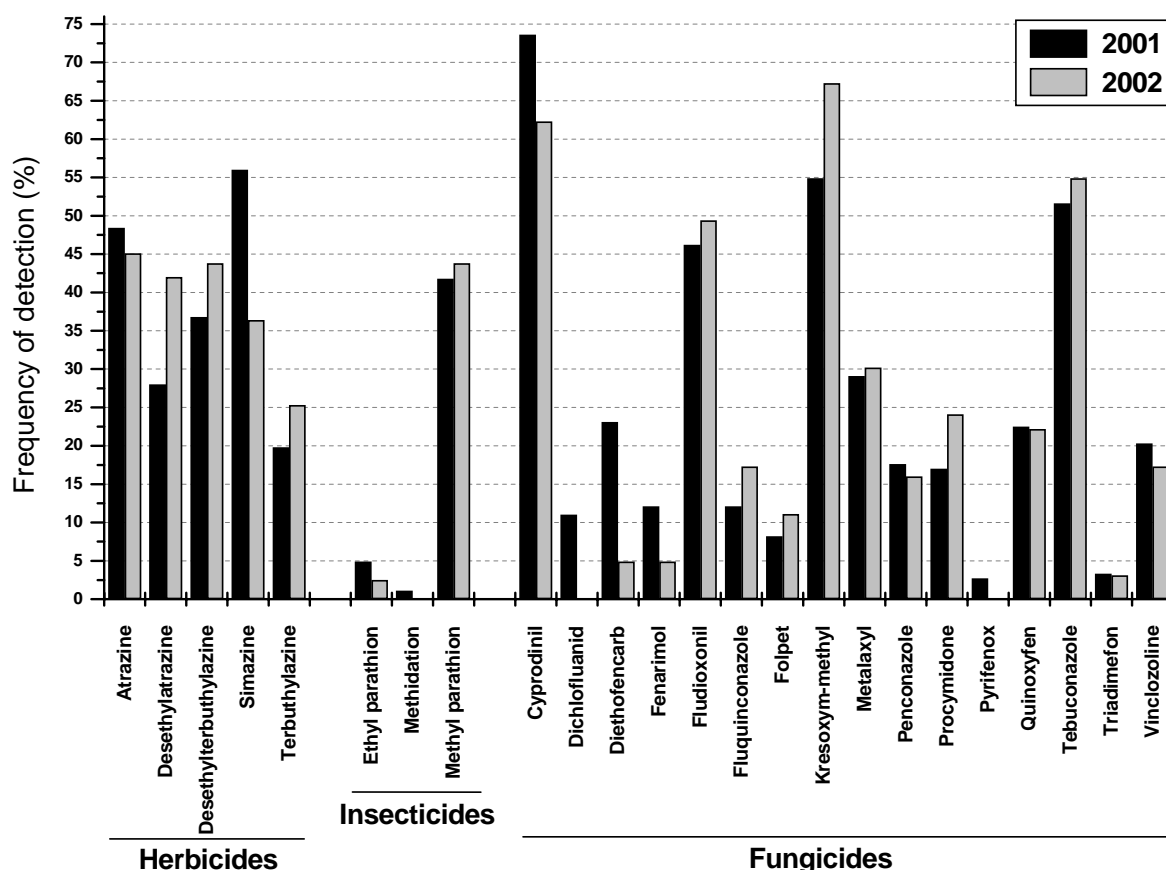


Figure 14: Frequency of detection (%) of pesticides detected in rain during the sampling campaigns 2001 and 2002. See data listed in Table 16.

Twenty-four of the 27 measured pesticides were detected above LoD at least once in 2001 and twenty-one in 2002 (no detections above LoD were found for dichlofluanid, methidation and pyrifeno in 2002). Many of the pesticides were detected at comparable frequencies

during both sampling campaigns. In both years, the most frequently detected compounds were the fungicides cyprodinil (2001: 73,6%, 2002: 62,3%), kresoxym-methyl (2001: 54,9%, 2002: 67,3%), tebuconazole (2001: 51,6%, 2002: 54,9 %) and fludioxonil (2001: 46,2%, 2002: 49,4%).

Table 16: Statistics on pesticides detected in rainwater from mid April 2001 through November 2001 (n = 182) and from mid April through early October 2002 (n = 162). Positive values only (> LoD) are considered.

Compound	Mean (ng l ⁻¹)		Median (ng l ⁻¹)		Max (ng l ⁻¹)		n > LoD		Freq (%)	
	2001	2002	2001	2002	2001	2002	2001	2002	2001	2002
Herbicides										
Atrazine	65,0	101,9	54,2	85,4	247	285	88	73	48,4	45,1
Desethylatrazine	37,8	42,4	27,6	33,9	116	188	51	68	28,0	42,0
Desethylterbuthylazine	21,3	22,7	21,1	14,9	37	64	67	71	36,8	43,8
Simazine	19,3	17,1	15,4	15,9	56	45	102	59	56,0	36,4
Terbuthylazine	36,1	32,4	20,7	21,4	111	107	36	41	19,8	25,3
Insecticides										
Ethyl parathion	29,6	29,3	25,8	28,7	55	32	9	4	4,9	2,5
Methidation	24,7	-	24,7	-	29	-	2	-	1,1	-
Methyl parathion	54,0	47,5	41,5	39,5	254	193	76	71	41,8	43,8
Fungicides										
Cyprodinil	30,1	59,5	23,1	18,5	204	1771	134	101	73,6	62,3
Dichlofluanid	38,2	-	34,5	-	87	-	20	-	11,0	-
Diethofencarb	40,6	20,3	21,3	14,8	204	51	42	8	23,1	4,9
Fenarimol	43,4	54,4	39,0	46,8	142	106	22	8	12,1	4,9
Fludioxonil	74,5	98,0	53,3	51,2	248	1321	84	80	46,2	49,4
Fluquinconazole	24,1	22,8	17,6	15,6	133	75	22	28	12,1	17,3
Folpet	150,1	88,7	101,9	69,9	352	290	15	18	8,2	11,1
Kresoxym-methyl	45,4	50,5	37,3	21,8	208	709	100	109	54,9	67,3
Metalaxyl	41,7	30,3	33,5	13,2	186	254	53	49	29,1	30,2
Penconazole	17,1	13,3	15,1	12,2	43	34	32	26	17,6	16,0
Procymidone	13,2	17,3	12,1	16,2	23	38	31	39	17,0	24,1
Pyrifenox	23,6	-	17,6	-	48	-	5	-	2,7	-
Quinoxifen	27,4	12,7	28,1	7,5	99	40	41	36	22,5	22,2
Tebuconazole	48,2	40,9	28,8	25,5	344	362	94	89	51,6	54,9
Triadimefon	28,0	44,8	22,6	38,6	62	99	6	5	3,3	3,1
Vinclozoline	13,9	22,4	13,0	14,6	28	68	37	28	20,3	17,3

Average concentrations were lower than 100 ng l^{-1} for all substances except folpet (mean value: $150,1 \text{ ng l}^{-1}$) in 2001 and atrazine (mean value: $101,9 \text{ ng l}^{-1}$) in 2002. Most pesticides, however, showed maximum concentrations higher than 100 ng l^{-1} , and in two instances levels above $1 \mu\text{g l}^{-1}$ were detected (cyprodinil and fludioxonil) (see par. 4.2.2). These extreme values are typical of areas where pesticides are applied (GLOTFELTY *et al.* 1990b, BUCHELI *et al.* 1998, CHARIZOPOULUS & PAPADOPOULOU-MOURIKIDOU 1999, COUPE *et al.* 2000).

Overall, average concentrations were similar to those measured in 2000 (see par. 4.1 and DE ROSSI & BIERL 2001, DE ROSSI *et al.* 2003), whereas maximum concentrations measured for 2001 and 2002 were higher than those found for 2000. Higher average and maximum concentrations of methyl parathion were measured for 2001 and 2002 than for 2000, but these values were still about half the values found by RIEFSTAHL (2000) for 1999.

A change in pesticide usage from 1999 to 2002 could be observed since, in 2002, some substances were less frequently detected and at lower concentrations (diethofencarb, penconazole, ethyl parathion, procymidone and simazine), while some others were not detected above LoD anymore (dichlofluanid, methidation and pyrifenox). Furthermore, the pesticides included in the list of investigated substances in the second phase of the project were those most frequently detected or found, though less frequently, at high concentrations (for example folpet).

Triazines concentrations were in the range of those detected by BESTER *et al.* (1995) in northern Germany, though higher values of simazine and lower values of atrazine were measured by the authors. SIEBERS *et al.* (1994) found maximum concentrations of atrazine in the range of $113\text{--}430 \text{ ng l}^{-1}$ and mean values between 44 ng l^{-1} and 105 ng l^{-1} in the filtrate from bulk rain samples collected between 1990 and 1992 at three sites in Lower Saxony (Germany).

BUCHELI *et al.* (1998) observed median and maximum concentrations of metalaxyl of 14 ng l^{-1} and 17 ng l^{-1} , respectively, in rain collected between February and October 1996 at Grütze (Switzerland). CHARIZOPOULUS & PAPADOPOULOU-MOURIKIDOU (1999) found mean concentrations of 140 ng l^{-1} and 30 ng l^{-1} of metalaxyl and fenarimol, respectively, in rain collected at the Axios river basin (Greece). Higher mean and maximum concentrations of metalaxyl were measured by HÜSKES & LEVSEN (1997) in Hannover (Germany) in 1992 (mean: 100 ng l^{-1} , maximum: 480 ng l^{-1}) than those found in 2001 and 2002 in Trier.

As observed above, average concentrations of the single substances measured in 2001 and 2002 were less than 100 ng l^{-1} , with few exceptions. However, it is noteworthy that, during the growing season, several pesticides were detected in each sample. Furthermore, only a small number of agrochemicals which are currently used in the area was analysed in this

study (see Appendix A, tables on pesticide applications). As a consequence, the presence in the atmosphere of pesticides other than those detected cannot be excluded. Hence, during the main application times, rainwater may exhibit total pesticide concentrations that markedly exceeds the European Union drinking water quality standard of 500 ng l^{-1} for total pesticides. This observation could be already confirmed by examining the total concentrations found in this study. Mean total pesticide concentrations measured during the two sampling campaigns are illustrated in Figure 15. Results show that during the growing season the total pesticide concentrations of the investigated compounds were considerable and, in some instances, well above the EU drinking water quality standard.

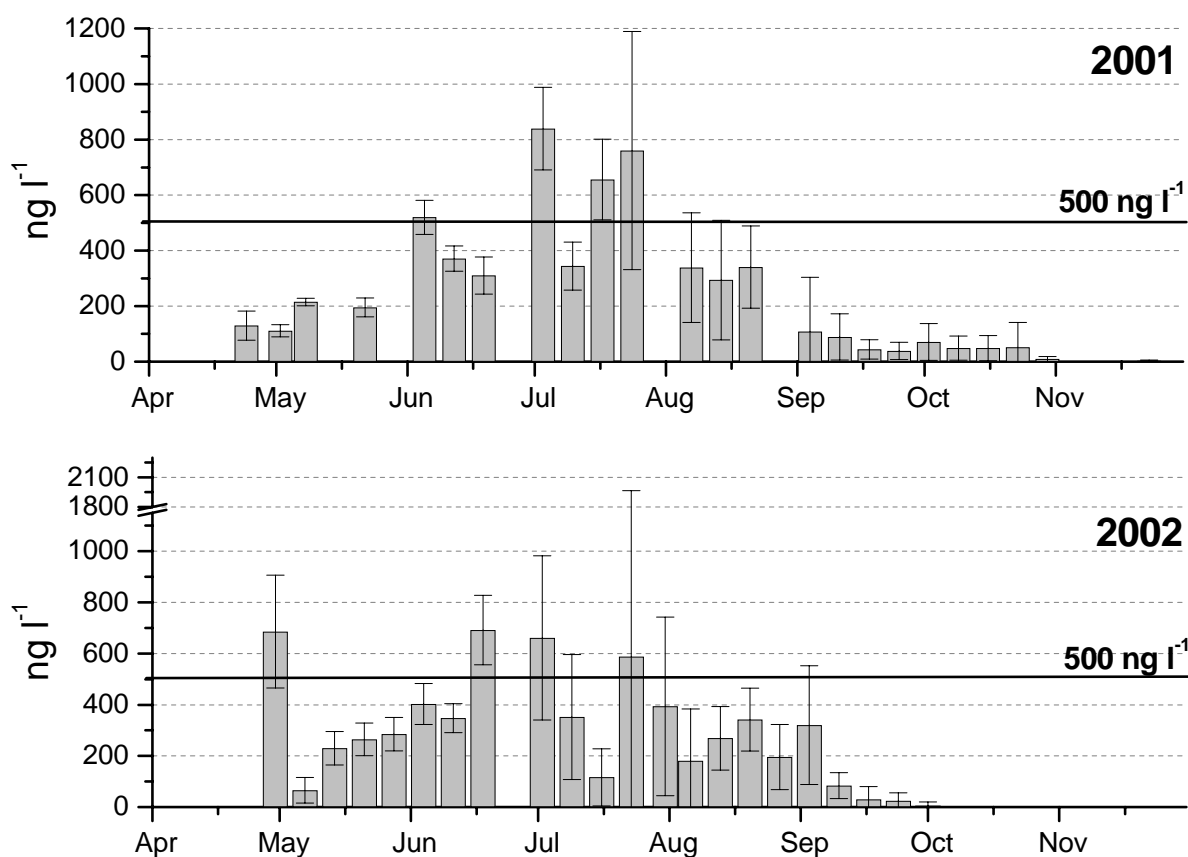


Figure 15: Mean total pesticide concentrations measured for 2001 and 2002. The error bars are the standard deviations of the 8 sampling sites. The solid lines visualize the European Union standard of 500 ng l^{-1} for total pesticide concentration in drinking water.

In 2001 and 2002 similar seasonal trends were observed (Figure 16). Herbicides were detected from the beginning of sampling (mid April) through August; insecticides were detected between May and September. Most fungicides were detected between June and September, while a few compounds of this class could be detected from the beginning of sampling (mid April) through September. Cyprodinil, fludioxonil, kresoxym-methyl, and tebuconazole were found above LoD until late October 2001. Of all substances, only

cyprodinil was detected at very low concentrations (less than 10 ng l^{-1}) in a few samples collected in November 2001. The highest concentrations occurred in the late spring and summer months, coinciding with application times and warmer temperatures.

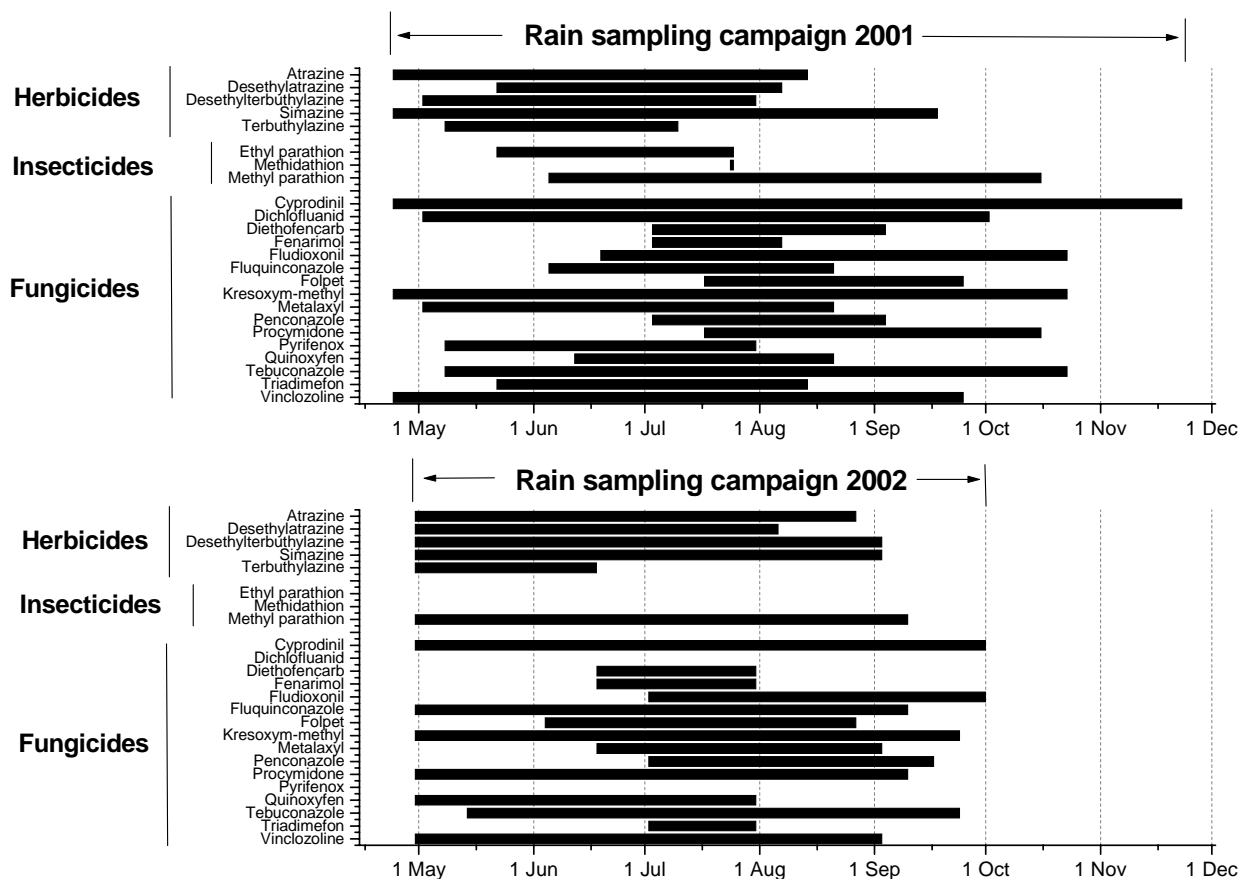


Figure 16: Temporal distribution of pesticides detected during the rain sampling campaigns 2001 (top graphic) and 2002 (bottom graphic).

4.2.2 Extreme values

The occurrence of extremely large concentrations in rain water depends on different factors: amount of pesticides present in the atmosphere, timing of rainfall events relative to application, amounts and intensity of the events, and duration of dry periods before the events. Several authors observed the highest concentrations during small rainfall events, especially after extended dry periods (GOOLSBY *et al.* 1997, VAN DIJK & GUICHERIT 1999). This fact is explained by the dynamic of a precipitation event. The first part of an event tends to scavenge most of the pesticides from the atmosphere. Rainfall occurring later in the event dilutes the concentration of pesticides that were deposited during the early part of the event (GOOLSBY *et al.* 1997).

4.2.2.1 The influence of precipitation amount

In agreement with the findings of other authors (GOOLSBY *et al.* 1997, BUCHELI *et al.* 1998), most of the pesticides investigated in this study exhibited higher concentrations when the amount of rainfall was small. Many substances reached their maximum concentrations at rain events that were less than 20 mm. As shown in Figure 17, this could be observed for all herbicides and metabolites (desethylatrazine and desethylterbuthylazine) both for year 2001 and 2002.

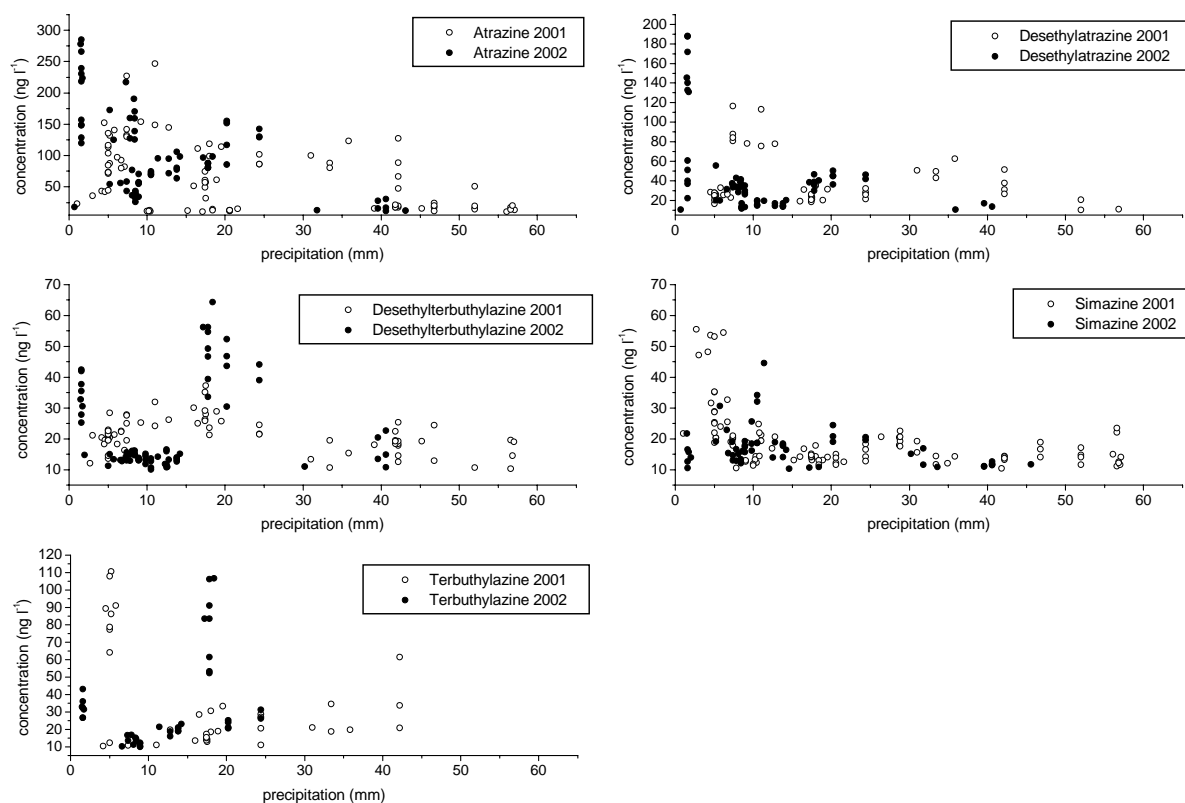


Figure 17: Scatter plots of herbicide and metabolite concentrations versus amount of precipitation.

Because of the rather high water solubilities and rather low Henry's law constants of the triazines, it can be expected that these compounds are readily washed out from the atmosphere if mainly present in the gas phase. This hypothesis was demonstrated by BUCHELI *et al.* (1998) by sequential sampling of rainwater from single rain events, where a significant drop in concentration of the first few millimetres of rain could be observed for the triazines investigated also in the present study.

Similar results were obtained for the insecticides ethyl parathion and methyl parathion and for most fungicides measured in 2002. In 2001, however, a more complex pattern could be observed for methyl parathion and some fungicides. A detailed analysis of these results will be the content of the following paragraph.

4.2.2.2 The influence of pesticide applications

In 2001, some samples, with a corresponding cumulative amount of rainfall more than 40 mm, had high concentrations of methyl parathion and of some fungicides which, in some instances, attained the highest levels measured during the whole sampling campaign. In these cases the amount of pesticides in the atmosphere and the intensity and timing of rainfall events relative to applications played a significant role in determining the concentration levels found in the rain water.

Figure 18 shows the scatter plot of methyl parathion concentration versus amount of precipitation for 2001. The highest concentrations were found in the samples collected on 24 July 2001 at the sites A, HM, MK and G. The samples were a composite of several rainfall events of different intensity and duration (daily precipitation amounts ranged from 0,8 mm to 27,7 mm). The cumulative amount of precipitation recorded during the week of sampling ranged from 46,8 mm (MK) to 57,1 mm (HM).

Unfortunately, since no information on applications of methyl parathion was available, it is not possible to make direct inferences on the correlation between these high concentrations and the use of the insecticide. However, it can be speculated that applications of methyl parathion, carried out in the area during the week of sampling, most likely account for the findings here described.

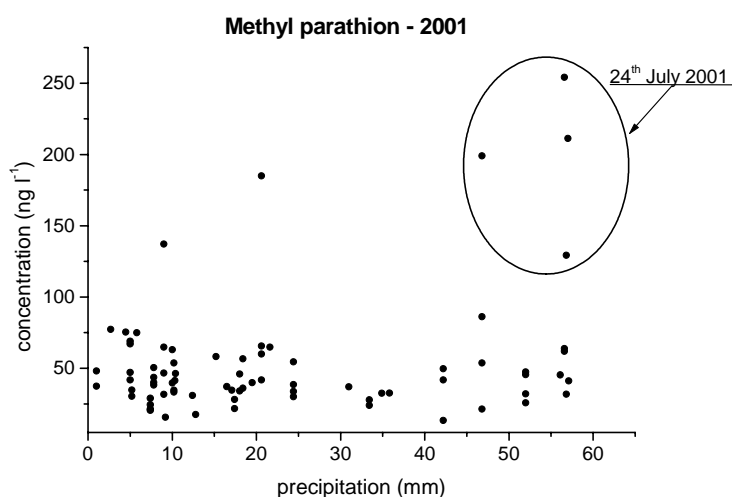


Figure 18: Scatter plot of methyl parathion concentrations versus amount of precipitation measured for 2001.

Methyl parathion is an insecticide which is used both in agriculture (including viniculture) and in urban environment (urban lawn, garden use). Its rather high vapour pressure ($0,41 \times 10^{-3}$ Pa at 25 °C) allows for high volatilisation rates after application as reported by KUBIAK (1999), who measured post-application volatilisation rates between 65% and 77% of the applied amount. COUPE et al. (2000) found that once in the atmosphere, methyl parathion is primarily distributed in the gas phase. Finally, because of its rather high water solubility and low Henry's law constant, methyl parathion is readily scavenged by wet deposition. It is conceivable that the rain events that occurred during the week of sampling, being mostly short, intense and alternated with dry periods (up to 2 days of dry conditions), contributed at different times to the effective washout of methyl parathion from the atmosphere without giving rise to a dilution effect typical of long rain events.

With the exception of the samples collected on 24 July 2001, the correlation between concentration levels and amount of precipitation is once again confirmed, with the highest concentrations detected during rainfall events less than about 20 mm.

Similar patterns were observed for the fungicides dichlofluanid, fenarimol, fludioxonil, folpet, kresoxym-methyl, metalaxyl, quinoxyfen and tebuconazole. Figure 19 shows the scatter plots of the concentrations of some of the above mentioned fungicides versus amounts of precipitation measured in 2001 and 2002. High concentrations, in some cases the highest values found over the whole growing season (see top graphic on the right), were measured in samples collected during the second and the third week of July 2001. In these two weeks, short but intense rainfall events intermittently occurred and the cumulative amounts of precipitation ranged from 46,8 mm to 57,1 mm. In 2002, only few instances were observed for folpet, fludioxonil and tebuconazole where high concentrations were associated with high cumulative amounts of precipitation.

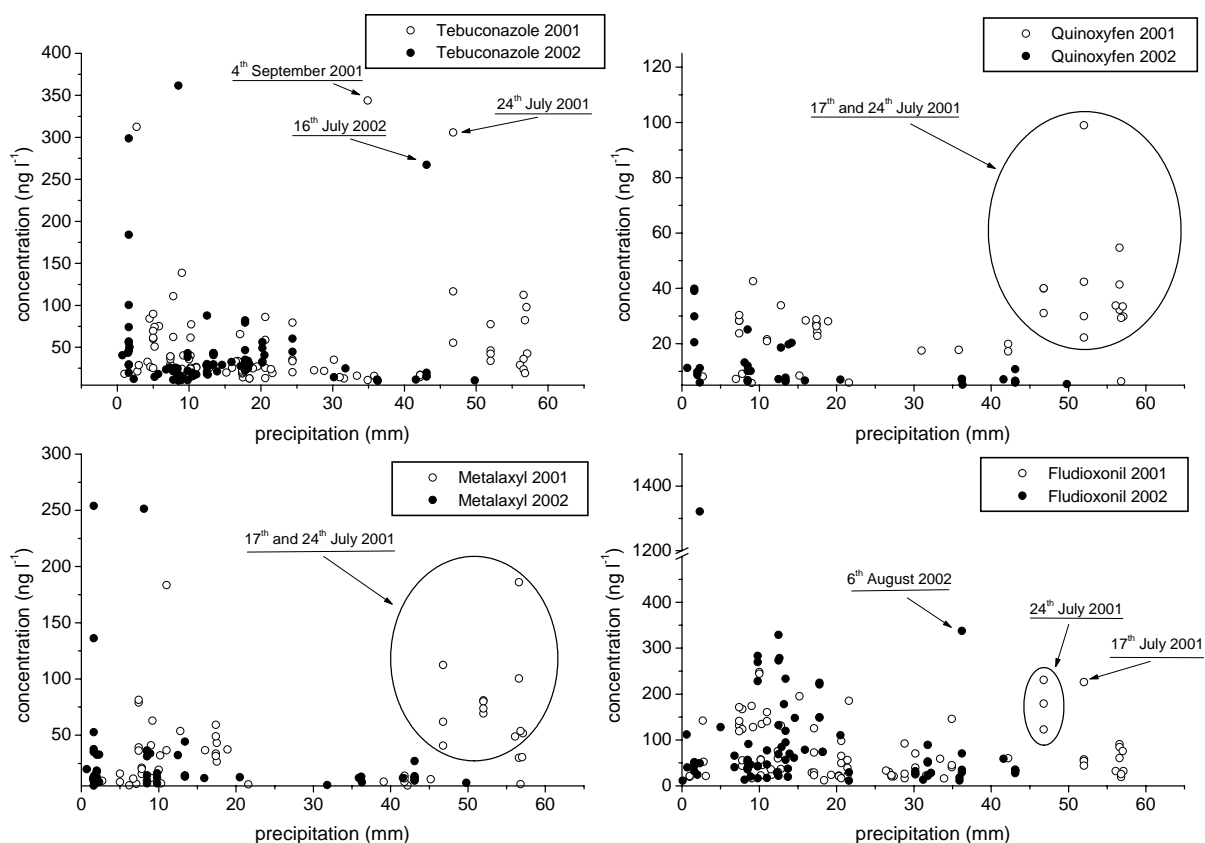


Figure 19: Scatter plots of fungicide concentrations versus amount of precipitation measured for 2001 and 2002.

The results shown in Figure 19 and those found for the other above mentioned fungicides must be completed by the following observations:

- These high concentrations were generally measured at less than 50% of the sampling sites.
- There is proof that the mentioned fungicides were applied in the area during the period of study.
- The main period of application of these substances is from June through August, in some cases through September.
- Given the economic structure of the vinicultural area of Trier (see par. 3.1.1), the existence of several small wine-growing activities has as a consequence that pesticides are applied from activity to activity at different times, most likely on different days of the same week.

Frequent applications, carried out at different times in the area, act as continuous sources of pesticides to the atmosphere from June through September. Furthermore, the occurrence of high concentrations measured only at few sampling sites suggests the correlation with local applications. Therefore, it can be concluded that local use and timing of rainfall events relative to applications played, in these cases, a significant role in determining the levels of pesticide concentration in rain water.

4.2.2.3 The realistic “worst case” situation

The highest concentrations measured over the whole study occurred in July 2002 at the “Schloss Marienlay” winery area (site M). Figure 20 shows the time-series of cyprodinil, fludioxonil and kresoxym-methyl concentrations measured at this site and the corresponding total precipitation recorded during the single sampling periods. On 23 July, cyprodinil and fludioxonil were found at concentrations of $1,77 \mu\text{g l}^{-1}$ and $1,32 \mu\text{g l}^{-1}$, respectively. At the same time 508 ng l^{-1} of kresoxym-methyl were measured.

There were some exceptional conditions associated with these findings. Two fungicide products containing the active ingredients cyprodinil, fludioxonil (product: Switch) and kresoxym-methyl (product: Strobby) were simultaneously applied in the vineyards located in the vicinity of the rain sampler on 16 July. Both fan mist-blowers and hand-held spray guns were used for application. Cyprodinil and fludioxonil were applied at this place for the first time during this growing season, while the first application of kresoxym-methyl occurred already on 4 July. A few hours after the application a short rainfall event occurred. The sample collected a few days later was a composite of this event and another short event which occurred the following day: altogether 2,3 mm of rain fell during the week of sampling.

It is likely that the first event immediately deposited the applied substances from the spray drift back onto the soil surface before they could be further dispersed in the atmosphere. In fact, during the same sampling period, very low concentrations of these fungicides or no detections at all were observed at the other sites.

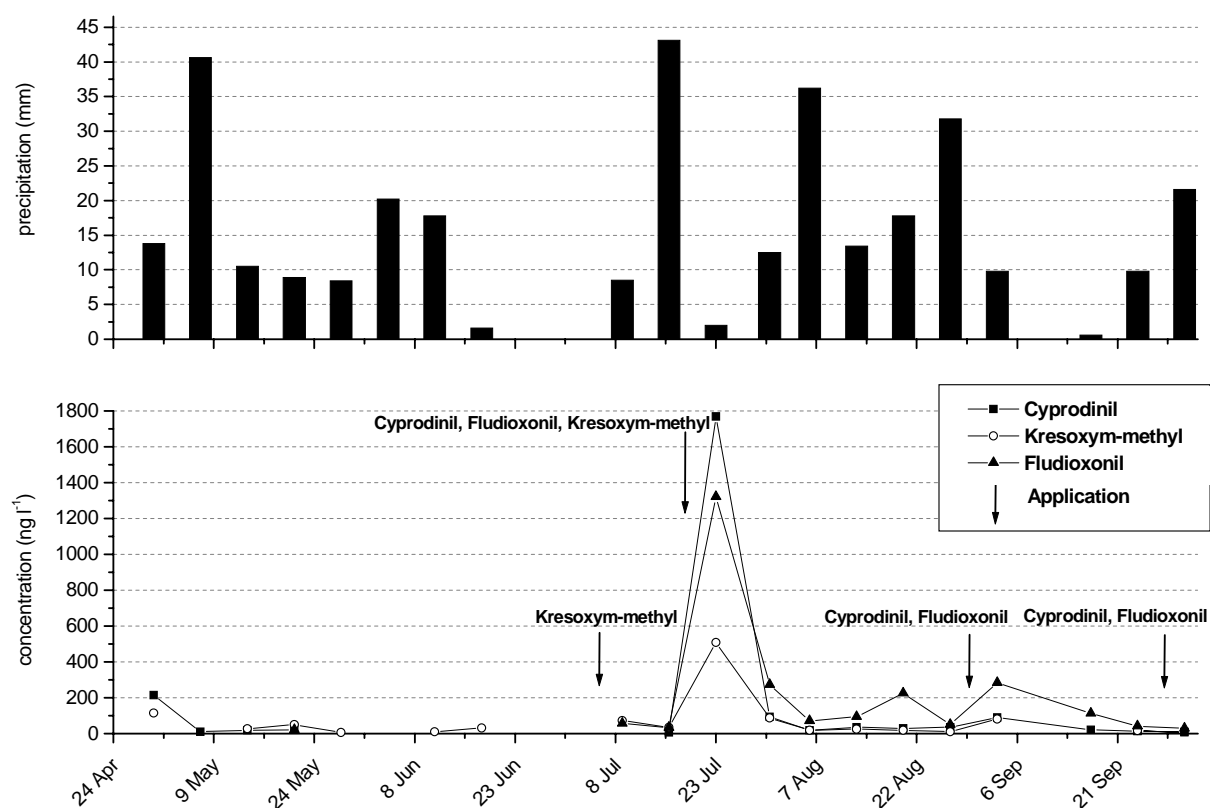


Figure 20: Time-series of cyprodinil, fludioxonil and kresoxym-methyl concentrations measured at the “Schloss Marienlay” winery area (M site) (bottom graphic) in 2002 and respective total precipitation per sampling period (top graphic).

The concentration levels found for the three fungicides mirrored the quantities which were used. The applied amount of kresoxym-methyl was about 3 times less than that of cyprodinil and about 2 times less than that of fludioxonil.

The findings described in this paragraph represent a realistic “worst case”. As it can be seen in Figure 20, applications of cyprodinil and fludioxonil carried out in August and September did not give rise to such extreme concentrations, although the amounts applied in August were about the same as those used in July. During the two years of sampling, this kind of situation was observed only once. However, though such cases do not happen frequently, the impact that these occasional high concentrations may have on surface water and ground water is difficult to determine and is not yet well understood.

4.2.3 Local emissions and atmospheric transport

One of the goals of the study was to investigate the occurrence of pesticides in the atmosphere in the area of Trier and their possible sources. To this purpose sampling sites were chosen at different locations in order to gain useful information on the spatial distribution of these substances.

As explained in chapter 2, the presence of pesticides in the atmosphere and rainfall is mainly the result of drift during application, volatilisation and adsorption of pesticides to particulates that undergo atmospheric transport or a combination of these processes. According to NATIONS & HALLBERG (1992) volatilisation may be the largest source of these chemicals in the atmosphere. Volatilisation may create gaseous concentration gradients, spreading vertically and laterally from application sites, which may be reflected in the concentrations in the local rainfall. Local scavenging, either from particles or from gases, may be the process responsible for the highest concentrations of pesticides measured at a certain sampling site.

Once in the atmosphere, modern pesticides can travel over distances of tens to hundreds of kilometres (see par. 2.2.2). Some of them may travel even further. The distance that airborne pesticides are transported depends upon their removal rates, *i.e.* dry and wet deposition and chemical reactions (MAJEWSKI & CAPEL 1995).

Determining the origin of pesticides found in the atmosphere of a certain area has always proven difficult. However, there are some ways that can provide information about possible source areas. The approaches used in this study include the observation of spatial distributions of pesticides detected in precipitation at the different sites during the two rain sampling campaigns (source-receptor relationship, par. 4.2.3.1) and the examination of the wind directions measured at the moment pesticides were occurring in rainwater (wind roses, par. 4.2.3.2). The combination of these two methods will help obtaining evidences on the origin of pesticides.

4.2.3.1 Source-receptor relationship

Pesticides, detected in air or precipitation at a certain sampling site, may originate from source areas located nearby or further away. By comparing the results from several sampling sites, inference can be made about the source and the distance a pesticide may have travelled (VAN DIJK & GUICHERIT 1999). If local sources dominate, a pesticide's concentration in precipitation may be highly variable, both in space and time. For instance, GEISSLER & SCHÖLER (1993) concluded from precipitation analysis at four sampling sites near Cologne in Germany, all located within 50 km of each other, that local sources must have been dominant, because input patterns differed greatly from site to site.

If pesticides originate from up to several hundreds of kilometres, a large degree of mixing and dilution occur during the atmospheric transport. As a result, deposition patterns at sampling sites within, e.g. 50 km of each other, are more similar, although distinct time trends may be visible (VAN DIJK & GUICHERIT 1999). CLEEMAN *et al.* (1995) concluded from the similarity in concentrations and seasonal trends of lindane in precipitation in different parts of Denmark that the source areas must have been located outside the country.

Finally, pesticides that originate from remote sources at many hundreds or even thousands of kilometres distance, will show very steady and gradual trends in concentrations in air and precipitation, both in space and in time. Alternatively, such a pattern may result from a very slow but prolonged release from residues in the soil. These concentrations are often referred to as background concentrations. (VAN DIJK & GUICHERIT 1999)

With this in mind, spatial distributions of the concentrations of the most frequently detected pesticides at the eight sampling sites over the two rain sampling campaigns were examined. Comparisons in terms of concentration levels (ng l^{-1}) could be made within each sampling campaign, since differences among the sites in weekly rainfall were small.

Different distributions were observed for different pesticides. A group of substances, mostly made up by the triazines and some of the fungicides analysed also during the screening campaign in 2000, exhibited similar concentration patterns at the different sampling stations. Another group, made up by the insecticide methyl parathion and several fungicides, showed input patterns which differed greatly from site to site. A detailed analysis of representative distribution patterns will be presented in the following part of this section.

Figure 21 shows the spatial distributions of the herbicides terbuthylazine and atrazine for 2002. Similar distributions were observed during the two sampling campaigns for both compounds and for simazine (simazine concentration levels were much lower).

Very small differences in concentrations among the sites were found over the two sampling campaigns. A distinct trend was visible, with higher concentrations being measured during the main application time typical for these herbicides (May and June). According to the examples discussed above, these distribution patterns indicate that the occurrence of atrazine, simazine and terbuthylazine in rainfall was most likely due to atmospheric transport from more distant areas where these herbicides were applied rather than local use. This observation is in agreement with the fact that plant protection products containing these active ingredients are not expected to be used in the area of study: simazine and terbuthylazine are not registered for use in the viniculture, and the herbicide atrazine has been banned in Germany since 1991. However, in the neighbouring countries like France, Luxembourg and Belgium the use of atrazine is still allowed. Although illegal use can never be completely ruled out, the findings described here together with an analysis of the wind

fields measured during the sampling campaigns (see par. 4.2.3.2) suggest that these countries could be the nearest possible source areas for these compounds.

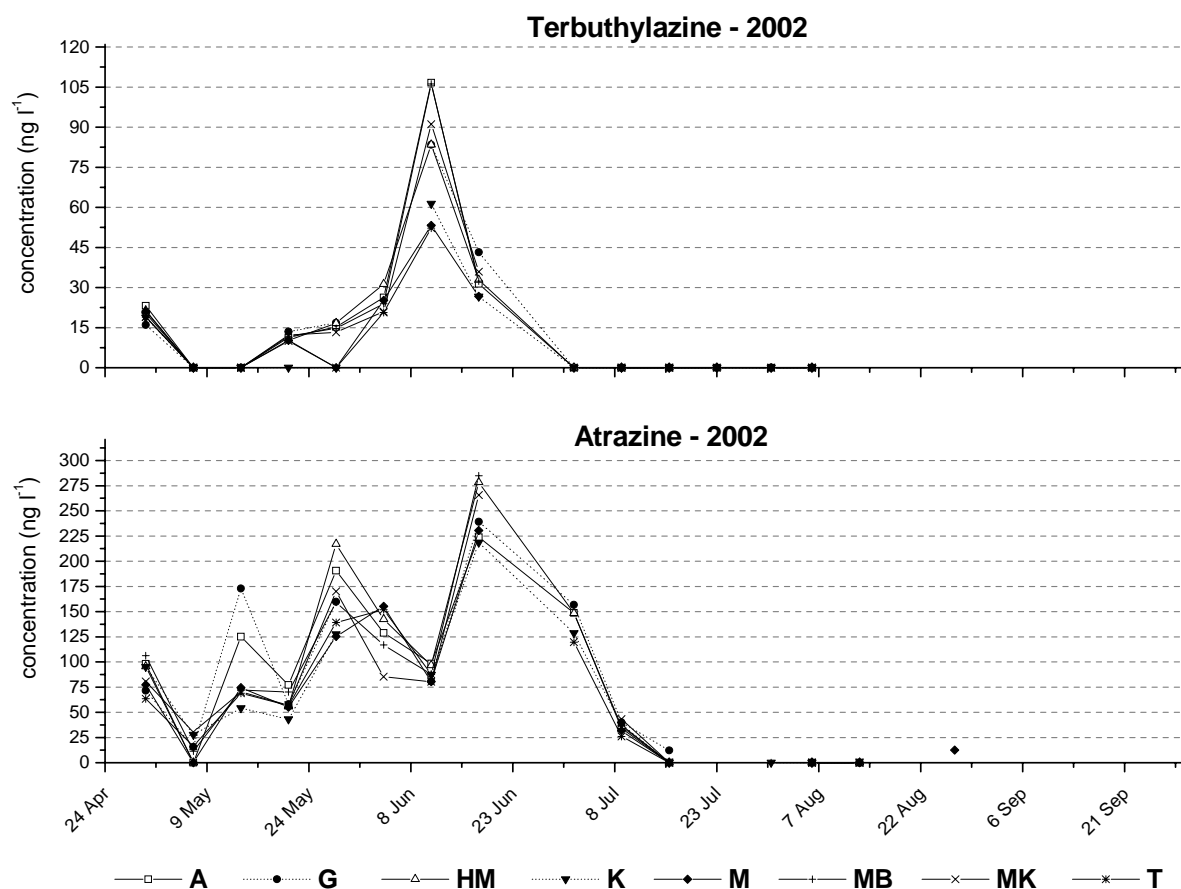


Figure 21: Time-series of terbuthylazine and atrazine concentrations (ng l^{-1}) observed at all sampling sites in 2002 (zero values represent $< \text{LoD}$ values).

A more complicated distribution pattern was observed for methyl parathion (Figure 22). During both growing seasons low concentrations were consistently found at the sites K and T, while at the sites A, HM, MK and MB high concentrations were occasionally measured. No information on local application of this compound was available. However, results reported by RIEFSTAHL (2000) pointed out that this insecticide is currently used in the area. The author's findings are in agreement with those of this study, where the highest concentrations and the highest differences from site to site were observed during the months of July and August of both years. Although differences in concentrations were less than 200 ng l^{-1} , they could not be explained by differences in precipitation amounts. This suggests the influence of local sources on the concentration of methyl parathion in precipitation.

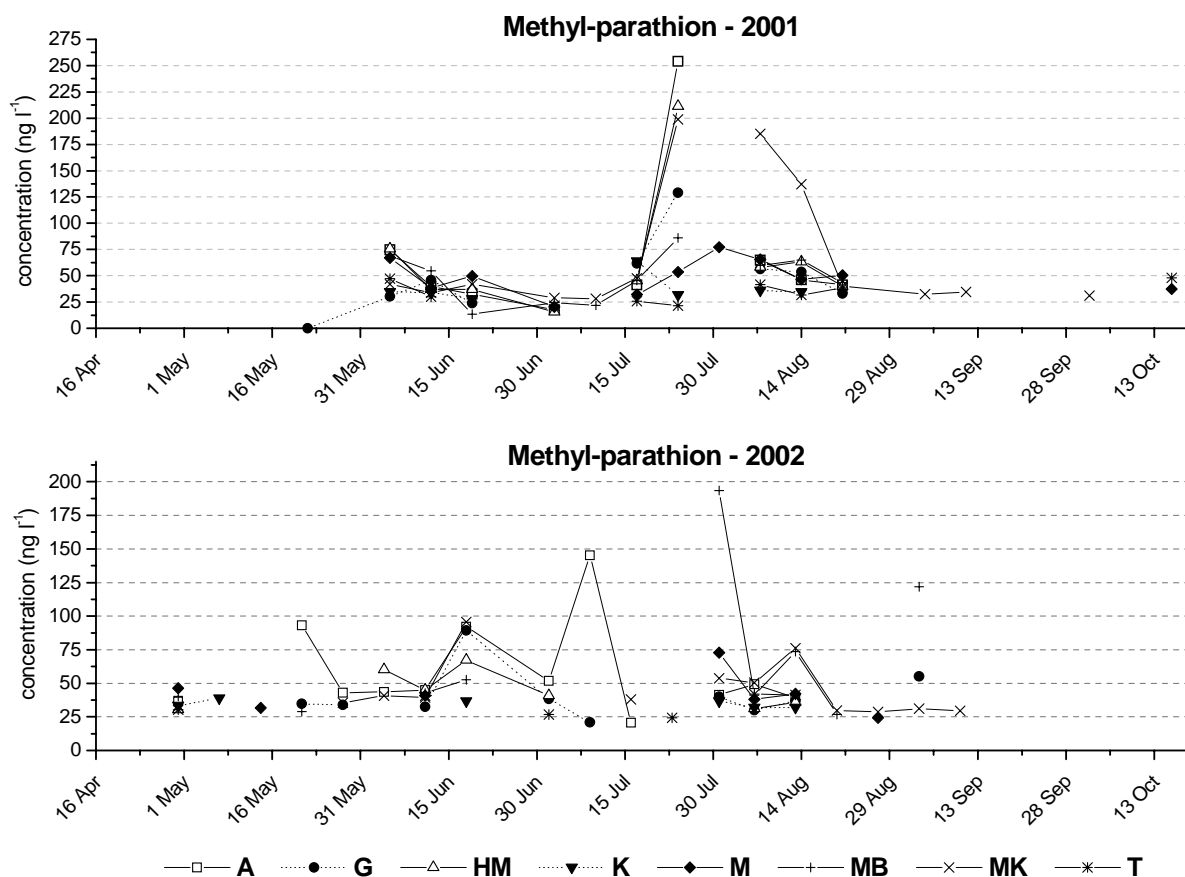


Figure 22: Time-series of methyl parathion concentrations (ng l^{-1}) observed at all sampling sites in 2001 and 2002 (zero values represent $< \text{LoD}$ values).

As expected, the most marked spatial variations were observed for substances belonging to the class of fungicides. This class of compounds is the most frequently used in wine-growing areas (par. 3.1.3). This holds also for the area of Trier, as it could be confirmed by the available information on pesticide applications carried out in this area between 2000 and 2002 (Appendix A). Local emissions play in this case the main role in determining the concentrations of these substances in the local precipitation and are reflected in characteristic spatial distributions, *i.e.* the highest concentrations are associated with local use and, during the high-use period, concentrations differ greatly from site to site.

Fungicides showing marked spatial variations were divided into two groups according to their distribution patterns.

Figure 23 shows the spatial distributions of two fungicides selected from the first group. This group is made up by those substances whose detection in rain water was limited to the main application period, namely dichlofluanid, fenarimol, fluquinconazole, folpet, metalaxyl, diethofencarb, fludioxonil and quinoxifen. During this time, concentration levels differed greatly from site to site. The highest concentrations were consistently detected at sites in

close proximity to vineyards (sites A and M) or at sites which turned out to be directly subject to pesticide emissions (post-application volatilisation followed by off-site drift) as a result of local air mass movements (local convective winds such as upslope and downslope winds) (sites HM, MB and MK). The lowest concentrations were constantly measured at the sites G and T. Concentration levels dropped to undetectable levels within a very short time at the end of the application period. The distribution pattern observed for diethofencarb during 2001 is illustrated in Figure 23 (top graph). With the exception of fludioxonil, the other substances belonging to this group showed similar patterns to that of diethofencarb. Fludioxonil showed a slight different distribution pattern, with higher frequencies and longer periods of detection (Figure 23, bottom graph). The higher frequency of detection and the more complicated distribution pattern found for this compound are most likely a consequence of a higher usage of pesticide products containing this active ingredient. Applications of fludioxonil carried out until the end of September account for the presence of this fungicide in rain water until October.

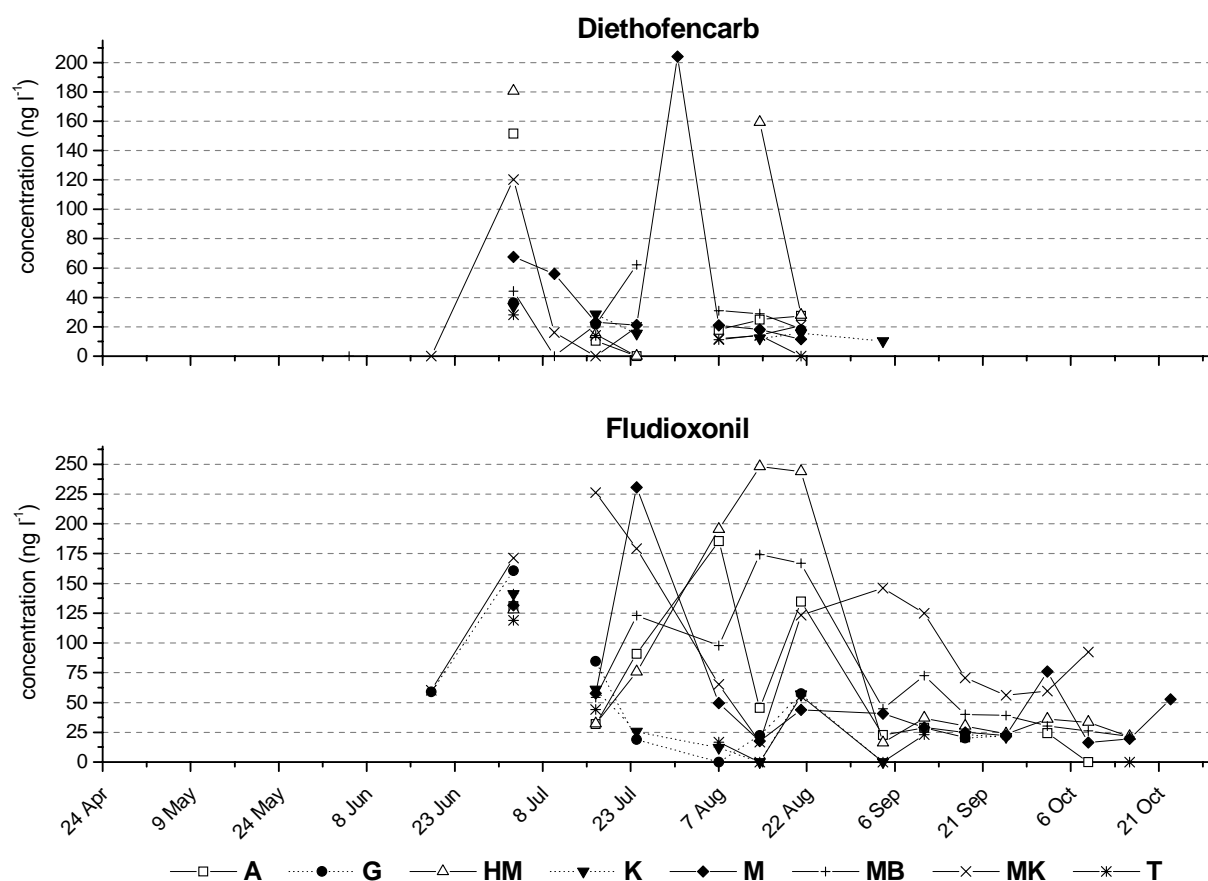


Figure 23: Time-series of diethofencarb and fludioxonil concentrations (ng l^{-1}) observed at all sampling sites in 2001 (zero values represent $< \text{LoD}$ values).

A second group of fungicides consisted of cyprodinil, kresoxim-methyl and tebuconazole. Unlike the substances of the first group, these chemicals were detected from the beginning of both sampling campaigns and showed a distinct distribution pattern which changed over the growing season. As shown in Figure 24 for the year 2001, similar concentrations were measured at all sites from mid-April through June, while differences from site to site greatly increased during July through early September. By mid-September, these fungicides were irregularly detected at a reduced number of sites. Analogous distributions were observed for 2002.

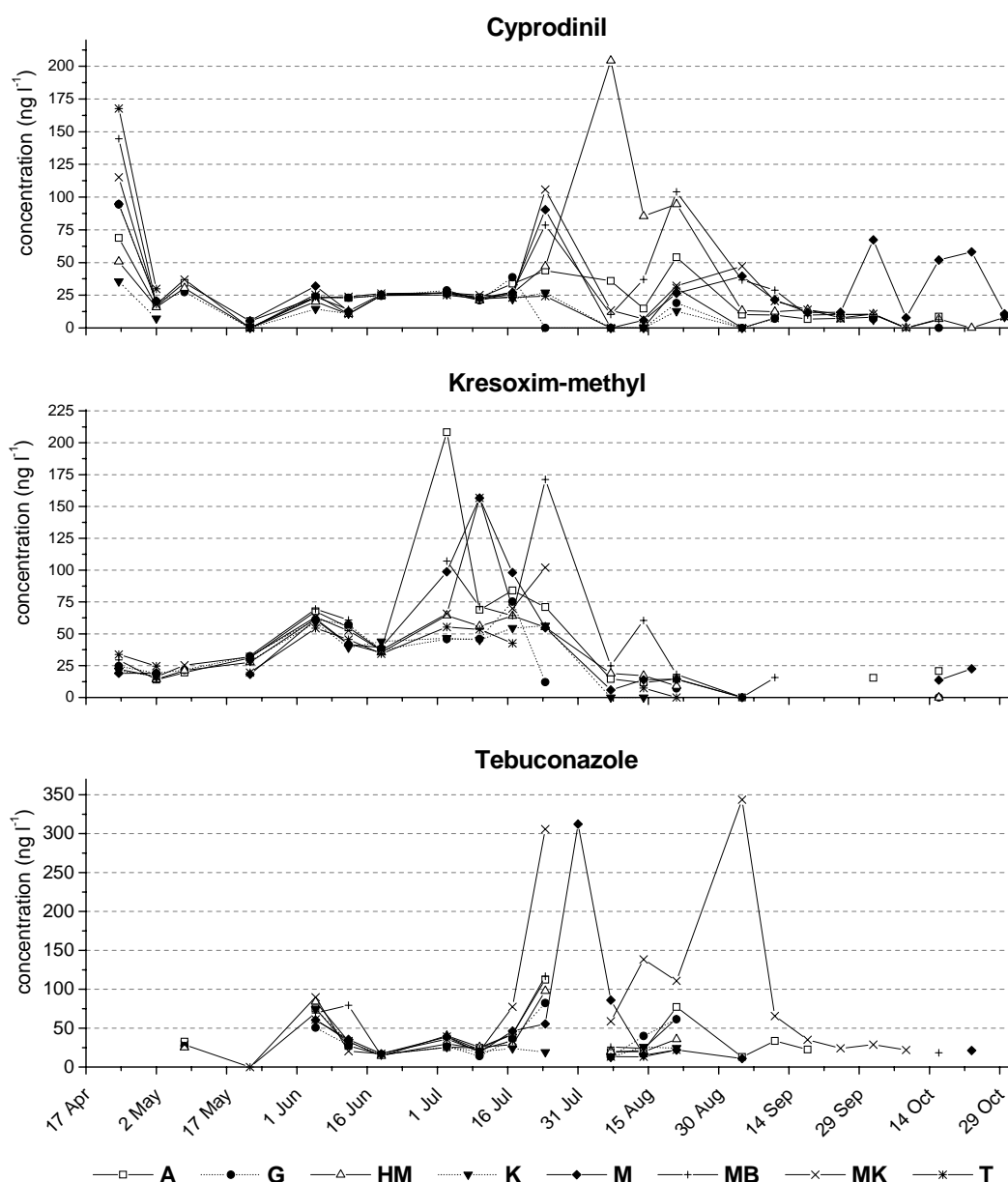


Figure 24: Time-series of cyprodinil, kresoxim-methyl and tebuconazole concentrations (ng l⁻¹) observed at all sampling sites in 2001 (zero values represent < LoD values).

The distribution patterns exhibited by cyprodinil, kresoxym-methyl and tebuconazole between July and September are similar to those observed for the fungicides of the first group during this time of the year. This period, characterised by high spatial variations, corresponds to the application period typical of the area of Trier. As for the fungicides of the first group, such distributions indicate a local source-effect influence on the concentration of these pesticides in precipitation from the close proximity to their field use.

The appearance of pesticides in precipitation before the local application time (April-June) could be due to soil erosion and volatilisation of carry-over residues in the warming soil (NATIONS & HALLBERG 1992). Alternatively, it could be the result of atmospheric transport from more distant areas whose growing season began earlier (MAJEWSKI & CAPEL 1995).

A distinction between the two processes was not possible in the frame of the project, however, the following observations could be made:

- If the presence of these chemicals in the atmosphere before the local application time is due to volatilisation processes, an increase in concentrations would be expected from April through June. In fact, during this period the average air temperature increases constantly. Higher air temperatures lead to higher vapour pressures thus increasing the volatilisation rates of a chemical. Consequently, higher concentrations in air and precipitation would be expected during the warmer months of May and June. The fact that concentration peaks of cyprodinil (both in 2001 and 2002) and kresoxym-methyl (in 2002) were detected at the beginning of the sampling (late April) and that no increasing concentration trends were observed between April and June markedly contrasts with the previous observation.
- Furthermore, sorption of pesticides to soil increases drastically when soil dries out (FERRARI *et al.* 2005 b). The increase of the sorption constant leads to a reduction of pesticide in the soil air and therefore also to a decrease of the volatilization flux. Unfortunately, no data on soil moisture were available and inferences can be made only on the basis of data on precipitation, air temperature (at 20 cm), relative humidity, soil temperature (at -5 cm) and solar radiation. Drier conditions did occur during May 2001 than during April and June 2001 (only 11,3 mm of rain were measured in May 2001, while in April and June 2001, 112,0 mm and 73,9 mm were measured, respectively). However, wetter conditions were measured in May 2002 than in April and June 2002. Consequently, drier soil conditions occurred during May 2001 can partly be responsible for lower volatilization fluxes and therefore lower rain concentrations found in May 2001 in comparison to those measured in April 2001. This, however, cannot explain the rain concentration pattern of kresoxym-methyl measured between April and June 2002.

- Finally, two physico-chemical properties that affect pesticide occurrence in the environment are the vapour pressure and soil half life (DT_{50}). The higher the vapour pressure of a substance, the higher its volatilisation rate; the higher the soil half life the more likely the pesticide persists and is available for transport in the environment. As shown in Table 17, cyprodinil, kresoxym-methyl and tebuconazole have vapour pressure and soil half life values bracketed by those of the fungicides included in the first group previously analysed. Therefore, if kresoxym-methyl, whose DT_{50} in soil is less than 1 day, is found in the atmosphere before the beginning of the local application period as a result of volatilisation of carry-over residues, this would be expected to happen also for other substances with similar properties, such as folpet, or with similar vapour pressures and higher DT_{50} values, such as fenarimol, metalaxyl and quinoxyfen. However, residues of these substances could not be detected before the local use began, although information on pesticide applications carried out in the previous years confirm the use of these chemicals.

Table 17: Vapour pressure and soil half life values (DT_{50}) of selected fungicides (TOMLIN 2000).

Group	Fungicide	Vapour pressure (mPa, 20 °C)	Soil half life (DT_{50}) (days)
I	Dichlofluanid	0,014	instable
	Diethofencarb	8,4	< 1-6
	Fenarimol	0,065 (25 °C)	14-130 (av. 79)
	Fludioxonil	$3,9 \times 10^{-4}$ (25 °C)	10-25
	Fluquinconazole	$6,4 \times 10^{-6}$	50-300
	Folpet	$2,1 \times 10^{-2}$ (25 °C)	4,3
	Metalaxyl	0,75 (25 °C)	10-40
	Quinoxyfen	$1,2 \times 10^{-2}$	224-508
II	Cyprodinyl	$4,7-5,1 \times 10^{-1}$ (25 °C)	20-60
	Kresoxym-methyl	$2,3 \times 10^{-3}$	< 1
	Tebuconazole	$1,7 \times 10^{-3}$	slow

Alternatively, the presence of cyprodinil, kresoxym-methyl and tebuconazole in rainfall before the beginning of the local application period could be the result of atmospheric transport processes. As explained in chapter 2 (par. 2.2.3), the distance a chemical can be transported in the atmosphere strongly depends on its atmospheric lifetime, this being the result of a combination of the different removal processes. Unfortunately, for most current-use pesticides the atmospheric lifetime is not known (VAN DIJK & GUICHERIT 1999). This holds for most fungicides analysed in this study. However, a classification of the different patterns of atmospheric deposition does appear useful as a first step in categorising the potential for different pesticides to be dispersed in the atmosphere (DUBUS *et al.* 2000). According to the

findings of the present study, it can be speculated that the fungicides of the second group exhibit longer atmospheric lifetimes than those of the first group and as a consequence can be transported over longer distances. However, such results could also be due to a preferential usage of the fungicides belonging to the second group in the source areas.

Distribution patterns exhibited by cyprodinil, kresoxym-methyl and tebuconazole during mid-April through June are similar to those previously described for the triazines. Consequently, it is conceivable that the presence of these chemicals in the rain collected during this period may be the result of atmospheric transport from more distant areas. However, once the local application time had started, these regional inputs became insignificant in comparison and were lost in the background.

4.2.3.2 Wind roses

Information on possible sources of pollutants deposited onto an area can be obtained by examining the wind direction at the moment these chemicals are occurring in air or rainwater (VAN DIJK & GUICHERIT 1999). Wind direction studies have been successfully used by several authors. By analysing the predominant wind direction, CLEEMAN *et al.* (1995) concluded that the sources of lindane found in precipitation in Denmark were most likely located in countries south and west of Denmark. Likewise, LODE *et al.* (1995) observed in Norway that atrazine and lindane, whose use was banned in the country before their investigation started, occurred in rainfall when easterly winds were blowing.

In the present study, wind direction was continuously measured at the meteorological station of the department of climatology of the University of Trier. The station was located at the site H (see par. 3.2.1 and Table 7).

According to the previous section (par. 4.2.3.1), the occurrence of atrazine, simazine and terbuthylazine in rainfall collected in the area of Trier was most likely due to atmospheric transport from more distant areas. In order to locate possible source areas, wind directions measured in correspondence of peak concentrations detected in precipitation samples were examined in detail. The results obtained from this analysis are shown in Figure 25 and Figure 26 for atrazine and terbuthylazine. The wind roses depicted in the figures represent the average wind direction measured during the sampling week corresponding to the collected sample. Both in 2001 and in 2002, peak concentrations were measured during sampling periods with air masses being consistently from west and south-west. This indicates that source areas located west and south-west, namely in the neighbouring countries Luxembourg and France, exerted a significant influence on the atmospheric occurrence of these substances over the area of Trier. Indeed, in these countries, these herbicides are still intensively used on maize crops and grapes as reported by several authors (CHEVREUIL &

GARMOUMA 1993, BINTEIN & DEVILLERS 1996, CHEVREUIL *et al.* 1996, SANUSI *et al.* 2000, MILLET 2003 personal communication).

Similar results were obtained for the occurrence of the fungicides cyprodinil, kresoxymethyl and tebuconazole in the rain before any local use began. These findings may be due to the use of products containing these active ingredients on cereal crops in more distant areas, located west and south-west of Trier. Alternatively, applications on grapes in areas where the growing season and, consequently, the spraying season started earlier may account for the occurrence of pre-application detections in the area of study.

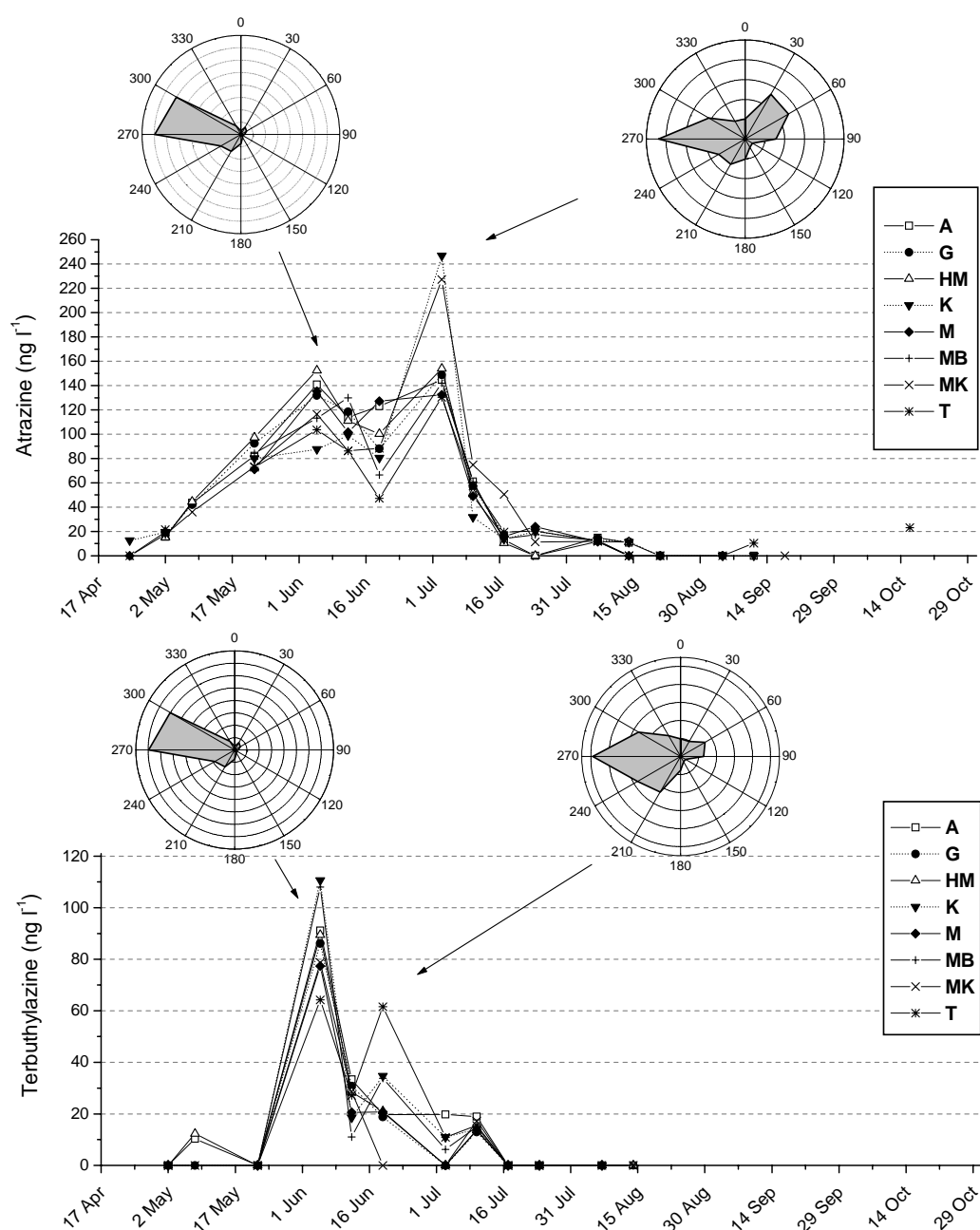


Figure 25: Time-series of atrazine (top graph) and terbuthylazine (bottom graph) concentrations (ng l⁻¹) and corresponding wind roses measured in 2001.

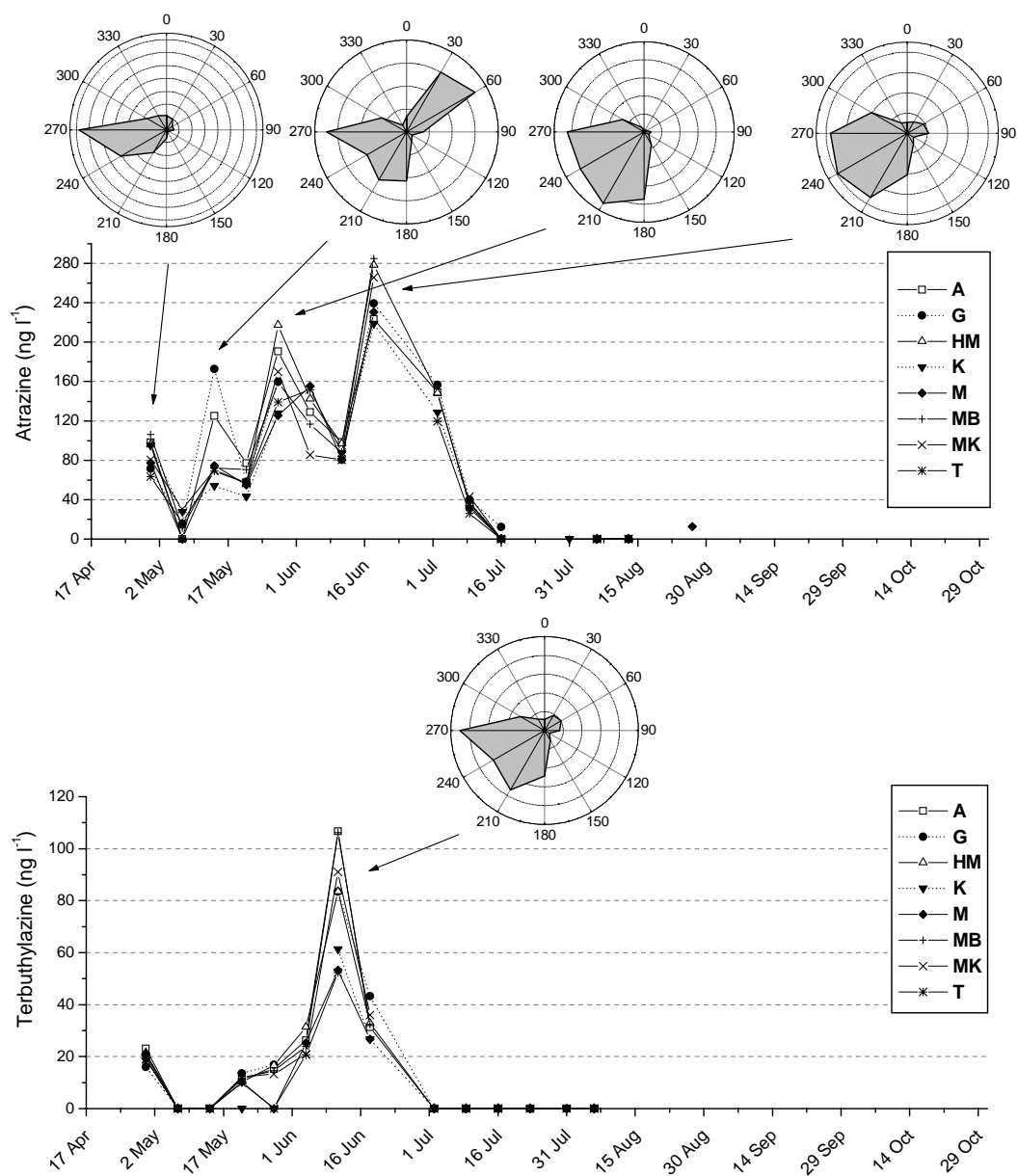


Figure 26: Time-series of atrazine (top graph) and terbutylazine (bottom graph) concentrations (ng l⁻¹) and corresponding wind roses measured in 2002.

4.2.3.3 Conclusions on local emissions and atmospheric transport

On the basis of the results previously discussed, the following conclusions can be drawn:

- The detection of pesticides in rainwater samples at times that cannot be related to the local spraying seasons and the detection of compounds that are believed not to be used in the vicinity of a sampling site indicate that there has been an atmospheric transport at least at a regional scale.
- Atmospheric transport from distant agricultural areas mainly accounted for the occurrence of triazines in rain, while local sources were the major contributor to the fungicide concentrations measured during the local application period.
- The fact that certain pesticides are registered in some countries, whereas their use is prohibited in others, greatly enhances the possibility to study the atmospheric transport of these compounds. Furthermore, by looking for the nearest agricultural or urban area in which a pesticide is used in substantial amounts it is possible to obtain information about its origin. From the distance between the sampling site and the possible source area inference can be made as to the minimum distance the pesticide has travelled through the atmosphere. By doing so and ruling out a possible illegal use of atrazine, terbuthylazine and simazine in the area of study, a travelling distance of at least 50 km for these chemicals seems to be plausible and in agreement with the results found in the literature. Several studies reported travelling distances for atrazine and simazine of at least 100-200 km (OBERWALDER & HURLE 1993, cited by VAN DIJK & GUICHERIT 1999, BESTER *et al.* 1995, LODE *et al.* 1995, VAN DIJK & GUICHERIT 1999, THURMAN & CROMWELL 2000) up to 1000 km (GLOTFELTY *et al.* 1990b, MAJEWSKI *et al.* 2000). Travelling distances for terbuthylazine of at least 50 km were reported by BESTER *et al.* (1995).

4.2.4 Transformation products

As explained in chapter 2 (par. 2.2.3.1), it has been demonstrated for several pesticides that the parent compound is not the only form that is present in the air, precipitation and fog. Transformation products of these pesticides have been investigated and detected in the atmosphere by several authors (see reviews by MAJEWSKI & CAPEL 1995 and by VAN DIJK & GUICHERIT 1999).

In this study three transformation products of the triazine herbicides were investigated: desisopropylatrazine, desethylatrazine and desethylterbuthylazine.

Desisopropylatrazine was never detected in any samples over the whole study. This can be explained by two observations: (a) the method used in this study for the multiresidue analysis

of pesticides in rainwater reported low recovery rates for this compound; (b) results from the literature show very low frequencies of detection and low concentration levels for this metabolite (MAJEWSKI & CAPEL 1995, GOOLSBY *et al.* 1997, BUCHELI *et al.* 1998, JAGER *et al.* 1998, CHARIZOPOULOS & PAPADOPOULOU-MOURKIDOU 1999). The lower frequency of detection and the lower concentrations of desisopropylatrazine found in the rain in comparison to desethylatrazine are most likely the result of the fact that the rate of the desisopropylation process (responsible for the formation of desisopropylatrazine) is slower than that the desethylation process (responsible for the formation of desethylated metabolites like desethylatrazine and desethylterbuthylazine) (JAGER *et al.* 1998).

Desethylatrazine was the most frequently detected metabolite of the herbicide atrazine. In agreement with the results reported in the literature (BUCHELI *et al.* 1998, JAGER *et al.* 1998), peak concentrations of desethylatrazine occurred with a delay of a few weeks with respect to its parent compound (Figure 27, bottom graph). In both years, desethylatrazine concentrations increased through May reaching the highest values in June, when the highest concentrations of atrazine occurred. After June, desethylatrazine concentrations decreased, mirroring the pattern of atrazine concentrations, though at lower values. By the end of July, desethylatrazine concentrations dropped under the limit of determination.

The ratio of the concentration of desethylatrazine to atrazine – the DAR ratio – has been used as an indicator of herbicide transport and ground-water and surface-water interaction in the environment. Low DAR values (median < 0,1) occur in streams during run-off shortly after application of atrazine. Higher DAR values (median about 0,4) occur later in the year after a considerable degradation of atrazine to desethylatrazine has occurred in the soil. (THURMAN *et al.* 1992, GOOLSBY *et al.* 1997, LIETZ 2003)

In this study, average DAR ratios were calculated for 2001 and 2002. Results are illustrated in Figure 27 (top graph). The DAR ratio changed markedly over the growing season from initial values of 0,30 (in 2001) and 0,19 (in 2002) to maximum values of 0,55 (in 2001) and 0,64 (in 2002). Overall, DAR values were higher than 0,1, a value commonly observed in rivers in USA (THURMAN *et al.* 1992). Atrazine is degraded to desethylatrazine both in the soil and in the atmosphere. PELLIZZETTI *et al.* (1990) showed that, in the atmosphere, atrazine degrades to desethylatrazine by photooxidative processes. The vapour pressure of desethylatrazine is two orders of magnitude lower than that of atrazine, thus desethylatrazine volatilizes from soil at a lower rate than atrazine. Therefore, even if a significant degradation of atrazine had taken place in the soil, resulting in DAR values of about 0,4, the DAR measured in the atmosphere should result lower than this value. Consequently, the high DAR values found in this study are indicative of degradation processes of atrazine occurred during the atmospheric transport. DAR values found in the literature for precipitation samples

are highly variable, but they are normally much higher than 0,1. The results of this study are consistent with the published data (see par. 2.2.3.1).

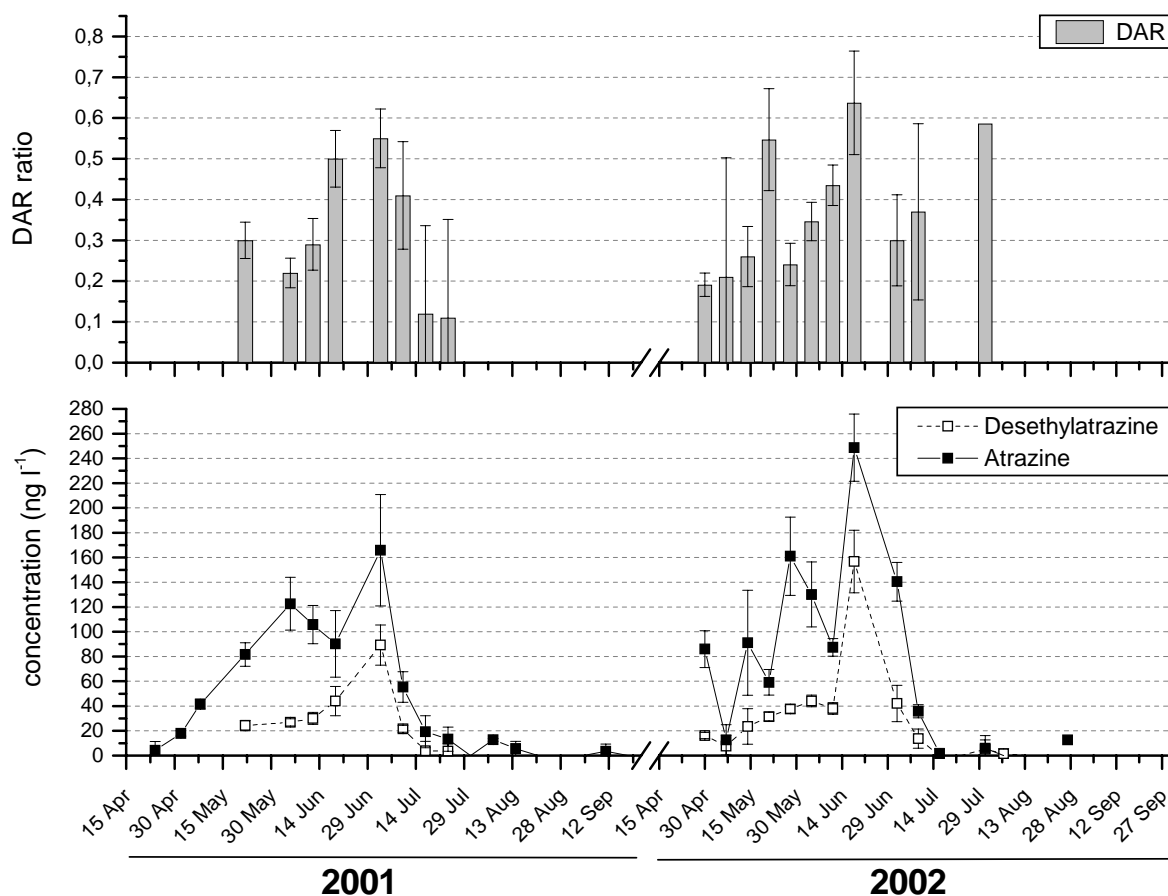


Figure 27: Desethylatrazine and atrazine average concentrations in precipitation (ng l^{-1} ; bottom graph) and average DAR values (top graph) for 2001 and 2002. Error bars represent the standard deviation among the sampling sites.

The time-series of desethylterbuthylazine concentrations compared to the parent compound presented differences between the two years (Figure 28). In 2001, desethylterbuthylazine highest concentration occurred nearly one month after the peak of terbuthylazine. Differently, in 2002, desethylterbuthylazine and terbuthylazine peak concentration occurred during the same sampling week. Unlike the results obtained for desethylatrazine and atrazine, both in 2001 and 2002, terbuthylazine concentrations dropped under the limit of determination by mid July, while desethylterbuthylazine could still be detected above this limit until August.

In the frame of this study it was not possible to explain these findings. Data on weather conditions occurred during the sampling campaigns were limited. Furthermore, no information on applications of terbuthylazine could be obtained.

One hypothesis is that peak concentrations of terbuthylazine detected in the two years reflected different periods of residence of this herbicide in the atmosphere. A deposition of

terbuthylazine by precipitation shortly after application, resulting in a short period of permanence in the atmosphere and, consequently, in a reduced time during which degradation processes might take place, could explain lower concentrations of the metabolite in comparison to those of the parent compound. Conversely, the longer the parent compound is dispersed in the atmosphere, the higher the probability that it undergoes degradation processes, thus leading to higher concentrations of the metabolite. Furthermore, atmospheric conditions during the transport like air temperature and aerosol concentration seem to be determining factors influencing the decomposition of terbuthylazine, as recently reported by Zetsch (2003).

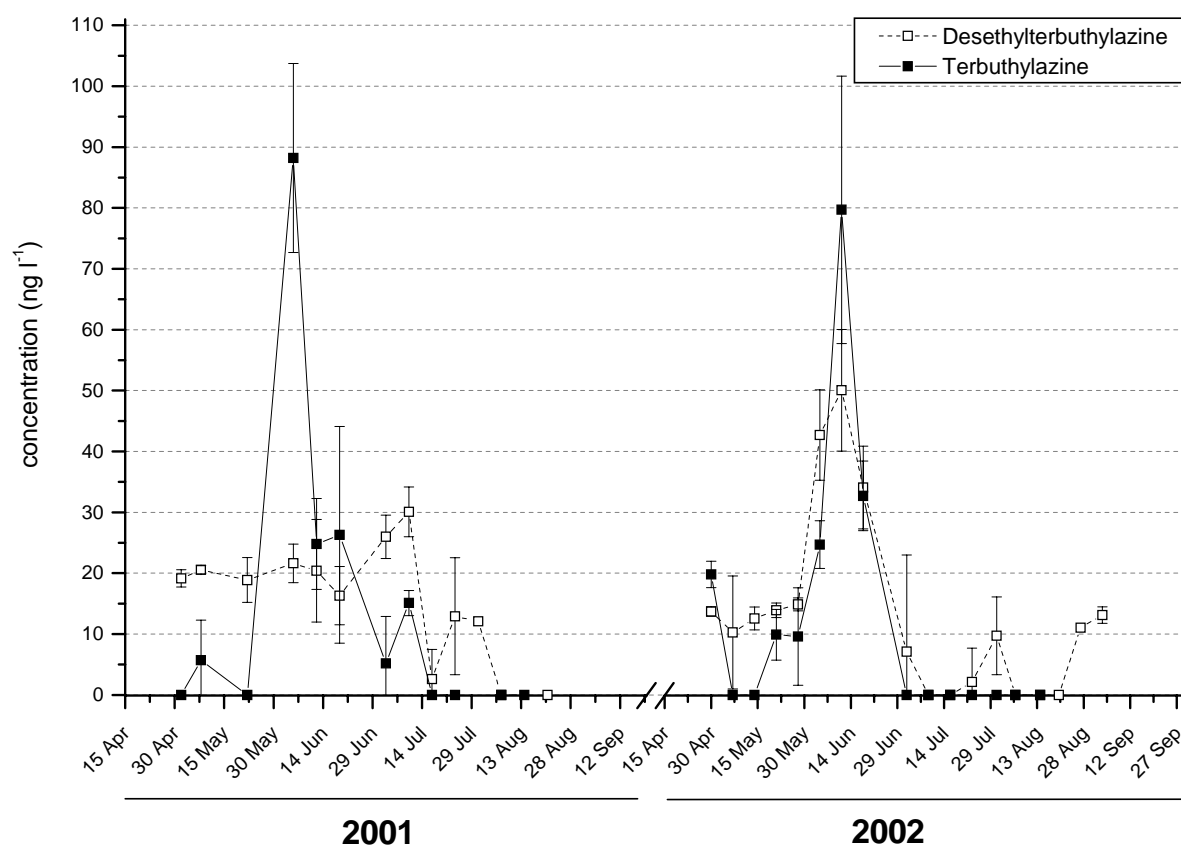


Figure 28: Desethylterbuthylazine and terbuthylazine average concentrations (ng l⁻¹) for 2001 and 2002. Error bars represent the standard deviation among the sampling sites.

A second explanation might be found in the phase in which the atmospheric transport occur. As previously explained, the degradation of triazines in the atmosphere is assumed to proceed mainly by reaction with OH radicals (see 2.2.3.1). If these compounds are transported in the aqueous phase (cloud or rain droplets), where the concentration of OH radicals is lower than that of the gas phase, the degradation rates are reduced leading to longer lifetimes of the parent compounds (HÜSKES & LEVSEN 1997).

Investigating and explaining the behaviour of pesticides and their metabolites in the atmosphere is a difficult task which requires further research. Pesticide transformation products are a significant key for achieving a more thorough understanding of the mass flux and the environmental fate of airborne pesticides. Furthermore, most oxidative reaction products are more polar and, consequently, more water soluble than their parent compounds (MAJEWSKI & CAPEL 1995, JAGER *et al.* 1998). Indeed, the water solubility of desethylatrazine is approximately two orders of magnitude higher than that of atrazine (see Table 10). Consequently, dealkylated products, being also generally more persistent than the parent compounds, can leach more easily in the soil and must be considered as hazardous pollutants for ground water contamination (MILLS & THURMAN 1994, GUZZELLA *et al.* 2003, SPALDING *et al.* 2003). In fact, one of the main reasons which lead to the banning of the use of the herbicide atrazine in Germany was the discovery of high levels of ground water contamination with atrazine and its primary metabolites desethylatrazine and desisopropylatrazine (JAGER *et al.* 1998, KÜCHLER *et al.* 2002). Concerns about these metabolites are also raised by their phytotoxicity (JAGER *et al.* 1998, VAN DIJK & GUICHERIT 1999).

4.2.5 Deposition

As previously discussed (see 4.2.2), concentration levels in rain strongly depends on the frequency, intensity and duration of precipitation events. For instance, high concentrations may be the result of short and intense precipitation events where pesticides are effectively scavenged from the atmosphere during the first minutes of the event (BUCHELI *et al.* 1998). However, in these cases, the high concentrations are offset by low precipitation volumes and do not significantly impact on the time-series of deposition flux. On the other hand, samples collected during a more significant storm may have lower overall rainwater concentrations, due to a dilution effect occurring in the total sample, but the amount of pesticide mass delivered to a region during this event may be considerable.

An example is shown in Figure 29. On 16 July 2002 a concentration of 35 ng l^{-1} of kresoxym-methyl was detected at Morscheid (site M) and a depositional flux of $1,519 \text{ } \mu\text{g m}^{-2}$ was calculated (Figure 29 – A). The sample collected the following week after a very short rain event (2,3 mm) attained a concentration level about 14 times higher (508 ng l^{-1}), but a corresponding lower depositional flux ($1,169 \text{ } \mu\text{g m}^{-2}$) (Figure 29 – B) was calculated if compared to the previous event.

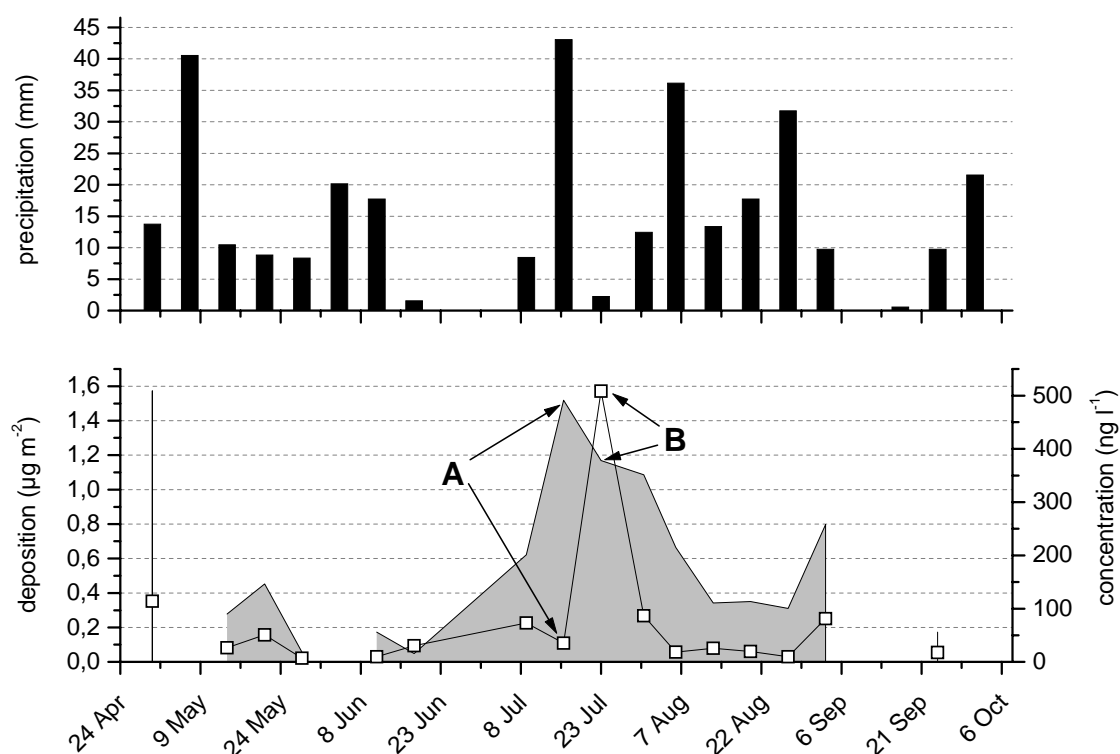


Figure 29: Deposition ($\mu\text{g m}^{-2}$, shaded area) and concentration (ng l^{-1} , solid line with square symbols) of kresoxym-methyl measured at the “Schloss Marienlay” winery area (M site) in 2002 (bottom graphic) and respective cumulative rainfall (mm) per sampling period (top graphic).

Concentration values in terms of ng l^{-1} do not allow to evaluate the atmospheric immissions of a substance, as no indication is given on the deposited mass. Furthermore, samples collected in different years cannot be easily compared to each other in terms of ng l^{-1} , as weather conditions, *i.e.* different rainfall amounts occurred during sampling, play an important role and must be taken into account. Consequently, in order to quantify the amount of pesticides deposited on the area of study and to facilitate the comparison between each sampling campaign, deposition amounts were calculated. The concentration of each pesticide compound in ng l^{-1} was multiplied by the actual rainfall amount in mm (l m^{-2}), measured at the closest weather station, to obtain the total depositional flux ($\mu\text{g m}^{-2}$) per sample and per growing season.

Average deposition loads for 2001 and 2002, calculated for classes of pesticides on a monthly basis, are shown in Figure 30.

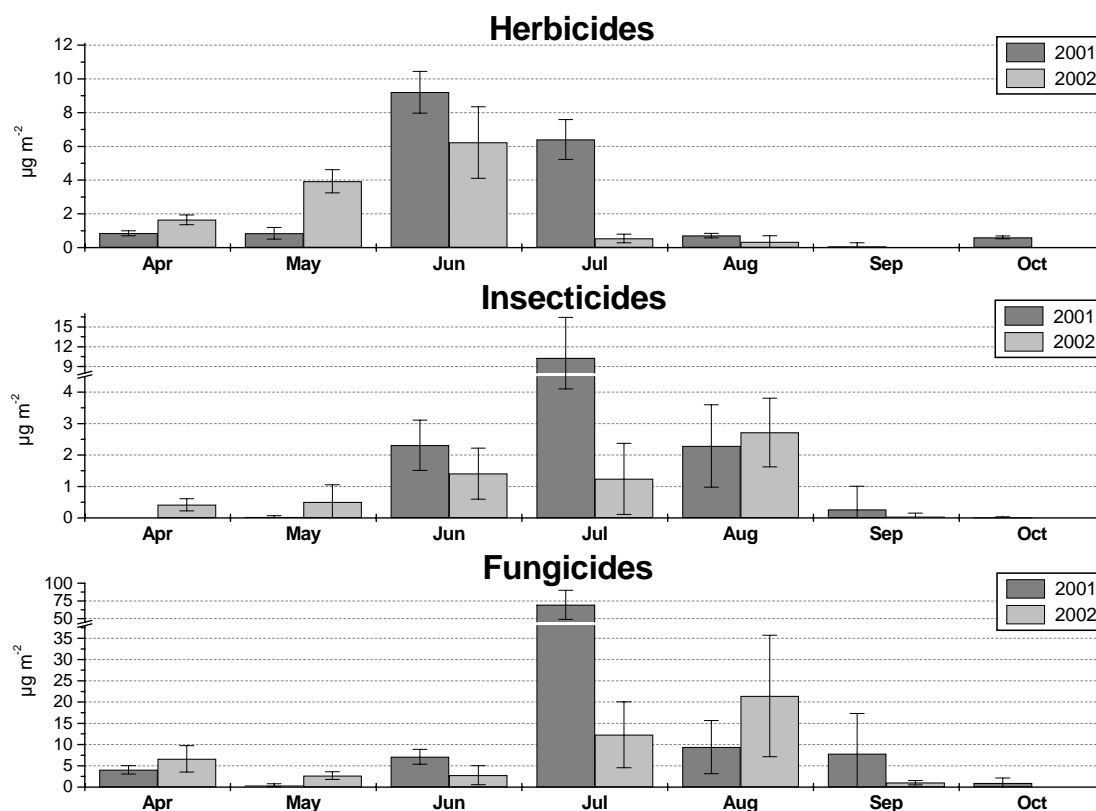


Figure 30: Average monthly deposition fluxes ($\mu\text{g m}^{-2}$) calculated for the 2001 and 2002 rain sampling campaigns. Herbicides = 3 active ingredients and 2 metabolites, Insecticides = 3 active ingredients, Fungicides = 16 active ingredients. The error bars represent the standard deviations of the 8 sampling sites.

As already observed for the temporal changes in the concentrations (ng l^{-1}), temporal variations of the calculated deposition loads strongly correlated with the main application times of the different classes of pesticides. The majority of herbicides (and their metabolites)

was deposited between April and July, when products of this class are mainly applied on maize crops. Insecticides and fungicides showed the highest depositions between June and August. During these months, insecticides are mainly applied on the oil-seed rape crops largely grown in Luxembourg and France, while smaller amounts of insecticides are used on grape crops (PERMESANG 2004, personal communication). Fungicides, instead, are largely applied from June through August in the vineyards of the area of study.

Depositional patterns were similar among the two years, but considerable variations existed in loadings by month (Figure 30). Higher depositions were measured in 2002 than in 2001 during April and May for all classes of pesticides, while in June, July and September 2002 loadings were smaller than in 2001. In August, deposition fluxes of fungicides and insecticides were larger in 2002 than in 2001, while the herbicide loadings were larger in 2001. Overall, these differences resulted in higher annual loadings measured for 2001 than for 2002 for all classes of pesticides (see Table 19 and Figure 31).

Variations among years might be attributed to two variables: differences in application practices and atmospheric conditions during and after application.

An analysis of fungicide use in 2001 and 2002 could be made on the basis of the available data (see Appendix A). Both in 2001 and 2002, eight applications were carried out in the Avelsbach wine-growing domain; the last applications were performed on 20 August 2001 and on 15 August 2002. In the area of Kasel and Morscheid (Ruwer valley) fungicides were applied 10 times in 2001 and 9 times in 2002; the last applications were performed on 7 September 2001 and on 30 August 2002. The fact that in 2001, both in the Avelsbach wine-growing domain and in the Ruwer valley the last applications were performed later in the year than in 2002 are an indication that in 2001 the growing season ended later than in 2002. This might explain the higher fungicide depositions found for September 2001.

In both years, the same application rates (l ha^{-1} or kg ha^{-1}) were used for the same fungicide products. However, the spectrum of used products varied considerably from year to year. For example, in 2002 no folpet- and kresoxim-methyl-containing products were applied in the Avelsbach wine-growing domain anymore (contrary to 2001). The use of other fungicide active ingredients, in part not included in the analytical program of this study, lead to an underestimation of deposition fluxes in 2002 and can, to a certain extent, explain the differences found for the total fungicide deposition between the two years. Given the limited available information, differences in pesticide usage for the complete study area could not be ascertained. However, since no severely widespread infections of the vines were reported for the year 2001 (PERMESANG 2004, personal communication), it can be assumed that, in the study area, no major changes were made in the fungicide application practice (*i.e.* number of applications and application rates) compared to the two examples discussed above.

The previous observations can provide some explanations for the differences observed in deposition loadings only for the class of fungicides. According to the results and discussions presented before in this work, the presence of insecticides in the rain in the study area is mainly due to local emissions, while herbicides seem to occur in precipitation mainly as a result of atmospheric transport. Since no information on insecticide and herbicide use were available, no inferences on the influence of application practices can be made for these two classes of compounds.

The second factor influencing deposition rates are atmospheric conditions. Local atmospheric processes during application are important in atmospheric transport and redeposition onto the soil. Furthermore, as observed in par. 4.2.2.3, the timing of the rainfall events relative to application plays a decisive role. The limited data on pesticide usage in the study area did not allow to perform a detailed investigation on weather conditions during and after single applications. However, a comparison between the two years in terms of the main meteorological parameters can provide some more explanations of these results. Precipitation amount, number of dry days, average temperature and wind speed calculated on a monthly basis for 2001 and 2002 are listed in Table 18.

Table 18: Monthly precipitation, number of dry days, temperature and wind speed measured in 2001 and 2002 in the study area. Data taken from the meteorological station of the agro-meteorological measuring network (Agrarmeteorologisches Meßnetz, AMM) of the Rheinland-Pfalz State located at the sampling site A.

	Precipitation (mm)		N.° dry days		Temperature (°C)		Wind speed (m s ⁻¹)	
	2001	2002	2001	2002	2001	2002	2001	2002
May	11,3	<u>46,3</u>	27	18	15,5	13,9	1,3	1,1
June	<u>73,9</u>	45,5	17	19	15,3	18,4	1,1	1,1
July	<u>133,1</u>	75,0	16	15	19,0	18,0	1,3	1,1
August	55,8	<u>112,9</u>	18	14	18,9	18,4	0,9	0,7

With some exceptions, number of dry days, temperature and wind speed values were similar between the two years. The greatest differences between the two years were found in terms of precipitation amount. These data provide a further explanation of the deposition results illustrated in Figure 30. The months with the highest precipitation amounts (underlined values) were those where the highest deposition fluxes were measured. Frequent rain events occurring around the time of applications result in a recurrent wash out of the atmosphere and the consequent deposition of the freshly emitted pesticides. On the other hand, periods with a high number of dry days and low precipitation amount (for example May 2001)

enhance the probability for the atmospheric pesticides to be dispersed and further transported in the atmosphere resulting in low deposition fluxes.

Similar differences in annual loadings were found by HATFIELD *et al.* (1996) in central Iowa from 1991 till 1994, where in 1992 loadings were less than half than those found in the other years of investigations. The authors explained the results with differences in atmospheric conditions and application amounts.

Nearly all of the deposition of the pesticides analysed in this study occurred during April through September. Low deposition fluxes were found in October. Rain samples collected at irregular intervals during November through March showed no detectable concentrations of the investigated substances (RIEFSTAHL 2000 and this work). Consequently, the sum of the deposition loads measured between April and September closely represent an estimation of the total annual wet deposition of pesticides (Figure 31).

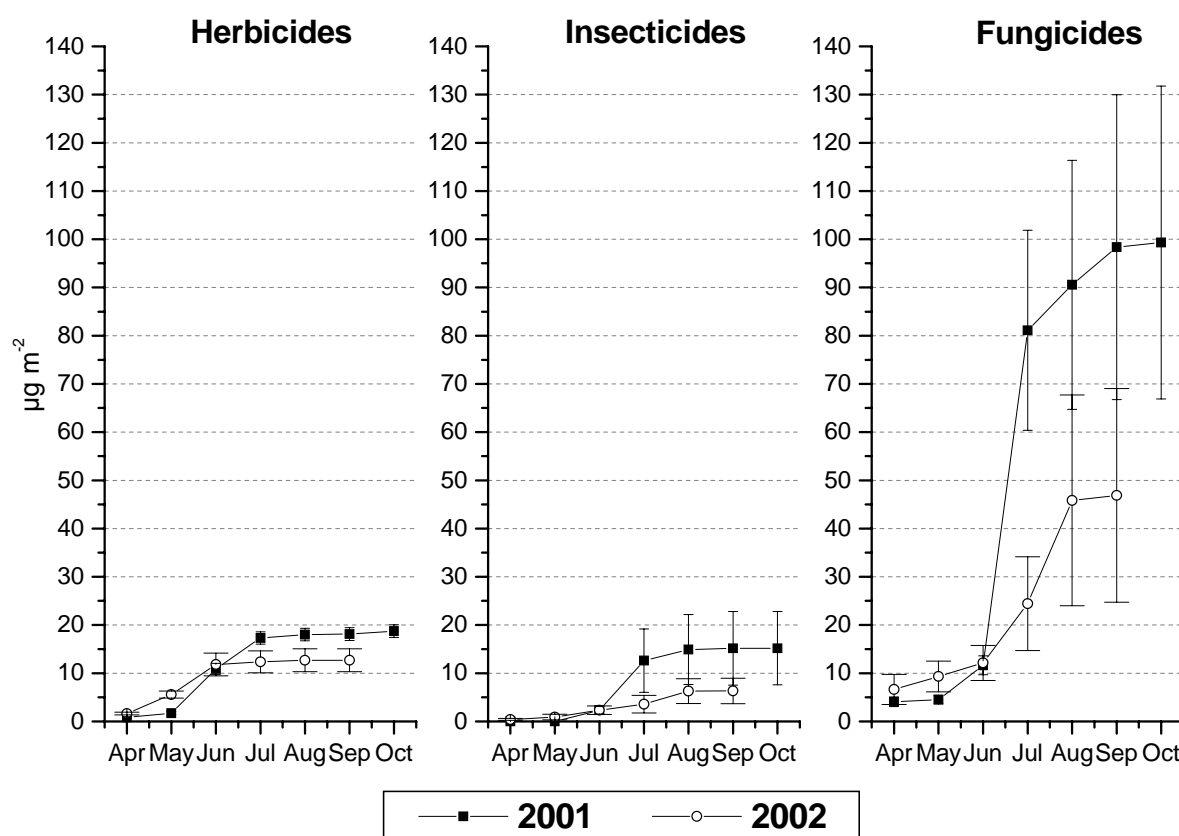


Figure 31: Average cumulative loads ($\mu\text{g m}^{-2}$) of herbicides, insecticides and fungicides deposited by rain in the study area during April through October 2001 and April through September 2002. The error bars indicate standard deviations of the 8 sampling sites.

The annual deposition loads measured for the three classes of pesticides at the different sampling sites in 2001 and 2002 are given in Table 19 and are illustrated in Figg. 32-34. As a comparison, deposition loads calculated for 2000 are shown only for herbicides and

insecticides. Depositions for the sampling stations M, MK and MB are not represented for 2000 as, in this year, sampling at these locations started later in the growing season (June-July). Since as of 2001 seven more fungicides were added to the list of investigated pesticides, it is not possible to compare the values from 2001 and 2002 with those found in 2000, therefore data collected for the class of fungicides in 2000 are not shown.

Table 19: Annual deposition loads ($\mu\text{g m}^{-2} \text{a}^{-1}$) measured for the three classes of pesticides at the eight sampling sites in 2001 and 2002.

Site	Herbicides		Insecticides		Fungicides	
	2001	2002	2001	2002	2001	2002
A	19,40	15,57	25,37	9,80	109,71	49,17
G	17,06	9,69	14,70	4,11	86,92	35,18
HM	16,08	14,14	20,20	4,43	116,28	34,67
K	18,11	8,83	8,16	4,22	68,13	15,44
M	19,73	13,23	10,21	5,83	92,83	56,34
MB	18,59	14,37	12,69	8,79	128,48	84,38
MK	19,14	13,77	24,89	9,66	139,71	68,52
T	16,93	11,95	5,09	3,83	44,89	32,53
Average	18,13	12,70	15,16	6,33	98,38	47,03

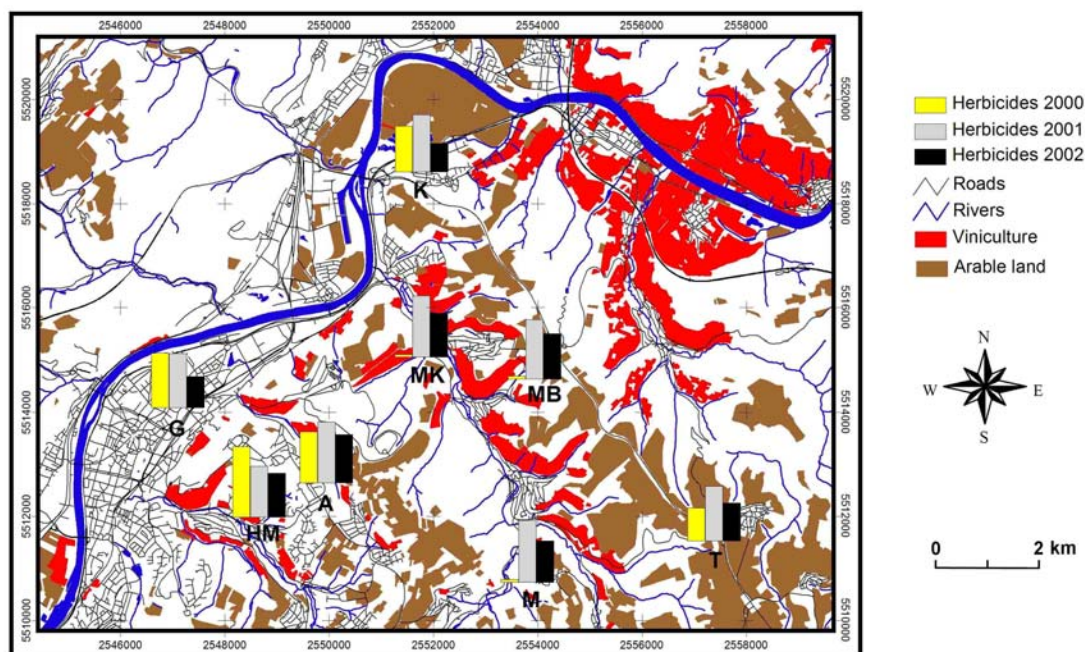


Figure 32: Annual deposition loads of herbicides and their metabolites measured at the eight sampling sites in 2000, 2001 and 2002. Data are listed in Table 19. Geospatial reference data (ATKIS - Basis - DLM; DGM) published with the permission of the Land Survey Office (Landesvermessungsamt) Rheinland-Pfalz, 06.10.2000 - Az.: 26 722-1.11; ESRI Data & Maps (2000).

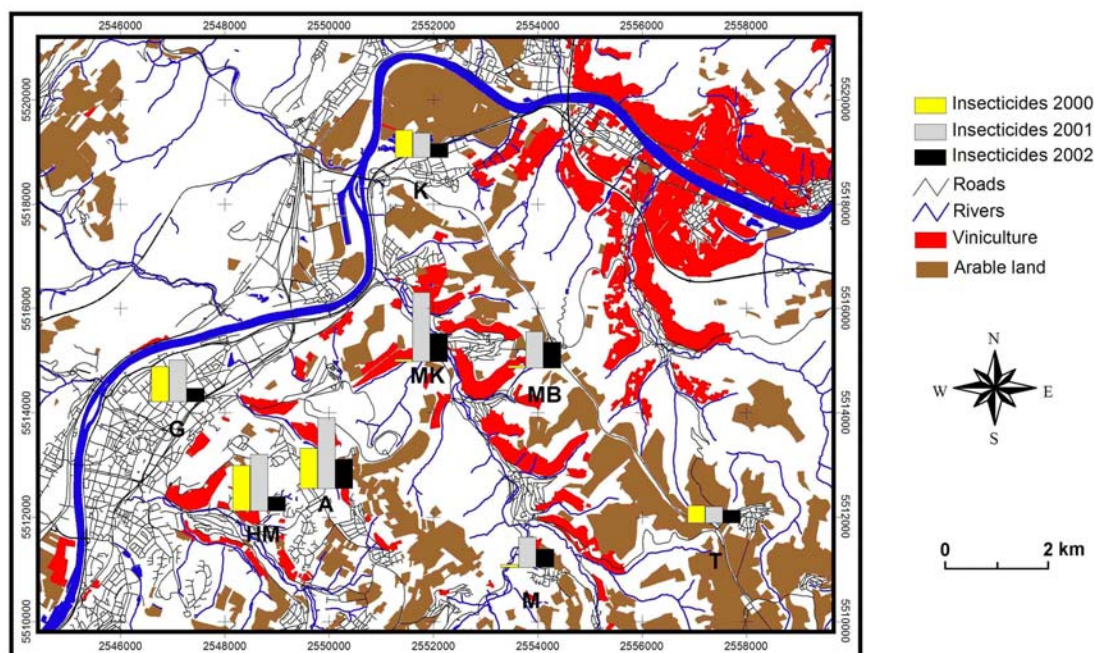


Figure 33: Annual deposition loads of insecticides measured at the eight sampling sites in 2000, 2001 and 2002. Data are listed in Table 19. Geospatial reference data (ATKIS - Basis - DLM; DGM) published with the permission of the Land Survey Office (Landesvermessungsamt) Rheinland-Pfalz, 06.10.2000 - Az.: 26 722-1.11; ESRI Data & Maps (2000).

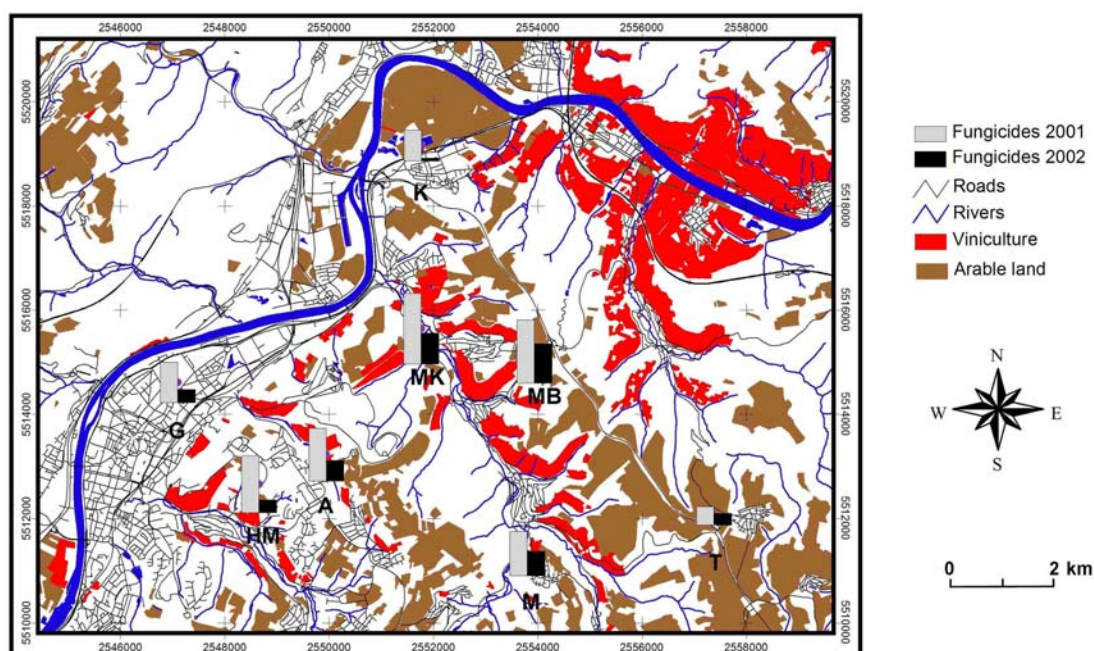


Figure 34: Annual deposition loads of fungicides measured at the eight sampling sites in 2001 and 2002. Data are listed in Table 19. Geospatial reference data (ATKIS - Basis - DLM; DGM) published with the permission of the Land Survey Office (Landesvermessungsamt) Rheinland-Pfalz, 06.10.2000 - Az.: 26 722-1.11; ESRI Data & Maps (2000).

The results obtained in terms of concentration values (ng l^{-1}) (see par. 4.2.3) are mirrored in the annual loadings. Very low differences in herbicide loads were observed among the sampling sites, while an increasing spatial variation was found for the classes of insecticides and fungicides.

On the basis of these results, it is plausible to consider the average annual deposition load of herbicides as a representative value of the study area, while for the insecticides and fungicides it is necessary to make some distinctions. For these two classes of pesticides, sampling sites were grouped according to the annual loadings recorded during the two years (see Table 20). In both years, the stations A and MK were subjected to the highest loadings of insecticides, while the less polluted sites resulted T and K. The same sites (A and MK), together with HM, M and MB recorded also the highest depositions of fungicides. It is remarkable that the site G, directly located in town where no applications of these pesticides are assumed, does not belong to the group with the lowest loadings, but in both years it was subjected to a middle level of deposition.

Table 20: Annual load levels ($\mu\text{g m}^{-2} \text{a}^{-1}$) of insecticides and fungicides measured at the eight sampling sites in 2001 and 2002.

Load Level	Insecticides		Fungicides	
	2001	2002	2001	2002
High	> 20 Sites: A, HM, MK	> 8 Sites: A, MB, MK	> 100 Sites: A, HM, MB, MK	> 49 Sites: A, M, MB, MK
Middle	$10 < x < 15$ Sites: G, M, MB	$4 < x < 6$ Sites: G, HM, K, M	$65 < x < 93$ Sites: G, K, M	$30 < x < 36$ Sites: G, HM, T
Low	< 8,2 Sites: K, T	< 4 Site: T	< 45 Site: T	< 16 Site: K

In order to put these results in some perspective, it is useful to compare the annual amounts of selected pesticides deposited by rain with the amounts typically used for pest control.

For the herbicide atrazine, banned in Germany since 1991, it is possible to refer to the applied amounts in the neighbouring countries. The maximum annual amount of atrazine applied is about 1 kg ha^{-1} in Luxembourg (ASCHMAN 2002, personal communication) and $1,5 \text{ kg ha}^{-1}$ in France (CHEVREUIL *et al.* 1996). If compared with these values, in 2001, the deposition of atrazine in the study area was approximately 0,012% and 0,008% of the amount typically used for the control of weeds on maize fields in Luxembourg and in France, respectively. In 2002, these values dropped to 0,009% and 0,006%, respectively.

For the insecticide methyl parathion (product: ME 605), the maximum annual amount allowed in the vine growing regions in Germany was 648 g ha^{-1} (as of September 2003, the use of

this product is not permitted anymore (BVL 2005)). At the sites A and MK, the deposition of methyl parathion was about 0,03% (in 2001) and 0,02% (in 2002) of the permitted amount. A corresponding lower percentage was calculated at the sites with middle and low load levels (less than 0,02% in 2001 and less than 0,008% in 2002).

The calculation of the maximum recommended amount for a single fungicide substance is a complicated task and can produce unrealistic values being affected by the following facts:

- The considered substance can be contained in different products (see for example the fungicide folpet in Table 21) that can be independently used from each other.
- A maximum number of applications per growing season is defined for each of these products.
- The maximum amount of a product which can be applied is a function of the growth stage of the plants; to this purpose recommended amounts are defined for four growth stages, with the last stage having the highest permitted amount.

Furthermore, the maximum recommended amounts do not necessarily correspond to the amounts actually applied in the study area. Although one product is allowed to be applied several times during the growing season, it is common practice to use different products with different active ingredients in order to avoid the development of pest populations which become resistant to a specific pesticide. The economic aspect plays also an important role in the choice of pesticides to be used. The fungicide substances investigated in this study (systemic fungicides) are very expensive and, therefore, they are used later in the season (as of June/July), when the danger of infections is higher or infections have already spread and more specific and effective treatments of the vines are required (PERMESANG 2002, personal communication).

The examples presented in Table 21 for the two fungicides cyprodinil and folpet will be discussed to better explain the difficulties of such a calculation. Application amounts recommended for other fungicide substances relevant for this study are listed in Appendix C.

Cyprodinil represents a simple case, as only one product containing this active ingredient is allowed in the viniculture (product: Switch) and only 2 applications are allowed per growing season. In the Avelsbach domain, Switch was applied one time both in 2001 and 2002, whereas in the area of Kasel it was applied one time in 2001 and two times in 2002 (see Appendix A). Therefore, it is reasonable to consider the maximum recommended amount for the GS75 (*i.e.* two applications resulting in 720 g ha^{-1} of active ingredient) as a realistic maximum amount applied in the area of study.

Table 21: Recommended application amounts of pesticides containing selected active ingredients (Source: Federal Office of Consumer Protection and Food Safety – Bundesamt für Verbraucherschutz und Lebensmittelsicherheit BVL).

Active ingredient	Product	Max. number of applications per growing season	Growth stage of plants (GS)*	Recommended application amount** of the product	Calculated max. application amount of the active ingredient
Cyprodinil	SWITCH (375 g kg ⁻¹ cyprodinil)	2	Basic amount	0,24 kg ha ⁻¹	180-720 g ha ⁻¹
			GS 61	0,48 kg ha ⁻¹	
			GS 71	0,72 kg ha ⁻¹	
			GS 75	0,96 kg ha ⁻¹	
Folpet	FOLPAN 500 SC (500 g l ⁻¹ folpet)	5	Basic amount	0,6 l ha ⁻¹	1500-6000 g ha ⁻¹
			GS 61	1,2 l ha ⁻¹	
			GS 71	1,8 l ha ⁻¹	
			GS 75	2,4 l ha ⁻¹	
Folpet	FOLPAN 80 WDG (800 g kg ⁻¹ folpet)	5	Basic amount	0,4 kg ha ⁻¹	1600-6400 g ha ⁻¹
			GS 61	0,8 kg ha ⁻¹	
			GS 71	1,2 kg ha ⁻¹	
			GS 75	1,6 kg ha ⁻¹	
Folpet	FORUM Star (600 g kg ⁻¹ folpet)	6	Basic amount	0,48 kg ha ⁻¹	1728-6912 g ha ⁻¹
			GS 61	0,96 kg ha ⁻¹	
			GS 71	1,44 kg ha ⁻¹	
			GS 75	1,92 kg ha ⁻¹	
Folpet	Ridomil Gold Combi (400 g kg ⁻¹ folpet)	3	Basic amount	0,6 kg ha ⁻¹	720-2880 g ha ⁻¹
			GS 61	1,2 kg ha ⁻¹	
			GS 71	1,8 kg ha ⁻¹	
			GS 75	2,4 kg ha ⁻¹	

* see Appendix D for further explanation.

** In the steep vineyards this amount can be increased of up to 25%.

Such a calculation cannot be made in the case of the active ingredient folpet. As reported in the Table 21, four products containing folpet are allowed for use in the viniculture. However, for the reasons explained above, the use of all these products during one growing season is very unlikely. A comparison with the available data on pesticide applications carried out in the area of study (Appendix A) shows that during the growing seasons 2001 and 2002 only three of these products were used: Folpan 500 SC, Forum Star and Ridomil Gold Combi. Specifically, in 2001 in the Avelsbach domain, Folpan 500 SC was applied only once and Ridomil Gold Combi twice. In 2002, no folpet-containing products were used in this domain. In the area of Kasel, three applications of Forum Star were carried out in 2001 and two in 2002, whereas Ridomil Gold Combi was applied only once in 2001. According to these data, the applied amount of folpet was much lower than the maximum recommended amount.

These two examples clearly show how the maximum recommended application amounts do not always equal those actually used in the study area. Thus, in order to obtain percentage values most possibly close to reality, it will be referred to a specific case.

For this calculation, pesticide applications carried out in the Avelsbach domain will be used and the deposition values measured at the sampling site A will be considered in detail. The measured deposition loads of selected fungicides will be reported as a percentage of the amounts applied in the Avelsbach domain in the years 2001 and 2002. These values, presented in Tables 22 and 23, show the deposited amount of selected substances as a function of the amounts applied in the vicinity of the sampling site. Since the site A belongs to those sites where the highest fungicide loadings were found, these percentages can be considered as the highest values calculated for the study area.

From the Tables 22 and 23 it can be seen that the percentages calculated for 2002 are lower than those for 2001. This is the direct result of two facts (previously discussed in this paragraph): (a) in both years, similar amounts per hectare of active ingredients were applied and (b) in 2002, lower deposition loads were measured than in 2001.

Compared to the amounts applied for pest control, the amounts deposited are very small: except for fenarimol and kresoxym-methyl in 2001, all the deposited amounts are well less than 0,1% (range 0,008% to 0,07%) of the application amounts. These values are similar to those found in the literature. Several authors report deposition values for single active ingredients in the order of or less than 0,1% of the application rate (GLOTFELTY *et al.* 1990b, BUSER 1990, HATFIELD *et al.* 1996, DÖRFLER & SCHEUNERT 1997, AKKAN *et al.* 2003).

Table 22: Deposited amounts, number of applications, applied amounts and loadings as percentage of the applied amounts of selected fungicides measured at the site A (Avelsbach domain) in 2001.

	Deposited amount ($\mu\text{g m}^{-2} \text{ a}^{-1}$)	Number of applications	Applied amount ($\text{g ha}^{-1} \text{ a}^{-1}$)	Percentage of the applied amount
Cyprodinil	10,70	1	337,5	0,03%
Fenarimol	4,13	2	40,37	0,10%
Fludioxonil	16,56	1	225	0,07%
Folpet	20,63	3	1400	0,01%
Kresoxym-methyl	17,28	2	177,5	0,10%
Quinoxifen	5,25	2	132,77	0,04%

Table 23: Deposited amounts, number of applications, applied amounts and loadings as percentage of the applied amounts of selected fungicides measured at the site A (Avelsbach domain) in 2002.

	Deposited amount ($\mu\text{g m}^{-2} \text{ a}^{-1}$)	Number of applications	Applied amount ($\text{g ha}^{-1} \text{ a}^{-1}$)	Percentage of the applied amount
Cyprodinil	7,05	1	360	0,02%
Fenarimol	0,17	2	41,86	0,004%
Fludioxonil	12,68	1	240	0,05%
Folpet	6,73	0	-	-
Kresoxym-methyl	9,97	0	-	-
Quinoxifen	1,11	2	137,69	0,008%

The contribution of such atmospheric inputs to a non-target ecosystem such as a surface-water body depends on its location in relation to agricultural areas. For surface-water bodies located in agricultural areas like vine growing regions and subject to riverine or other surface runoff inputs from the treated areas, the contribution of atmospheric deposition of pesticides is negligible if compared to other sources. RÜBEL (1999) measured fungicide loads in superficial runoff samples collected in the Mosel-Saar-Ruwer vine growing region in the range of $\mu\text{g ha}^{-1}$ to mg ha^{-1} . Furthermore, the author underlined the importance of the vineyard roadways as one of the most important source of pesticides to surface-water bodies. The author observed on these tracks numerous spills of fungicide mixtures coming from leakages in the storage tanks used for pesticide applications. These spills result in high concentrated sources of active ingredients (up to several mg m^{-2}) (ALTMAYER & TWERTEK 2002) that can be easily mobilized during rain events and reach surface-water bodies. Finally, according to ALTMAYER & TWERTEK (2002) about 70% to 80% of the pesticide inputs to surface-water bodies in vine growing regions are the result of the cleaning of field crop sprayers.

The low pesticide input from precipitation is not a concern in rural areas where the impact of other sources is much more important. However, because of atmospheric dispersion and transport of contaminants, deposition in precipitation affects all parts of the environment and can convey residues to non-target sites, such as organic crops and sensitive ecosystems, like protected areas or drinking water reservoir. The potential impacts of these aerial pesticide inputs are as yet uncertain because of the limited available information on long-term eco-toxicological effects of pesticides at low concentrations. A number of papers have suggested effects on non-target organisms from aerial deposition of pesticides in Europe (DUBUS *et al.* 2000). DE JONG *et al.* (1995) estimated that fungi and vascular plants from over 25% of the Netherlands would be subject to non-target side effects from atrazine. CHEVREUIL *et al.* (1996) suggested that the combined effect of a mixture of pesticide compounds could possibly produce adverse impacts at concentrations below their individual toxic threshold values.

The potential contribution of pesticides from the atmosphere to ground water depends on the pesticide levels in atmospheric deposition and on the portion of ground-water recharge that is derived from precipitation. The greatest contribution is likely to occur when precipitation is the major source of recharge and the unsaturated zone is highly permeable, particularly if there are macropores, cracks, or fissures in the soil (SHAFFER *et al.* 1979, THOMAS & PHILLIPS 1979, SIMSON & CUNNINGHAM 1982). Contamination of ground water by pesticides with greater solubility in water than that of the organochlorine insecticides (like those investigated in this study) does occur, but how much of this contamination can be attributed to atmospheric deposition is not known (MAJEWSKI & CAPEL 1995).

4.2.6 Summary and conclusions on rain sampling campaigns

Rain samples were weekly collected at eight sites located in the vinicultural area of Trier, from mid April through November 2001 and from mid April through early October 2002. Altogether 182 samples were collected in 2001 and 162 samples in 2002, and analysed for 24 pesticides and 3 metabolites.

The main results of the rain sampling campaigns can be summarised as follows:

- Twenty-four of the 27 measured pesticides were detected above LoD at least once in 2001 and twenty-one in 2002. In 2001 and 2002 similar seasonal trends were observed. Most pesticides were detected from the beginning of sampling; herbicides were detected until August, while insecticides and most fungicides were detected until September. Three fungicides could be detected above LoD until late October 2001, while the fungicide cyprodinil could be detected at very low concentrations until November 2001.

- In both years, the highest detection frequencies and highest concentrations were found for the class of fungicides. The most frequently detected compounds were the fungicides cyprodinil, kresoxym-methyl, tebuconazole and fludioxonil. The highest concentrations were measured in the summer months, coinciding with application times and warmer temperatures.
- Average concentrations of the single substances were less than 100 ng l⁻¹, with a few exceptions. However, total concentrations were considerable and in some instances well above the EU drinking water quality standard of 500 ng l⁻¹ for total pesticides.
- The occurrence of triazines in rain, for which there are no legal uses in Germany, was related to transport through the atmosphere from areas where the use of these active ingredients is still permitted. Accordingly, a travelling distance of at least 50 km was calculated for atrazine, terbuthylazine and simazine.
- Local sources were identified as the major contributor to the occurrence of the insecticide methyl parathion and fungicides in rain detected during the local application period.
- The investigation of a few metabolites showed the importance of pesticide transformation products as a significant key in more fully understanding the mass flux and the environmental fate of airborne pesticides.
- Annual deposited amounts calculated for atrazine were between 0,009% and 0,012% of the maximum annual amount applied in Luxembourg and between 0,006% and 0,008% of the maximum annual amount applied in France. Annual deposited amounts calculated for methyl parathion and for selected fungicides resulted between 0,004% and 0,10% of the maximum annual amount allowed to be applied in the vine growing areas in Germany.

The contribution of such atmospheric inputs to a non-target ecosystem such as a surface-water body depends on its location in relation to agricultural areas. For surface-water bodies located in agricultural areas like vine growing regions and subject to riverine or other surface runoff inputs from the treated areas, the contribution of atmospheric deposition of pesticides is negligible if compared to other sources. However, because of atmospheric dispersion and transport of contaminants, deposition in precipitation affects all parts of the environment and can contribute residues to non-target sites, such as organic crops and sensitive ecosystems, like protected areas or drinking water reservoir. The potential impacts of these aerial pesticide inputs are as yet uncertain because of the limited available information on the long-term eco-toxicological effects of pesticides at low concentrations.

4.3 Air sampling campaigns

Altogether seven air sampling campaigns were carried out during the growing season 2002. Of these, four campaigns were started following pesticide applications performed in the Avelsbach domain (general data are summarised in Table 24). During these campaigns, different sampling times were chosen (between 1 h and 24 h) in order to investigate on a detailed basis the temporal variations of air concentrations of the applied substances. Unfortunately, only four of the applied active ingredients were comprised in the list of the investigated substances. Air samples were taken at the stations AA, W and H (see sampling sites description in 3.2.1).

The remaining three sampling campaigns were carried out as of the end of August, when the investigated substances were not applied anymore in the area of study. In order to detect lower air concentrations, longer sampling times were chosen (24 h samples only). Since the portable battery operated sampler at the location W did not allow sampling times longer than 10 hours, samples were taken only at the sampling stations AA and H. General information about these campaigns are listed in Table 25.

The sampling stations AA and W were chosen in order to gain detailed information on pesticide dispersion in the atmosphere following application. The site W was located in the vineyards where pesticides were applied; the site AA was located about 300 m downwind of the site W and about 100 m from the edge of the treated area. According to main wind direction data collected during the sampling, the station H was not directly affected by pesticide applications carried out in the Avelsbach domain, and can be considered as an indicator of average pesticide concentration in the gas and particle phases of the study area. Figure 35 shows the Avelsbach domain, the two sampling sites AA and W and the area where the investigated active ingredients were applied (shaded area).

In the first part of this section (par. 4.3.1), only results on the substances applied in the Avelsbach domain will be presented and discussed in details. In the second part (par. 4.3.2), all sampling campaigns will be presented and discussed taking into consideration the whole spectrum of detected substances.

Table 24: Air sampling campaigns following pesticide applications carried out in the Avelsbach domain during the early and middle growing season 2002.

Sampling Campaign	May	June 1	June 2	July
Pesticide Application	23–24 May Delan: 600 ml ha ⁻¹ Sulphur: 3 kg ha ⁻¹	5 June Vento: 300 ml ha ⁻¹ Melodi: Multi 2 kg ha ⁻¹	19–20 June A: Delan: 400 ml ha ⁻¹ Flint: 0,1 kg ha ⁻¹ B: Flint: 0,2 kg ha ⁻¹ Forum: 1,5 l ha ⁻¹	17–18 July A: Equation Pro: 650 g ha ⁻¹ Vento: 400 ml ha ⁻¹ B: Switch: 0,96 kg ha ⁻¹ Teldor: 1,6 kg ha ⁻¹
Active ingredient application	Dithianon: 450 g ha ⁻¹	Fenarimol *: 17,9 g ha ⁻¹ Quinoxifen *: 59 g ha ⁻¹ Iprovalicarb: 120 g ha ⁻¹ Tolyfluanid: 750 g ha ⁻¹	A: Dithianon: 300 g ha ⁻¹ Trifloxystrobin: 50 g ha ⁻¹ B: Trifloxystrobin: 100 g ha ⁻¹ Dimethomorph: 225 g ha ⁻¹	A: Cymoxanil: 195 g ha ⁻¹ Famoxadone: 146 g ha ⁻¹ Fenarimol *: 23,9 g ha ⁻¹ Quinoxifen *: 78,7 g ha ⁻¹ B: Cyprodinil *: 360 g ha ⁻¹ Fludioxonil *: 240 g ha ⁻¹ Fenhexamid: 816 g ha ⁻¹
Size of treated area	Ca. 18,6 ha	Ca. 16 ha	A: ca. 2,6 ha B: ca. 16 ha	A: ca. 18,6 ha B: ca. 11,9 ha
Duration of sampling	22–27 May	6–7 June	19–21 June 24–28 June	18–23 July 29–31 July
Site AA (n)	7	2	8	6
Site W (n)	6	2	2	6
Site H (n)	-	1	9	6
Note		Sampling was terminated because of a rain event		

* Substances analysed in this study

Table 25: Air sampling campaigns, not related to specific pesticide applications, carried out during the late growing season 2002.

Sampling Campaign	August	September 1	September 2
Duration of sampling	26–27 August	5–9 September	16–20 September
No. samples – Site AA	1	4	4
No. samples – Site W	-	-	-
No. samples – Site H	1	4	4
Note	Sampling was terminated because of a rain event		

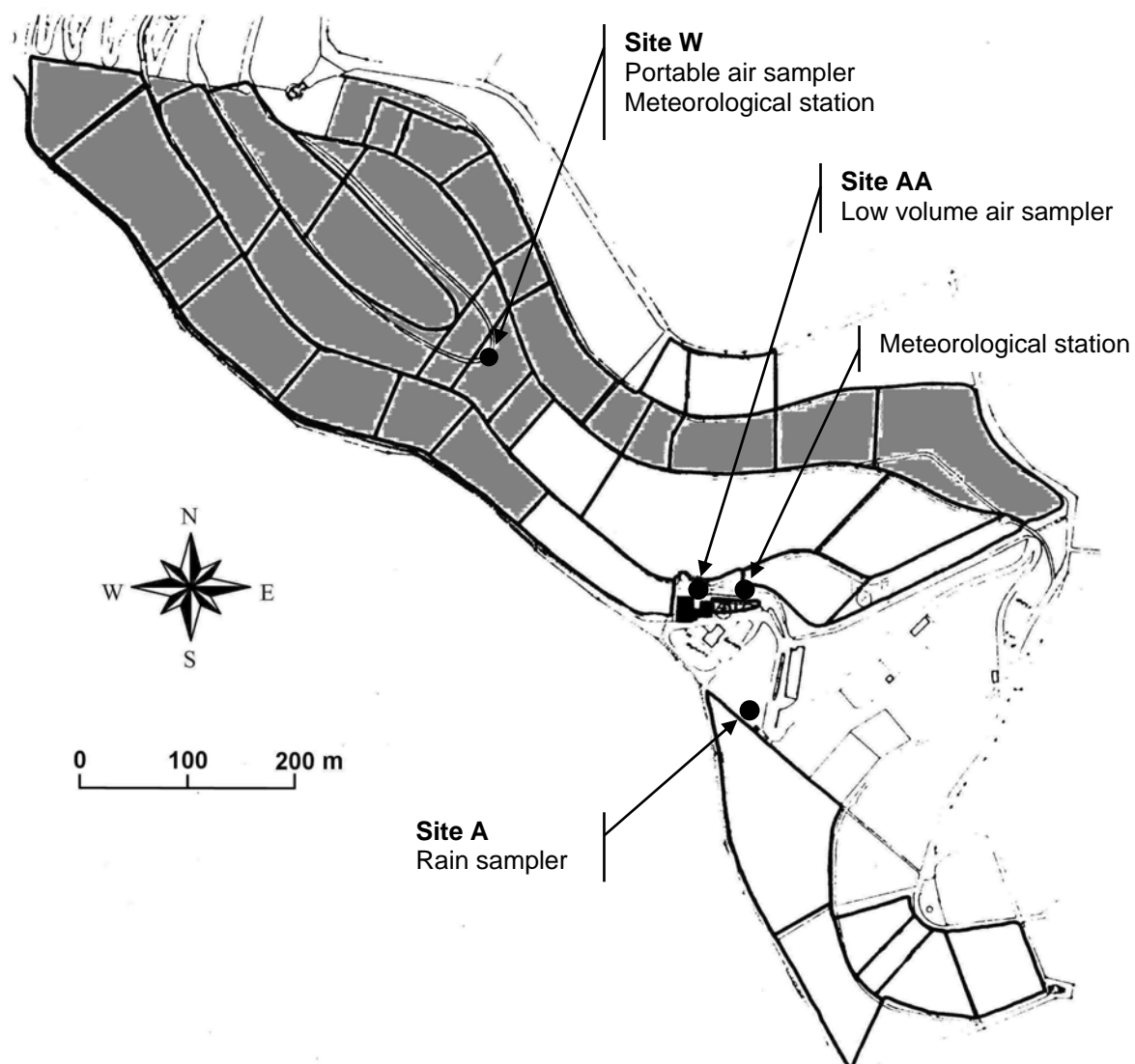


Figure 35: Avelsbach wine-growing domain. Air sampling and rain sampling sites, and meteorological stations. The shaded area represents the area where the investigated active ingredients were applied during the growing season 2002.

4.3.1 Sampling following pesticide applications in the Avelsbach domain

In this section, results of the air sampling campaigns carried out during the growing season 2002 (see Table 24 and 25) will be presented and discussed focusing on the applied active ingredients fenarimol, quinoxifen, cyprodinil and fludioxonil. Only the sampling sites AA and W will be considered. The sampling campaign carried out in May 2002 will be discussed in the next section, as none of the pesticides applied in the Avelsbach domain was included in the list of the investigated substances.

4.3.1.1 Sampling campaigns June 1 and June 2

The sampling campaign June 1 was started early in the morning on 6 June as pesticide application on 5 June lasted all day. Unfortunately, a heavy rain event occurred on 7 June and caused the early termination of the campaign. For this reason, a second campaign was started on 19 June (campaign June 2) when another application was carried out in the domain (see Table 24). During this application none of the investigated substances was used. For this reason, the results of these two campaigns will be presented together as the presence of quinoxifen in the collected samples is assumed to be the direct consequence of the application carried out on 5 June.

Sampling site W

Because of several equipment and power failures of the portable battery operated sampler, only the two samples collected during the campaign June 1 could be processed. Details are listed in Table 26.

Table 26: Air sampling campaign June 1, sampling site W.

Sample	W7	W8
Date	6 June	6–7 June
Time	8:40 – 16:40	17:00 – 01:00
Predominant wind direction	SW	N
Average wind speed	0,6 m s ⁻¹	0,3 m s ⁻¹
Average air temperature	17,9 °C	17,5 °C
Sampling flow	15,5 l min ⁻¹	15,5 l min ⁻¹
Sampled air volume (standard volume)	7,409 m ³	7,410 m ³
TSP	9,4 µg m ⁻³	6,7 µg m ⁻³
Quinoxifen (gas phase)	n.d.	n.d.
Quinoxifen (particle phase)	2,1 ng m ⁻³	4,8 ng m ⁻³
Fenarimol (gas and particle phase)	n.d.	n.d.

Sampling site AA

During the campaigns June 1 and June 2, pesticide concentrations at the site AA were determined only in the particle phase (PM₁₀). Details are listed in Table 27.

Table 27: Air sampling campaigns June 1 and June 2, sampling site AA.

Sample	AA8	AA9	AA10	AA11	AA12
Date	6 June	6–7 June	19 June	20 June	20 June
Time	8:52 – 16:52	17:08 – 1:08	15:45 – 19:45	6:00 – 12:00	13:00 – 19:00
Duration of sampling	8 h	8 h	4 h	6 h	6 h
Predominant wind direction	SW	N-NW	NW	SW	W-SW
Av. wind speed	0,6 m s ⁻¹	0,3 m s ⁻¹	0,7 m s ⁻¹	1,0 m s ⁻¹	2,5 m s ⁻¹
Av. air temperature	17,9 °C	17,5 °C	27,3 °C	21,0 °C	25,7 °C
Sampling flow	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹
Sampled air volume (standard volume)	7,907 m ³	7,910 m ³	3,895 m ³	5,955 m ³	5,866 m ³
PM ₁₀	11,4 µg m ⁻³	29,1 µg m ⁻³	61,6 µg m ⁻³	36,9 µg m ⁻³	27,3 µg m ⁻³
Quinoxifen (PM ₁₀)	1,8 ng m ⁻³	1,6 ng m ⁻³	2,6 ng m ⁻³	1,8 ng m ⁻³	1,7 ng m ⁻³
EF* quinoxifen	156,0 µg g ⁻¹	55,8 µg g ⁻¹	41,8 µg g ⁻¹	49,5 µg g ⁻¹	62,4 µg g ⁻¹
Fenarimol (gas and particle phase)	n.d.	n.d.	n.d.	n.d.	n.d.

*EF: Enrichment Factor

(Table 27 – continued)

Sample	AA13	AA14	AA15	AA16	AA17
Date	21 June	24–25 June	25–26 June	26–27 June	27–28 June
Time	8:27 – 16:27	11:09 – 11:09	11:50 – 11:50	12:35 – 11:45	11:48 – 11:48
Duration of sampling	8 h	12 h	12 h	11 h 10'	12 h
Predominant wind direction	S-SW, W, NW	NW, NE	NE	SW	NW, NE
Av. wind speed	0,8 m s ⁻¹	0,8 m s ⁻¹	0,7 m s ⁻¹	1,18 m s ⁻¹	0,96 m s ⁻¹
Av. air temperature	21,2 °C	17,8 °C	18,8 °C	20,5 °C	15,9 °C
Sampling flow	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹
Sampled air volume (standard volume)	7,956 m ³	24,277 m ³	24,178 m ³	23,043 m ³	24,192 m ³
PM ₁₀	44,0 µg m ⁻³	23,5 µg m ⁻³	26,1 µg m ⁻³	30,4 µg m ⁻³	38,0 µg m ⁻³
Quinoxifen (PM ₁₀)	1,3 ng m ⁻³	0,4 ng m ⁻³	0,5 ng m ⁻³	0,4 ng m ⁻³	0,4 ng m ⁻³
EF* quinoxifen	29,9 µg g ⁻¹	18,6 µg g ⁻¹	17,9 µg g ⁻¹	14,6 µg g ⁻¹	10,6 µg g ⁻¹
Fenarimol (gas and particle phase)	n.d.	n.d.	n.d.	n.d.	n.d.

*EF: Enrichment Factor

The few samples collected at the site W do not allow a discussion on the temporal variation of pesticide concentration in the air. It is worth noting that no pesticides were detected in the gas phase, most likely because of the low air temperatures occurred during sampling.

A direct comparison between quinoxifen concentrations detected in the particle phase the day after application at the sites W and AA can be made only keeping in mind that two different classes of particles were collected, namely total suspended particles (TSP) and PM_{10} .

In contrast, the set of data collected at the site AA gives a good representation of the temporal variation of the applied active ingredient quinoxifen. Results are listed in Table 27 and illustrated in Figures 36-38.

The highest concentrations in the air were detected fourteen days after application (see Figure 36). This can be explained with the application carried out in the domain between 19 and 20 June, despite the fact that no quinoxifen containing products were applied. During these two days, tractors were driving through the vineyards to apply the mixture of pesticides. These agricultural activity caused soil and plant particles with old residues of the pesticide quinoxifen to enter the atmosphere. Indeed, more dust was measured than usual, as confirmed by the analysis of PM_{10} concentrations (Figure 37). The direct consequence of this fact was a higher concentration of quinoxifen in the air. This, however, does

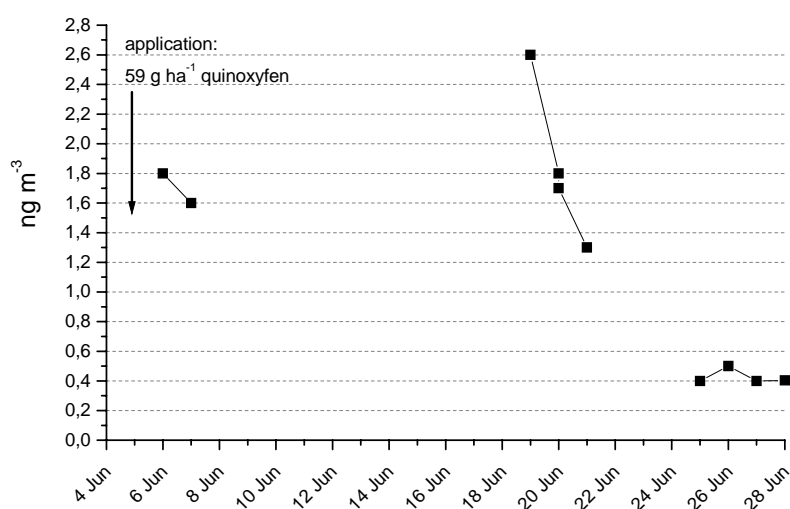


Figure 36: Quinoxifen concentrations in PM_{10} ($ng\ m^{-3}$) measured at the sampling site AA during the campaigns June 1 and June 2.

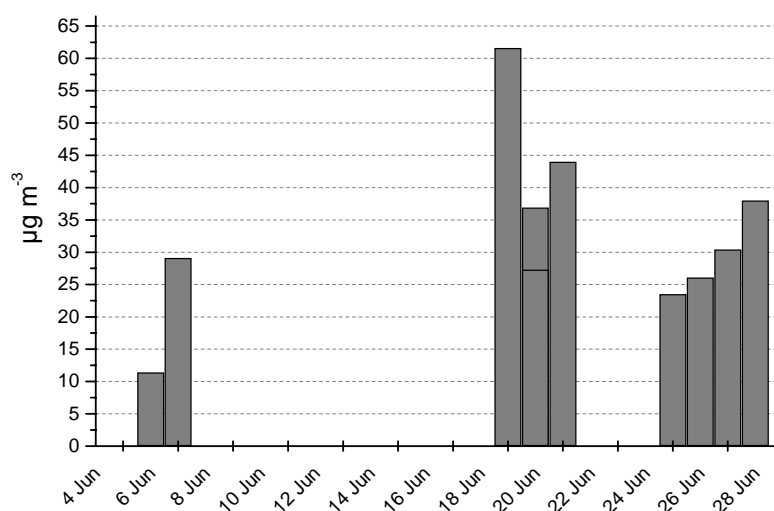


Figure 37: PM_{10} concentrations ($\mu g\ m^{-3}$) measured at the sampling site AA during the campaigns June 1 and June 2. The bar corresponding to 20 June represents two samples.

not necessarily correlate with the chemical load of the collected dust. In fact, the air concentration of a substance in terms of ng m^{-3} directly depends on two factors: the amount of airborne particles by which the substance is transported and the concentration level of this substance on the particles. Consequently, the higher the particulate phase concentration, the higher might result the air concentration of the substance in terms of ng m^{-3} . A more detailed description of the characteristics of the particles is provided by the enrichment factor (EF). The EF is given by the ratio of the absolute amount of a detected compound to the absolute amount of collected particulate matter to which the compound was ad-/absorbed and is expressed in terms of $\mu\text{g g}^{-1}$. The EF is independent of the amount of collected dust and describes the degree of chemical load of the particles.

Figure 38 shows the calculated EF values of the samples collected at the site AA during the campaigns June 1 and June 2. The highest EF was detected the day following application (6 June, $\text{EF} = 156,0 \mu\text{g g}^{-1}$) and after that a constant decrease was observed. This shows that the chemical load of the particles constantly decreased with time after the end of treatment. Therefore, the higher air concentration of quinoxifen observed fourteen days after application was due to higher PM_{10} concentrations in the air and not to a chemical enrichment of the particles

with the investigated fungicide. These particles presented a lower chemical load than those collected during the sampling campaign June 1. Twenty-three days after application, air concentration levels of quinoxifen were 22% of the values measured one day after application, whereas the load of the particles (EF) dropped to 6,9% of the initial load.

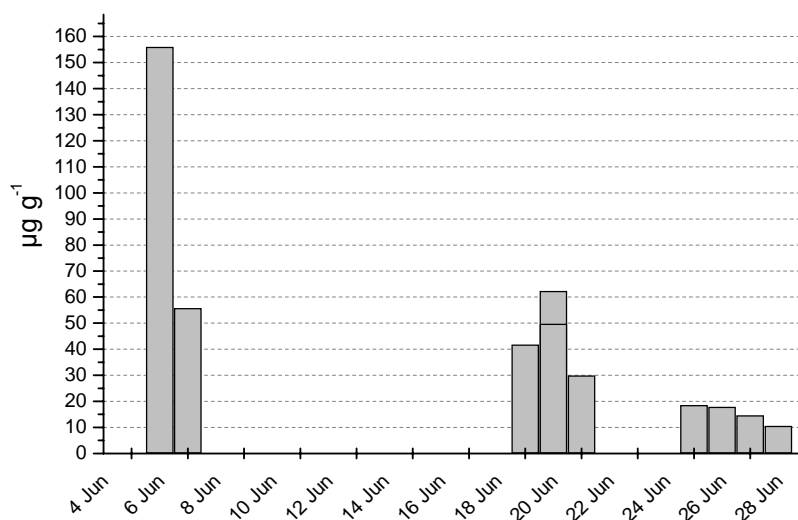


Figure 38: Enrichment factor ($\mu\text{g g}^{-1}$) calculated for quinoxifen detected in PM_{10} . The bar corresponding to 20 June represents two samples.

4.3.1.2 Sampling campaign July

Four of the investigated substances were applied in the Avelsbach domain on 17 and 18 July (see Table 24). This sampling campaign was started on 18 July, about one hour after the application was terminated. Both particulate and gaseous phase samples were collected at the sites W and AA.

Sampling site W

A detailed description of the sampling campaign July, carried out at the site W, is given in Table 28 and the measured air concentrations are listed in Table 29. Because of equipment failures, only four of the collected samples can be used for discussion.

Table 28: Details on the air sampling campaign July, sampling site W.

Sample	W11	W12	W14	W15
Date	18 July	19 July	22 July	29 July
Time	12:25 – 20:25	12:09 – 20:09	11:50 – 21:50	11:48 – 21:48
Duration of sampling	8 h	8 h	10 h	10 h
Predominant wind direction	N-NW	W	W	NE, S
Av. wind speed	1,0 m s ⁻¹	1,0 m s ⁻¹	1,0 m s ⁻¹	1,0 m s ⁻¹
Av. air temperature	19,6 °C	22,7 °C	19,3 °C	30,6 °C
Sampling flow	15,5 l min ⁻¹	15,5 l min ⁻¹	15,5 l min ⁻¹	15,5 l min ⁻¹
Sampled air volume (standard volume)	7,422 m ³	7,425 m ³	9,128 m ³	9,256 m ³

Table 29: Air concentrations detected at the site W during the air sampling campaign July.

Sample	W11	W12	W14	W15
TSP (µg m ⁻³)	33,7	22,9	19,7	51,9
Particle phase (ng m⁻³)				
Cyprodinil	45,4	18,1	10,8	6,4
Quinoxifen	5,5	4,0	3,1	3,1
Fludioxonil	2,7	3,3	2,4	2,1
Fenarimol	n.d.	n.d.	n.d.	n.d.
Gas phase (ng m⁻³)				
Cyprodinil	n.d.	37,0	1,2	< 0,5
Quinoxifen	n.d.	3,6	n.d.	n.d.
Fludioxonil	n.d.	n.d.	n.d.	n.d.
Fenarimol	n.d.	n.d.	n.d.	n.d.
EF (µg g⁻¹)				
Cyprodinil	1347,2	790,4	548,2	123,3
Quinoxifen	163,2	174,6	157,4	59,7
Fludioxonil	80,1	144,1	121,8	40,5

Of the applied substances, only cyprodinil, fludioxonil and quinoxifen could be detected. Of these, only cyprodinil and quinoxifen were detected both in the gaseous and particulate phases. This can be explained by the fact that these two substances have higher vapour pressures than fludioxonil (see Table 10). However, though having a higher vapour pressure

than quinoxifen, the fungicide fenarimol was never detected. The applied amount of fenarimol was about 37% of that of quinoxifen and 8% of that of cyprodinil. As a consequence, a lower amount used during application and a lower sensitivity of the analytical method for fenarimol likely account for the failure in detecting this fungicide during the study.

Immediately after the end of treatment, 100% of cyprodinil and quinoxifen was found in the particle phase. The following day, when a higher air temperature occurred, 67% of the total amount of cyprodinil and 47% of the total amount of quinoxifen was found in the gas phase. These results are a little confusing as the highest gas phase concentrations were expected to be found in the sample collected immediately after the end of application. The following observation might provide an explanation. Spraying pesticides through spray nozzles produces a spectrum of droplets diameters. The smallest droplets remain airborne and are dispersed as spray drift, whereas larger droplets can be transported by the wind and deposited some distance outside the target area. It is conceivable that, being the sampler located in the middle of the vineyard where application took place, all droplets produced during application were trapped on the filter surface during the first sampling, thus making impossible a separation between gas and particle phase.

The total air concentration, *i.e.* the sum of particulate and gaseous phase, was higher one day after application for all the applied substances (see Table 29). Most likely, volatilisation processes from soil and leaf surfaces were enhanced at the higher temperatures measured during the second day of sampling. Eleven days after the treatment, the applied fungicides could be detected only in the particle phase, and the total air concentrations dropped to 11,6%, 40,8% and 63,6% of the maximum concentrations for cyprodinil, quinoxifen and fludioxonil, respectively.

The highest EF for cyprodinil was found immediately after application; eleven days later it dropped to 9,2% (see Figure 39). Quinoxifen and fludioxonil presented the highest EF values one day after application; eleven days after treatment these values dropped to 34,2% and 28,1% of the

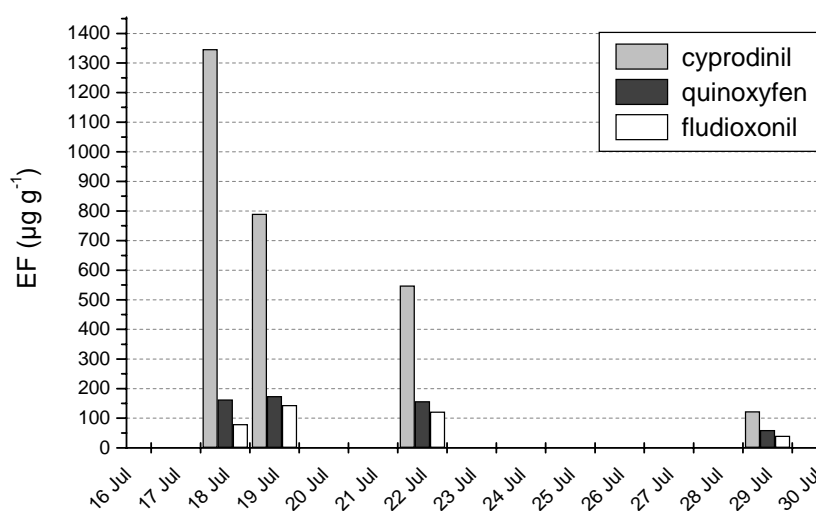


Figure 39: Enrichment factor ($\mu\text{g g}^{-1}$) calculated for cyprodinil, quinoxifen and fludioxonil detected at the sampling site W.

maximum EF calculated for quinoxifen and fludioxonil, respectively. Cyprodinil concentrations on the particulate decreased faster with time than those of quinoxifen and fludioxonil. According to these results it is possible to assume that cyprodinil has a shorter atmospheric residence time than quinoxifen and fludioxonil.

Sampling site AA

Details on the sampling campaign July carried out at the sampling site AA are listed in Table 30. Results are given in Table 31.

It is worth noting that this sampling campaign was characterized by two different sampling times: samples AA18 and AA19 are 8h samples, samples AA20-AA23 are 24h samples. Those samples that processed a greater volume of air, i.e. 24h samples, had a greater chance of detecting very low levels of airborne pesticides. This explains why fludioxonil could only be detected in the 24h samples.

Nevertheless, despite longer sampling times, the active ingredient fenarimol was never detected.

Table 30: Details on the air sampling campaign July, sampling site AA.

Sample	AA18	AA19	AA20	AA21	AA22	AA23
Date	18 July	19 July	20–21 July	22–23 July	29–30 July	30–31 July
Time	12:34 – 20:34	12:20 – 20:20	12:09 – 12:09	12:01 – 12:01	11:56 – 11:56	13:11 – 13:11
Duration of sampling	8 h	8 h	24 h	24 h	24 h	24 h
Predominant wind direction	N-NW	W	W-SW, NE	E-NE, W	NE	SW
Av. wind speed	1,0 m s ⁻¹	1,0 m s ⁻¹	1,1 m s ⁻¹	0,8 m s ⁻¹	0,7 m s ⁻¹	0,7 m s ⁻¹
Av. air temperature	19,6 °C	22,7 °C	19,9 °C	16,2 °C	24,9 °C	21,8 °C
Sampling flow	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹	1 m ³ h ⁻¹
Sampled air volume (standard volume)	7,976 m ³	7,893 m ³	23,818 m ³	24,225 m ³	23,449 m ³	23,562 m ³

Table 31: Air concentrations detected at the site AA during the air sampling campaign July.

Sample	AA18	AA19	AA20	AA21	AA22	AA23
PM ₁₀ (µg m ⁻³)	61,4	45,6	25,6	9,9	31,6	20,4
Particle phase PM₁₀ (ng m⁻³)						
Cyprodinil	9,6	5,6	7,4	3,8	3,6	2,9
Quinoxifen	1,8	1,6	1,2	0,8	1,1	1,1
Fludioxonil	< 1,3*	< 1,3*	1,1	1,0	1,1	1,1
Fenarimol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Gas phase (ng m⁻³)						
Cyprodinil	n.d.	n.d.	n.d.	n.d.	< 0,204	0,229
Quinoxifen	1,0	0,740	0,225	< 0,204**	n.d.	< 0,204**
Fludioxonil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fenarimol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
EF (µg g⁻¹)						
Cyprodinil	156,4	122,8	289,1	383,8	113,9	142,2
Quinoxifen	29,3	35,1	46,9	80,8	34,8	53,9
Fludioxonil	n.d.	n.d.	43,0	101,0	34,8	53,9

* Limit of determination calculated for 8h samples.

** Limit of determination calculated for 24h samples.

As expected, for all detected fungicides lower total air concentrations were measured than those found at the site W (located in the vineyard) (Figure 40). Of the four applied substances, only cyprodinil and quinoxifen could be detected both in the gas and particle phases. For these two fungicides, concentration values in terms of ng m⁻³

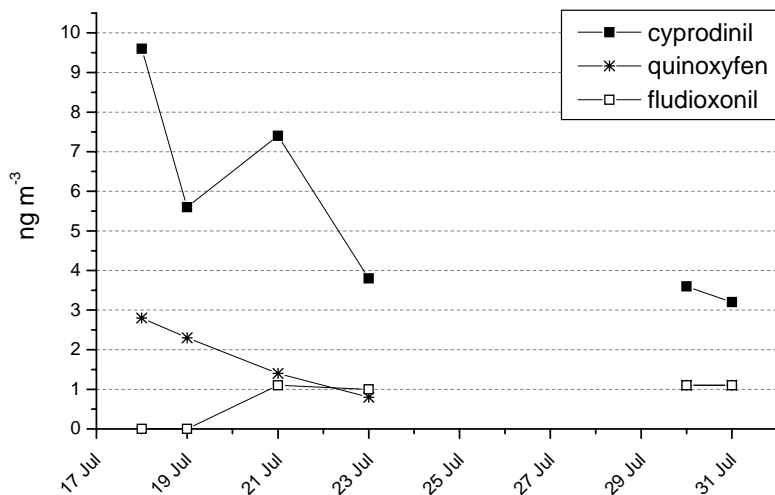


Figure 40: Total air concentrations (ng m⁻³) measured for cyprodinil, quinoxifen and fludioxonil at the sampling site AA during the campaign July.

decreased with time; the highest levels were detected immediately after application. Thirteen days after application total air concentrations dropped to 30,2% and 39,3% of the maximum values for cyprodinil and quinoxifen, respectively.

Fludioxonil could only be found in the particle phase and at concentration levels that were more or less constant and close to the limit of determination.

At both sites W and AA, higher concentrations were measured for cyprodinil than for quinoxyfen and fludioxonil. This can be explained by the following two observations: (a) a higher amount of cyprodinil was applied during 17 and 18 July (see Table 24); (b) cyprodinil has the highest vapour pressure and therefore a tendency to volatilise more easily than quinoxyfen and fludioxonil. However, as observed at the site W, cyprodinil air concentrations decreased faster with time than those of quinoxyfen and fludioxonil.

The calculated EF values showed a different temporal variation than that observed for the total air concentration levels (Figure 41). The highest EF values for all three detected fungicides were not measured right after application, but five days later. An explanation can be found in the analysis of the wind directions measured during sampling. The wind roses show that different source areas must have

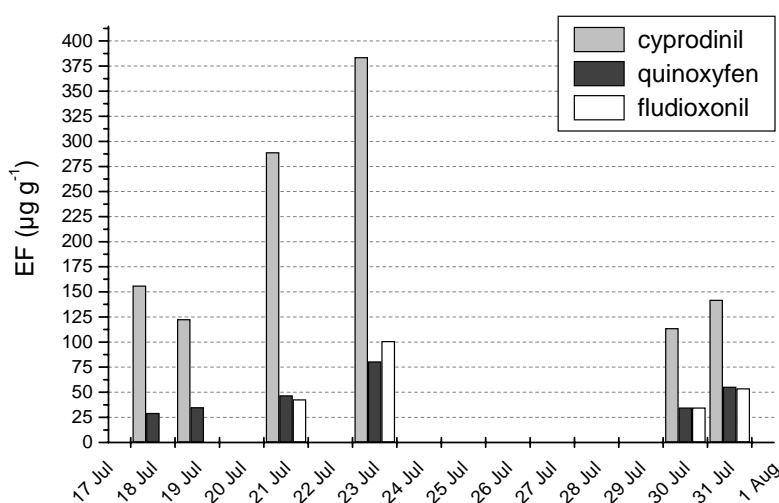


Figure 41: Enrichment factor ($\mu\text{g g}^{-1}$) calculated for cyprodinil, quinoxyfen and fludioxonil detected at the sampling site AA during the sampling campaign July.

contributed to the observed pattern. The predominant winds measured during 18 and 19 July were from a north-north-westerly and westerly direction, respectively. Very little or no contribution came from the east. This implies that the source area of the samples collected between 18 and 21 July was mainly the Avelsbach domain area, where pesticides were applied on 17 and 18 July. Wind directions measured between 20 and 30 July showed an increasing contribution from the north-east. The vine-growing area which extends along the valley of the river Ruwer is located about 3 km north-east and east of the sampling site AA. It is possible that the higher EF values measured four and five days after the application are related to pesticide treatments that took place in this area. Unfortunately, though very plausible, this explanation cannot be confirmed given the lack of information on pesticide applications carried out in the Ruwer valley.

EF values calculated for the samples collected at the site W do not show such a pattern. Two factors may account for this result: (a) the sampling station W was located in the vineyards of the Avelsbach domain and, therefore, directly subjected to the emissions resulting from

pesticide applications carried out in that specific area; (b) the sampling system used at the site W was designed for the collection of total suspended particles (TSP) and those particles have a shorter atmospheric travel distance than the particles collected at the site AA, namely PM_{10} . Therefore, it is expected that samples collected at the station W are far less affected by source areas other than the Avelsbach domain than samples collected at the station AA.

These results show the importance of the enrichment factor as a parameter that can provide a better description of the composition and loading of the particles. It can reveal differences among samples that could not be found by analysing air concentration values in terms of $ng\ m^{-3}$. As a consequence, different source areas can be identified as potential contributors to the air masses collected during sampling.

4.3.1.3 Sampling campaigns August, September 1 and September 2

Three more sampling campaigns were carried out during the late growing season 2002. It must be kept in mind that the last application of pesticides analysed in this study was performed on 17 and 18 July, right before the beginning of the sampling campaign July, described in the previous paragraph.

In order to detect lower levels of airborne pesticides, only 24h samples were collected. Since these long sampling periods were not supported by the portable battery operated sampler at the site W, sampling was performed only at the site AA. Details and results of the sampling campaigns are listed in Tables 32 and 33.

During the last three sampling campaigns carried out in the late growing season 2002, a different wind field was observed than that measured during the middle growing season. A predominant wind component was measured from an easterly and north-easterly direction, whereas during the months of June and July the main winds were from a westerly direction. As a consequence, the Avelsbach domain did not play a major role as source area, but different source areas accounted for the results reported in this paragraph.

In general, air concentrations constantly decreased with time from one sampling campaign to the other. During each sampling campaign more or less constant concentration values were measured for all detected fungicides (see Figure 42).

Sixty-four days after the last application, total air concentrations dropped to 6,3% and 22,2% of the maximum values measured right after the end of treatment on 18 July for cyprodinil and quinoxifen, respectively.

Table 32: Details on the sampling campaigns August, September 1 and September 2, sampling site AA.

Sample	AA24	AA25	AA26	AA27	AA28
Date	26-27 Aug.	5-6 Sept.	6-7 Sept.	7-8 Sept.	8-9 Sept.
Time	10:34 – 10:34	8:35 – 8:35	8:47 – 8:47	9:05 – 9:05	10:56 – 9:08
Duration of sampling	24 h	24 h	24 h	24 h	22,2 h
Predominant wind direction	E-NE	E-NE	E-NE, W-SW	E-NE, S-SW	S
Av. wind speed	m s^{-1}	m s^{-1}	m s^{-1}	m s^{-1}	m s^{-1}
Av. air temperature	21,0 °C	16,0 °C	15,8 °C	16,4 °C	18,2 °C
Sampling flow	$1 \text{ m}^3 \text{ h}^{-1}$	$1 \text{ m}^3 \text{ h}^{-1}$	$1 \text{ m}^3 \text{ h}^{-1}$	$1 \text{ m}^3 \text{ h}^{-1}$	$1 \text{ m}^3 \text{ h}^{-1}$
Sampled air volume (standard volume)	23,754 m^3	24,200 m^3	24,241 m^3	24,073 m^3	22,118 m^3

(Table 32 – continued)

Sample	AA29	AA30	AA31	AA32
Date	16-17 Sept.	17-18 Sept.	18-19 Sept.	19-20 Sept.
Time	11:10 – 9:46	9:53 – 9:53	10:02 – 9:55	10:00 – 10:00
Duration of sampling	22,6 h	24 h	23,9 h	24 h
Predominant wind direction	E-NE	NE	N-NE	NE, N-NW
Av. wind speed	m s^{-1}	m s^{-1}	m s^{-1}	m s^{-1}
Av. air temperature	11,9 °C	11,9 °C	14,3 °C	16,8 °C
Sampling flow	$1 \text{ m}^3 \text{ h}^{-1}$	$1 \text{ m}^3 \text{ h}^{-1}$	$1 \text{ m}^3 \text{ h}^{-1}$	$1 \text{ m}^3 \text{ h}^{-1}$
Sampled air volume (standard volume)	23,170 m^3	24,568 m^3	24,176 m^3	24,110 m^3

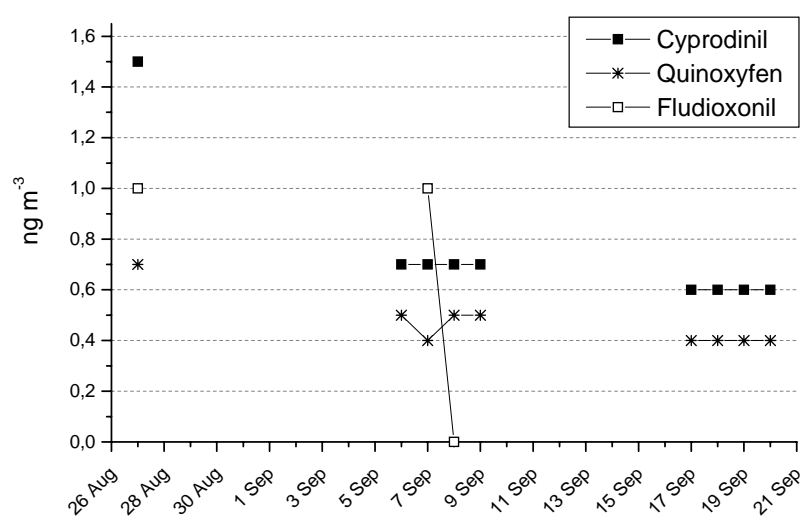
**Figure 42:** Concentrations (ng m^{-3}) measured for cyprodinil, quinoxifen and fludioxonil in PM10 at the sampling site AA during the campaigns August, September 1 and September 2.

Table 33: Air concentrations detected at the site AA during the air sampling campaigns August, September 1 and September 2.

Sample	AA24	AA25	AA26	AA27	AA28
PM ₁₀ (µg m ⁻³)	31,6	23,6	24,3	30,7	25,3
Particle phase PM₁₀ (ng m⁻³)					
cyprodinil	1,5	0,7	0,7	0,7	0,7
quinoxifen	0,7	0,5	0,4	0,5	0,5
fludioxonil	1,0	n.d.	1,0	< 0,407*	n.d.
Gas phase (ng m⁻³)					
cyprodinil	< 0,204*	< 0,204*	n.d.	n.d.	n.d.
quinoxifen	< 0,204*	< 0,204*	n.d.	n.d.	n.d.
fludioxonil	n.d.	n.d.	n.d.	n.d.	n.d.
EF (µg g⁻¹)					
cyprodinil	47,5	29,7	28,8	22,8	27,7
quinoxifen	22,2	21,2	16,5	16,3	19,8
fludioxonil	31,6	-	41,2	< 13,3	-

* Limit of determination calculated for 24h samples.

(Table 33 – continued)

Sample	AA29	AA30	AA31	AA32
PM ₁₀ (µg m ⁻³)	22,0	26,9	17,0	27,8
Particle phase PM₁₀ (ng m⁻³)				
cyprodinil	0,6	0,6	0,6	0,6
quinoxifen	0,4	0,4	0,4	0,4
fludioxonil	n.d.	n.d.	n.d.	n.d.
Gas phase (ng m⁻³)				
cyprodinil	n.d.	n.d.	< 0,204*	< 0,204*
quinoxifen	n.d.	n.d.	< 0,204*	< 0,204*
fludioxonil	n.d.	n.d.	n.d.	n.d.
EF (µg g⁻¹)				
cyprodinil	27,3	22,3	35,3	21,6
quinoxifen	18,2	14,9	23,5	14,4
Fludioxonil	-	-	-	-

* Limit of determination calculated for 24h samples.

4.3.1.4 General evaluation of the sampling campaigns following applications in the Avelsbach domain: the dissipation process

Once a substrate (agriculture commodity, body of water, wildlife, soil, etc.) has been exposed to a chemical, dissipation processes begin immediately. The initial residue dissipates at an overall rate that is a composite of the rates of individual processes (volatilization, washing off, leaching, hydrolysis, microbial degradation, etc.) (SEIBER 1985). For simple dissipation, such as occurs in the application of pesticides and resulting exposure from residues in food or water or air, the typical result is that concentrations of overall residue (parent plus products) decrease with time after the end of exposure or treatment (SEIBER 2002).

A dissipation curve was plotted for cyprodinil and quinoxyfen (Figure 43). Total air concentration values measured during the sampling campaigns July, August, September 1 and September 2 were used as data set for these curves. It is worth reminding that, during the growing season 2002, the last application of cyprodinil and quinoxyfen in the Avelsbach domain was carried out right before the beginning of the sampling campaign July. However, it cannot be ruled out that other source areas (where these active ingredients might have been applied at different times) contributed to the air masses collected during sampling (see par. 4.3.1.2, sampling site AA). Both graphics show a first-order decline process, where the remaining residue concentration is asymptotic to the time axis.

The dissipation rate of cyprodinil and quinoxyfen was also plotted as a first-order plot with $\ln C/C_0$ against time (Figure 44). Using the best fit linear regression through the points, empirical atmospheric residence times (τ_a , see par. 2.2.3) of 14,6 days and 20,8 days were calculated for cyprodinil and quinoxyfen, respectively. These results are in accordance with previous observations made in this study, where cyprodinil concentrations were found to decrease more rapidly with time than quinoxyfen concentrations and, consequently, a shorter atmospheric residence time was hypothesised for cyprodinil.

These findings are also confirmed by the physico-chemical properties of the substances object of study. Of all applied active ingredients that were analysed, cyprodinil has the highest vapour pressure, hence a tendency to volatilise easier than the other substances. This explains, in part, the higher air concentrations measured after the end of treatment. Furthermore, cyprodinil has a higher water solubility (about two order of magnitude higher than that of quinoxyfen) that allows for an efficient removal from the atmosphere by wet depositional processes. Quinoxyfen, on the other hand, has the lowest water solubility and the highest H value, all conditions that are not favourable for wet depositional processes. This is also confirmed by the results of the rain sampling campaigns, where higher detection frequencies and concentrations were found for cyprodinil than for quinoxyfen (Figure 50).

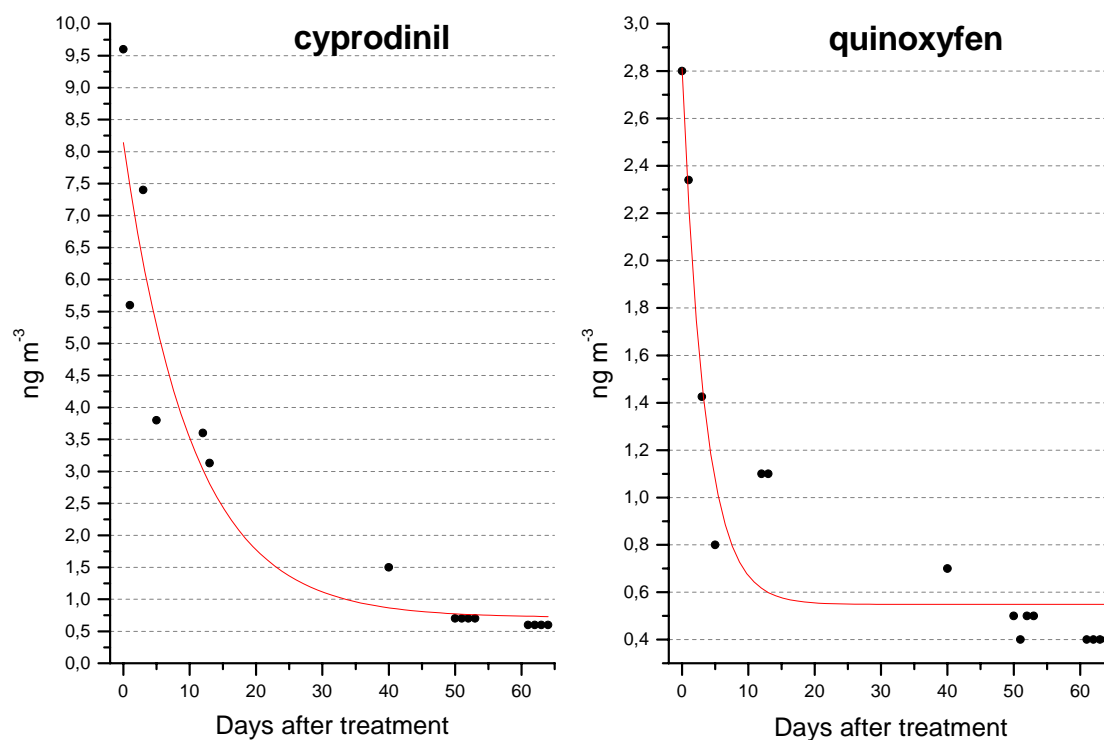


Figure 43: Atmospheric dissipation rate of cyprodinil (left plot) and quinoxyfen (right plot) as a dissipation curve. Day 0 is the day of the end of treatment and of the first sample.

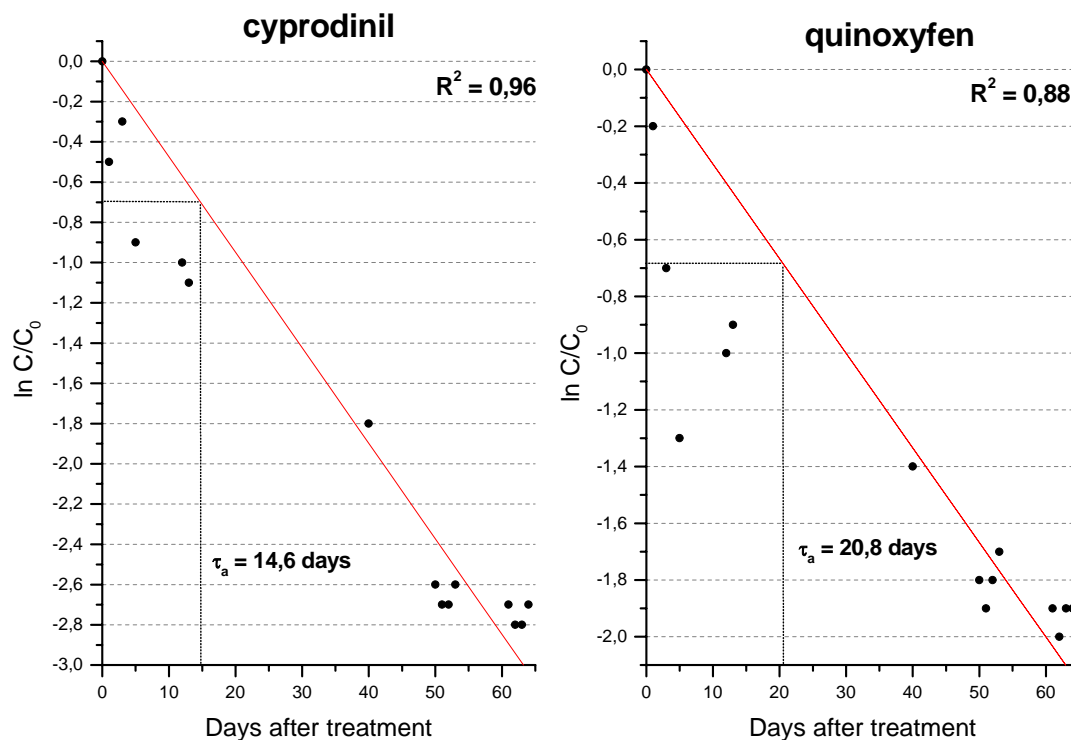


Figure 44: Atmospheric dissipation rate of cyprodinil (left plot) and quinoxyfen (right plot) as a first-order plot. Day 0 = day of end of treatment and of the first sample; C_0 = concentration of day 0; C = concentration of time t ; τ_a = atmospheric residence time.

4.3.2 Air sampling campaigns during the growing season 2002

In this section, all results found during the air sampling campaigns carried out in the growing season 2002 will be presented. Details on the air sampling campaigns carried out at the station H are summarized in Appendix E; details on the campaigns carried out at the stations AA and W are given in the previous section (par. 4.3.1).

4.3.2.1 Occurrence of pesticides

Results of the air sampling campaigns found at the stations H, AA and W are summarized in Tables 34-36 and illustrated in Figures 45-48.

Table 34: Statistics on pesticides detected in TSP and in the gas phase from June 2002 through September 2002 at the sampling station H (n = 25). Positive values only (> LoD) are considered.

Compound	min	max	median	n > LoD	freq (%)
TSP (ng m ⁻³)					
Herbicides					
Atrazine	0,050	0,075	-	2	8
Desethylatrazine	-	-	0,106	1	4
Desethylterbuthylazine	0,033	0,187	0,092	7	28
Simazine	0,030	0,200	-	2	8
Terbuthylazine	0,030	0,229	0,097	8	32
Insecticide					
Methyl parathion	0,052	0,152	0,064	5	20
Fungicides					
Cyprodinil	0,009	0,746	0,041	24	96
Diethofencarb	0,029	0,523	0,092	6	24
Fenarimol	-	-	0,016	1	4
Fludioxonil	0,018	0,301	0,036	14	56
Fluquinconazole	0,032	0,086	0,038	3	12
Folpet	0,413	5,477	1,057	25	100
Kresoxym-methyl	0,019	0,744	0,049	19	76
Metalaxyl	0,016	1,392	0,171	12	48
Penconazole	0,014	0,073	0,030	9	36
Quinoxifen	0,010	0,302	0,049	22	88
Tebuconazole	0,019	1,598	0,065	8	32
Gas phase (ng m ⁻³)					
Cyprodinil	0,017	0,280	0,048	14	56
Kresoxym-methyl	0,033	0,060	0,046	4	16
Metalaxyl	0,032	0,121	-	2	8
Quinoxifen	0,016	0,047	0,019	7	28

Table 35: Statistics on pesticides detected in PM₁₀ and in the gas phase from June 2002 through September 2002 at the sampling station AA (n = 32). Positive values only (> LoD) are considered.

Compound	min	max	median	n > LoD	freq (%)
PM ₁₀ (ng m ⁻³)					
Insecticide					
Methyl parathion	1,3	1,4	1,3	3	9
Fungicides					
Cyprodinil *	0,6	9,6	0,7	23	72
Diethofencarb	-	-	1,4	1	3
Fludioxonil *	1,0	1,1	1,1	6	19
Folpet	1,7	19,4	3,7	22	69
Kresoxym-methyl	1,0	3,1	1,0	9	28
Metalaxyl	0,6	2,2	0,6	6	19
Quinoxifen *	0,4	2,6	0,6	26	81
Tebuconazole	0,6	16,0	1,4	8	25
Gas phase (ng m ⁻³)					
Cyprodinil *	-	-	0,3	1	3
Folpet	0,8	0,9	-	2	6
Metalaxyl	0,3	1,2	0,9	3	9
Quinoxifen *	0,2	1,0	0,7	3	9

* Active ingredient applied in the vicinity of the sampling station (see par. 4.3.1).

Table 36: Statistics on pesticides detected in TSP and in the gas phase from June 2002 through September 2002 at the sampling station W (n = 6). Positive values only (> LoD) are considered.

Compound	min	max	median	n > LoD	freq (%)
TSP (ng m ⁻³)					
Fungicides					
Cyprodinil *	6,4	45,4	14,4	4	67
Fludioxonil *	2,1	3,3	2,5	4	67
Folpet	2,3	6,9	2,9	4	67
Quinoxifen *	2,1	5,5	3,5	6	100
Gas phase (ng m ⁻³)					
Cyprodinil *	1,2	37,0	-	2	33
Quinoxifen *	-	-	3,6	1	17

* Active ingredient applied in the vicinity of the sampling station (see par. 4.3.1).

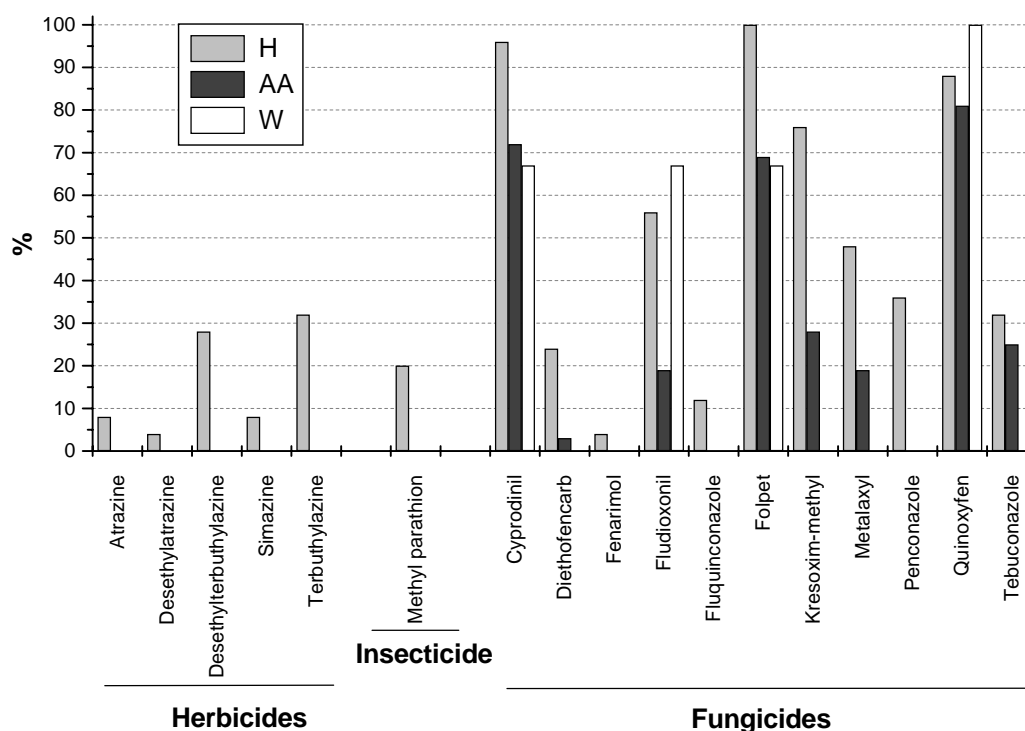


Figure 45: Frequency of detection (%) for each pesticide detected in the particle phase above LoD during the air sampling campaigns carried out in the growing season 2002.

Seventeen of 27 pesticides analysed were detected at least once in air (gas- and particle-phase) from the station H. Nine pesticides were detected at the station A, while only four pesticides were detected at the station W. The highest number of pesticides was detected at the sampling site H. This site was equipped with a high-volume sampler that allowed for the collection of greater volumes of air, thus enhancing the chance of collecting very low levels of airborne pesticides. Indeed, minimum concentration levels detected at the site H are in many cases about one or two orders of magnitude lower than those measured at the other two sites.

As expected on the basis of available data on local pesticide applications, the highest frequencies of detection were found for the class of fungicides. The most frequently detected pesticides at all sites were the fungicides quinoxifen (81-100%), folpet (67-100%) and cyprodinil (67-72%) (see Figure 45 and Tables 34-36).

No herbicides nor herbicide metabolites were detected at the stations AA and W. On the contrary, three herbicides and two metabolites were sporadically detected at the site H (detection frequencies between 4% and 32%). This result can be explained by the following observations:

- According to the results of the rain sampling campaigns previously discussed in this study, the main application time for these substances and, consequently, their occurrence in the atmosphere, is the early growing season, *i.e.* from April until July. The first air sampling campaign at the site H started in June, thus the useful time to detect these substances in the air was rather short. Indeed, herbicides and metabolites were detected only during the sampling campaigns carried out in June.
- There is no legal use in Germany for atrazine and simazine, while the use of terbuthylazine is not permitted in the viniculture (one of the main agricultural activities in the area of study). Therefore, no or very few emissions were expected from local sources and, consequently, lower air concentrations and lower frequencies of detection.

The highest pesticide concentrations were detected at the sites W and AA, the two sampling stations located very close to emitting sources (see Figure 46, top and central graphs). Overall, the highest concentration was measured at the site W for cyprodinil (45,4 ng m⁻³ in TSP and 37,0 ng m⁻³ in the gas phase). This is well explained by the fact that this active ingredient was applied in the vineyard where the sampler was located. High concentrations were also measured for folpet (6,9 ng m⁻³ in TSP) and quinoxifen (5,5 ng m⁻³ in TSP, 3,6 ng m⁻³ in the gas phase). At the site AA, the pesticide with the highest concentrations was folpet (19,4 ng m⁻³ in PM₁₀), followed by tebuconazole (16,0 ng m⁻³ in PM₁₀) and cyprodinil (9,6 ng m⁻³ in PM₁₀). During the growing season 2002, no folpet nor tebuconazole containing products were applied in the Avelsbach domain, but, given the high levels measured, it can be assumed that these substances were applied in the close vicinity of the domain.

The pesticide with the highest concentrations at the site H was folpet (5,477 ng m⁻³ in TSP), followed by tebuconazole (1,598 ng m⁻³ in TSP) and metalaxyl (1,392 ng m⁻³ in TSP). Lower concentrations were measured for other fungicides, the herbicides and the insecticide methyl parathion (see Figure 46, bottom graph).

A comparison with data from the literature is not straightforward as there is limited information on the current-use pesticides analysed in this study. Most studies are focused on organochlorine and organophosphorus pesticides, there are several studies on triazines herbicides and only a few studies focus on fungicides. No literature values were found for the fungicides detected at high concentrations in this study.

A direct comparison can be made only for methyl parathion, the herbicides and metabolites detected in this study (see Table 37). Maximum concentration levels measured in the area of study for these substances are much lower than those reported in the literature. It must be noted that all results given in Table 37 were found in areas where the listed pesticides were applied.

An indirect comparison can be made in terms of concentration ranges for the fungicides. Concentration values in the range of ng m^{-3} or higher are measured at sites where pesticides are applied or in the close vicinity. These values are related to local applications. Concentration values in the range of pg m^{-3} are often related to transport through the atmosphere.

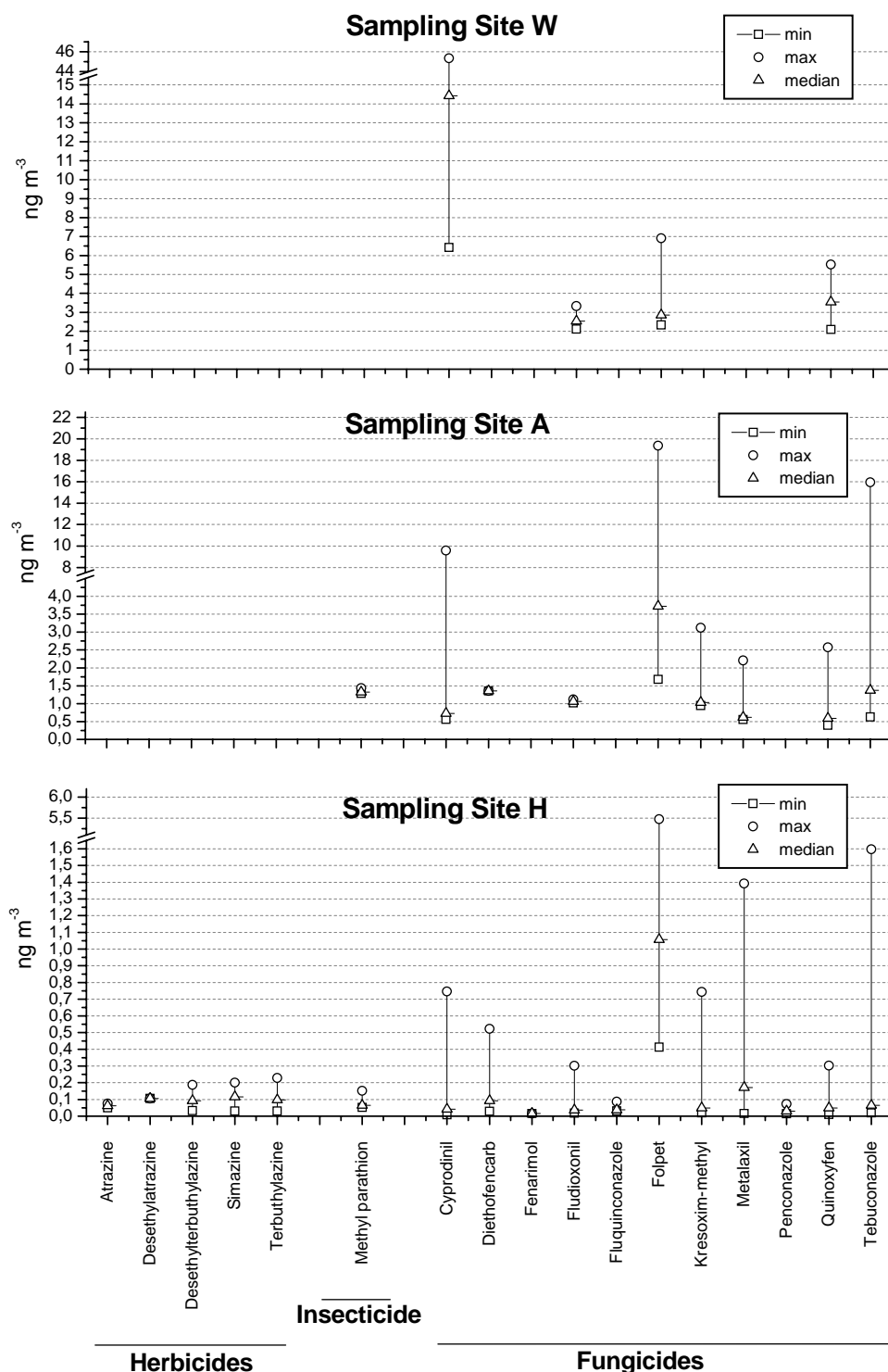


Figure 46: Minimum, maximum and median concentration values for each pesticide detected in the particulate phase above LoD during the growing season 2002.

Table 37: Data from the literature on selected pesticides relevant for this study.

Active ingredient	Max (ng m ⁻³)	Median (ng m ⁻³)	Reference / Study area
Atrazine	51,26 (urban site, gas+particle phase) 5,97 (rural site, gas+particle phase) 1,4 (remote site, gas+particle phase)	20,03 (urban site, gas+particle phase, mean) 2,13 (rural site, gas+particle phase, mean) 0,29 (remote site, gas+particle phase, mean)	Sanusi <i>et al.</i> (1999) / Alsace and Vosges regions (Eastern France)
Atrazine	2 (gas-phase)	-	Chevreuil <i>et al.</i> (1996) / Paris area
Atrazine	8,5	1,2 (gas phase, mean)	Peck & Hornbuckle (2005) / Iowa
Atrazine	0,019 (urban site, particle phase) 0,42 (agric. site, particle phase) 2,6 (agric. site, gas phase)	0,058 (agric. site, particle phase)	Coupe <i>et al.</i> (2000) / Mississippi
Atrazine	2,8 (gas+particle phase)	1,1 (gas+particle phase)	Majewski <i>et al.</i> (1998) / Mississippi river
Atrazine	20 (gas+particle phase)	3,7 (gas+particle phase, mean)	Glottfelty <i>et al.</i> (1990b) / Maryland
Desethylatrazine	1,3	0,51 (mean)	Peck & Hornbuckle (2005) / Iowa
Desethylatrazine	0,8 (gas phase)	-	Chevreuil <i>et al.</i> (1996) / Paris area
Desisopropyl- atrazine	1,2	1,2 (mean)	Peck & Hornbuckle (2005) / Iowa
Methyl parathion	1200 (middle of application field) 420 (5m from edge of application field)	210 (middle of application field, mean) 170 (5 m from edge of application field, mean)	Siebers & Gottschild (1998) / Berlin
Methyl parathion	6,0	2,2 (mean)	Peck & Hornbuckle (2005) / Iowa
Methyl parathion	0,99 (urban site, gas phase) 0,4 (agric. site, particle phase) 62 (agric. site, gas phase)	2,5 (agric. site, gas phase)	Coupe <i>et al.</i> (2000) / Mississippi
Methyl parathion	26 (urban site, gas phase) 520 (application site, gas phase)	4,8 (urban site, gas phase, mean)	Baker <i>et al.</i> (1996) / California

(Table 37 – continued)

Active ingredient	Max (ng m ⁻³)	Median (ng m ⁻³)	Reference / Study area
Methyl parathion	0,85 (gas+particle phase)	0,07 (gas+particle phase)	Majewski et al. (1998) / Mississippi river
Simazine	3 (gas phase)	-	Chevreuril <i>et al.</i> (1996) / Paris area
Simazine	0,4	0,23 (mean)	Peck & Hornbuckle (2005) / Iowa
Simazine	0,35 (gas+particle phase)	0,15 (gas+particle phase, mean)	Glottelty <i>et al.</i> (1990b) / Maryland
Terbuthylazine	206 (middle of application field) 12 (at the edge of application field)	-	Mülleder (1997), cited by AKKAN (2003) / Baden-Württemberg
Terbuthylazine	3 (gas phase)	-	Chevreuril <i>et al.</i> (1996) / Paris area

Time series from site H and AA for selected fungicides are shown in Figure 47 and Figure 48, respectively. These time series show characteristic temporal patterns that are related to local application times. Concentration spikes were observed for all fungicides during the months of June and July, the typical application period for systemic fungicides. Lower concentration levels were measured during August and September.

At the end of the growing season, only four fungicides were detected above LoD. For these substances total air concentrations decreased to between 5,0% and 19,6% of the highest values measured during all air sampling campaigns (Table 38).

Table 38: Residues measured in the last sample of the air sampling campaigns as % of maximum values. Total air concentrations are used for the calculation.

Compound	Max (ng m ⁻³)	Max concentration detected on	Concentration measured in the last sample (20.09.2002) (ng m ⁻³)	% of the max
Sampling Station H				
Cyprodinil	0,884	21.07.2002	0,044	5,0%
Fludioxonil	0,301	30.07.2002	0,026	8,6%
Folpet	5,477	30.07.2002	0,455	8,3%
Sampling Station AA				
Cyprodinil	9,6	18.07.2002	0,6	6,3%
Folpet	19,4	30.07.2002	3,8	19,6%
Quinoxifen	2,6	19.06.2002	0,4	15,4%

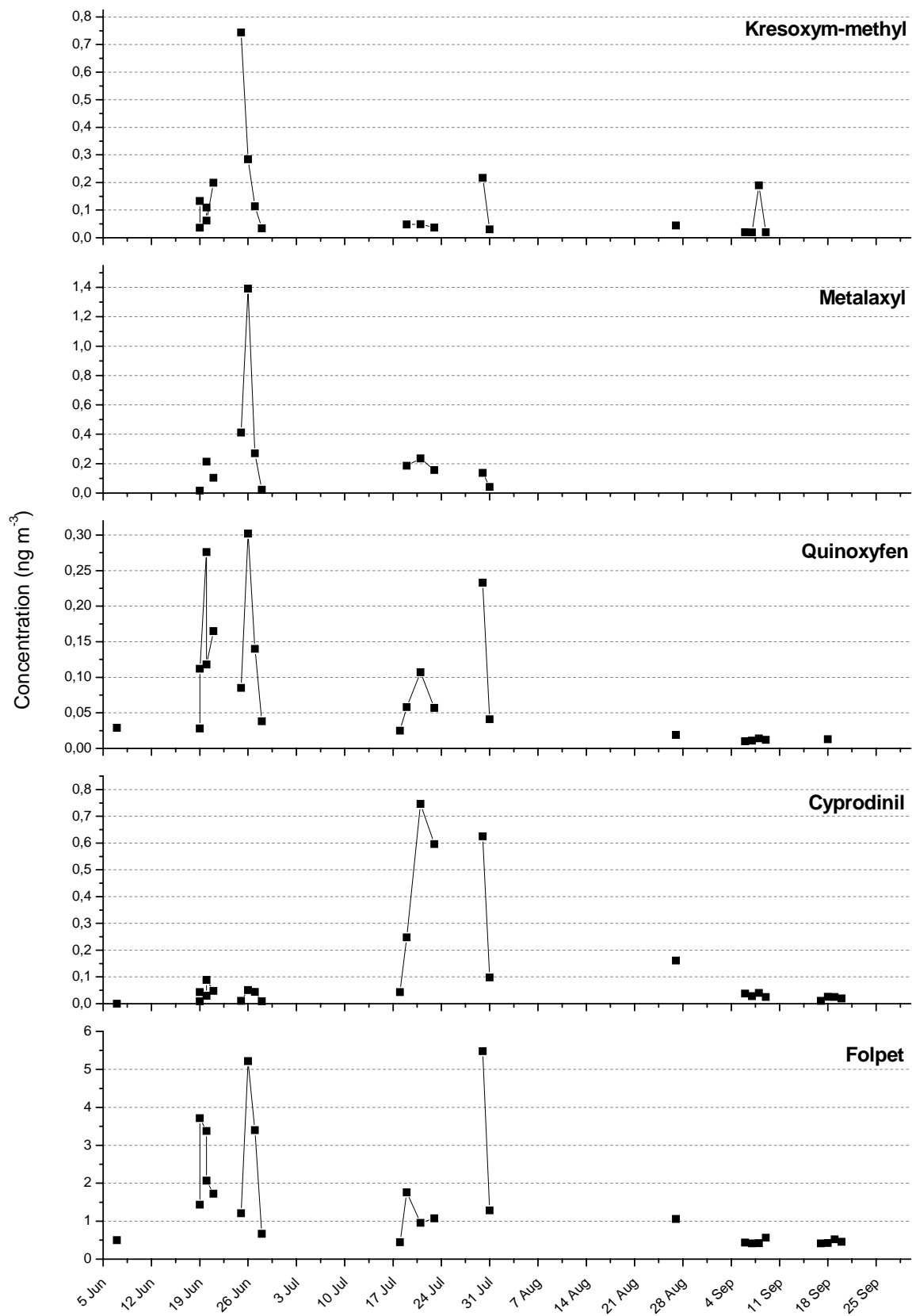


Figure 47: Concentration time series for selected fungicides detected in TSP at the sampling site H. Zero values represent < LoD values.

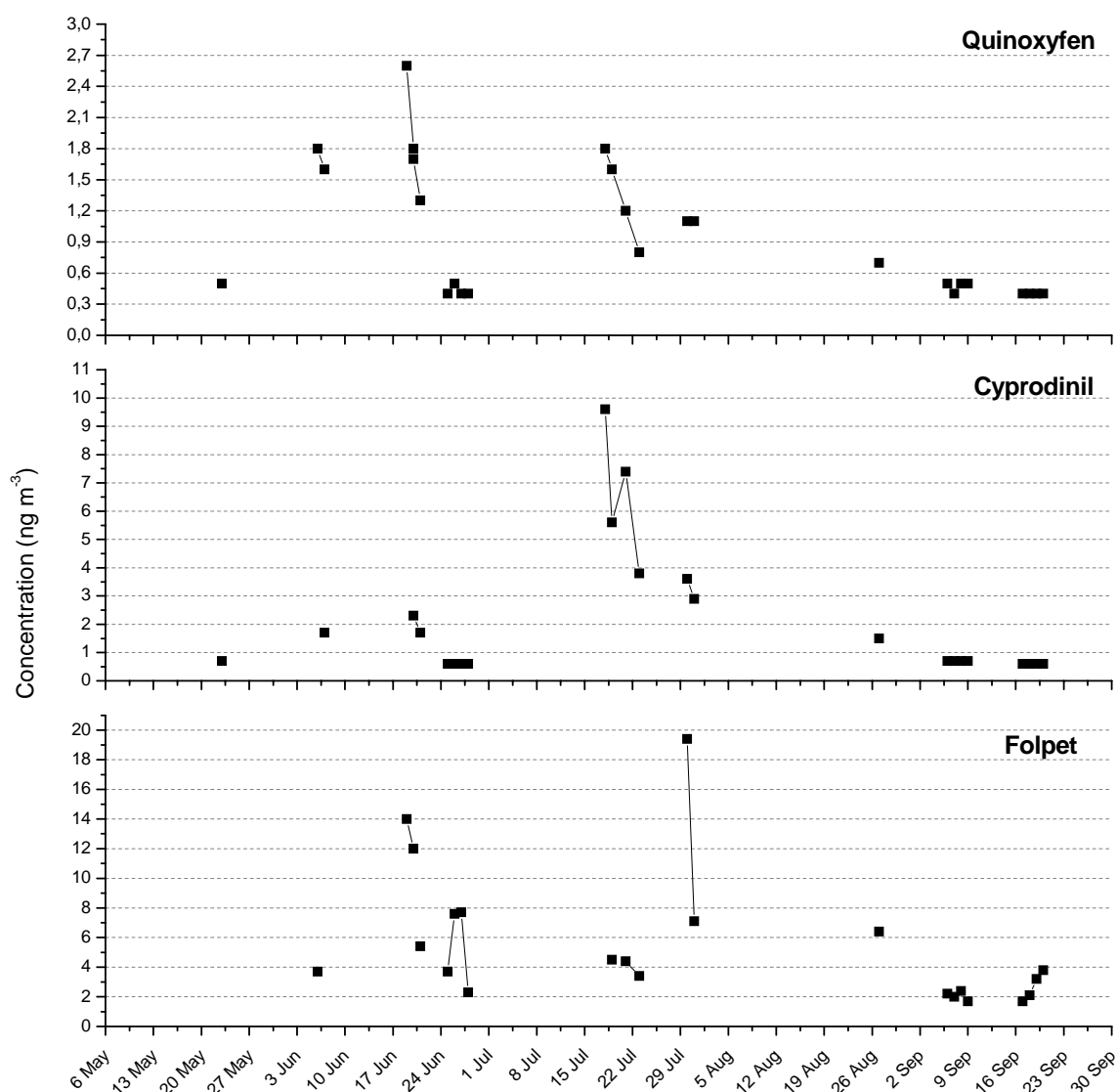


Figure 48: Concentration time series for selected fungicides detected in PM₁₀ at the sampling site AA. Zero values represent < LoD values.

4.3.2.2 Gaseous and particulate phase distribution

Once in the atmosphere, a compound will distribute among the aqueous, gaseous and particulate phases based on the physical and chemical properties of the compound, such as Henry's law constant, water solubility and vapour pressure, and on the conditions of the atmosphere, such as temperature, moisture content and the type and concentration of particulate matter (see par. 2.2.1). The phase distribution of the compound strongly affects the behaviour, transport and ultimate fate of the compound in the atmosphere. (COUPE *et al.* 2000)

In this study, pesticides were detected largely or exclusively in the particulate phase (PM₁₀ and TSP). Only five of the 17 pesticides detected in the particulate matter were detected also

in the gas-phase. Detection frequencies in the gas phase were very low, with the highest values being measured at the station H. At this site, the most frequently detected compound was cyprodinil (56%) followed by quinoxyfen (28%), kresoxym-methyl (16%) and metalaxyl (8%) (see Table 34). At the sites AA and W, four and two fungicides, respectively, were sporadically detected in the gas phase (see Table 35 and Table 36).

These results are in accordance with the findings of TURNBULL (1995) who pointed out the tendency of modern pesticides towards particle phase partitioning, revealing their less volatile nature in comparison to organochlorine pesticides.

Phase distribution for cyprodinil and quinoxyfen observed at the sampling site H is illustrated in Figure 49. The fraction of cyprodinil measured in the gas phase varied from 11% to 66%, with a median value of 53%, that of quinoxyfen varied from 10% to 63%, with a median value of 54%. Distribution of these two compounds between gaseous and particulate phase did not correlate well with the average temperature measured during sampling ($R^2=0,15$ and $0,48$ for cyprodinil and quinoxyfen, respectively) nor with the concentration of particulate matter (TSP) ($R^2=0,04$ and $0,31$ for cyprodinil and quinoxyfen, respectively).

Similar results were found by SANUSI *et al.* (1999) in their study on gas-particle partitioning of selected pesticides. The authors found a group of pesticides, with vapour pressure values similar to those of cyprodinil and quinoxyfen, that showed a variable gas phase independent of the temperature. The description of the gas-particle partitioning for those compounds could be improved by using relative humidity in addition to the three parameters considered for other pesticides, namely temperature, TSP and vapour pressure. MAJEWSKI & CAPEL (1995) also reported of several studies that investigated the effect of humidity on gas-particle partitioning. Results show that as the water vapour content of the atmosphere increases, the percentage of pesticides sorbed to the particulate material decreases.

In this study, correlation values calculated for cyprodinil and quinoxyfen between relative humidity measured during sampling and relative abundance of the gas phase were $0,63$ and $0,95$, respectively.

SANUSI *et al.* (1999) suggested the existence of a competition mechanism between water molecules in the gas phase and pesticides to adsorb on the receiving sites of the particles. By this mechanism, increase in the atmospheric relative humidity induces a simultaneous increase of pesticides in the gas phase.

This could partly explain why, despite higher temperatures measured in June, no quinoxyfen was found in the gas phase at the site H. During these campaigns lower values of relative humidity were observed. On the contrary, quinoxyfen was found in considerable amount in the gas phase from July until September, when lower temperatures and higher relative humidity values were measured (Figure 49).

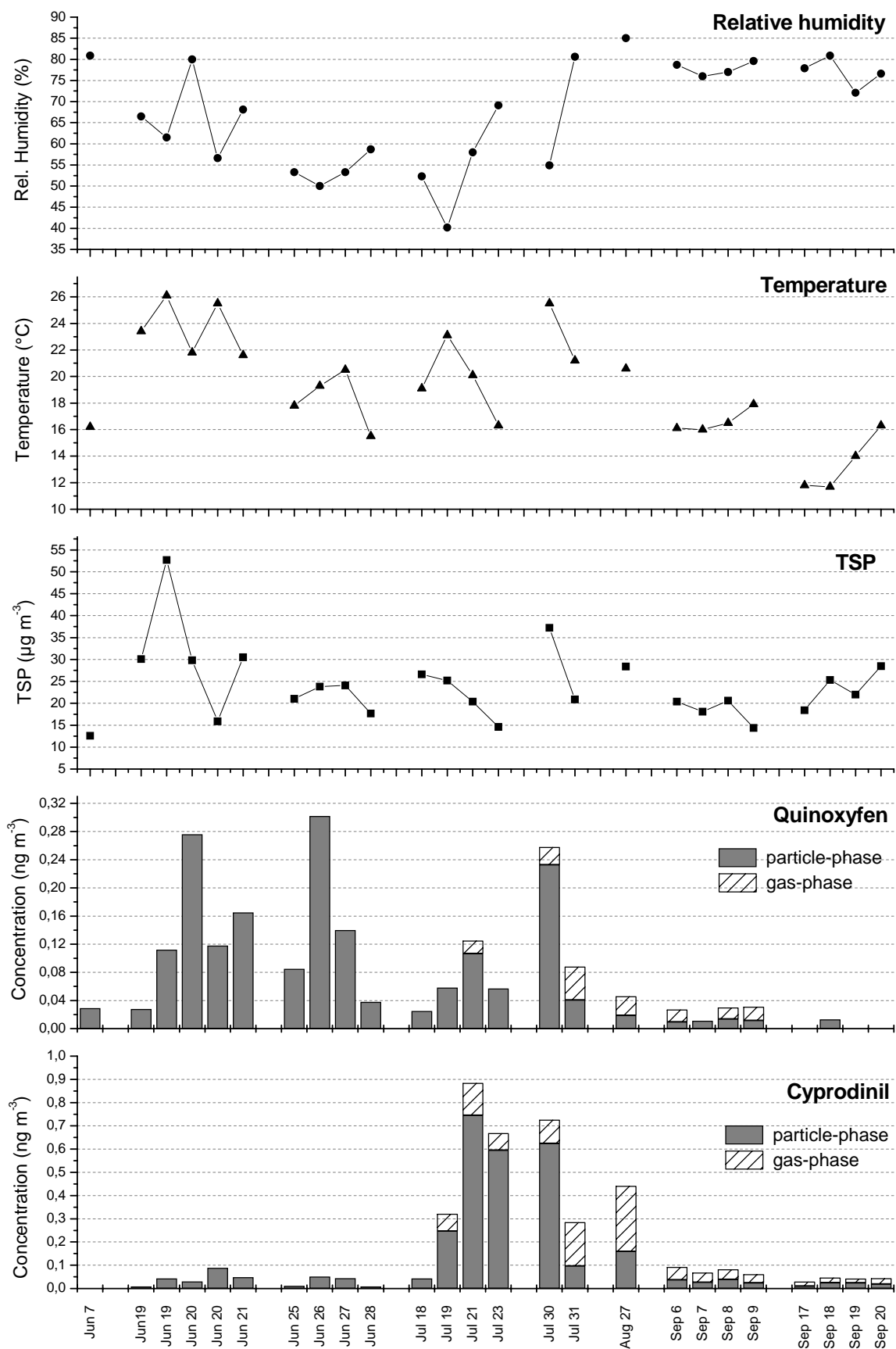


Figure 49: Phase distribution of cyprodinil and quinoxifen, TSP, average temperature and average relative humidity measured at the site H.

4.3.3 Occurrence of pesticides in rain and in air samples

Overall, fungicides were the most frequently detected pesticides both in the rain and the air samples.

A direct comparison between pesticides found in the air and in the rain samples can be made for the sampling sites H and A. Figure 50 shows detection frequencies of pesticides analysed in rain and air at the sampling sites A and H during the growing season 2002; results are shown only for those pesticides detected both in the air and rain samples.

At the site H, three fungicides were detected in more than 50% of the rain samples, namely kresoxym-methyl (70%), cyprodinil (50%) and tebuconazole (50%), whereas five fungicides could be found in more than 50% of the air samples, namely folpet (100%), cyprodinil (96%), quinoxifen (88%), kresoxym-methyl (76%) and fludioxonil (56%).

A different picture was observed at the site A, where eight pesticides (two herbicides, one herbicide metabolite, one insecticide and four fungicides) were detected in more than 50% of the rain samples, namely cyprodinil (88%), kresoxym-methyl (71%), tebuconazole (71%), methyl parathion (71%), fludioxonil (65%), simazine (65%), atrazine (53%) and desethylatrazine (53%). Only three fungicides could be detected in more than 50% of the air samples, namely quinoxifen (81%), cyprodinil (72%) and folpet (69%).

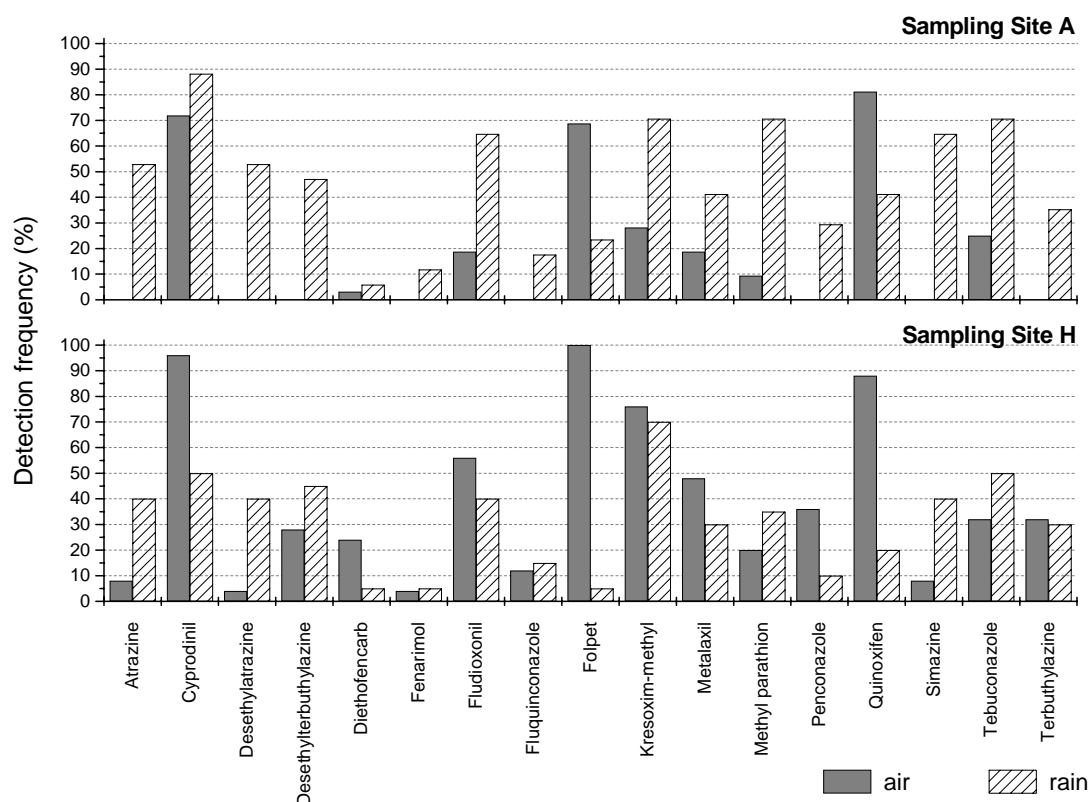


Figure 50: Detection frequency of selected pesticides in air and rain measured at the site A and H during the growing season 2002.

The pesticide with the highest concentrations in rain was atrazine at the site H (278,3 ng l⁻¹) and kresoxym-methyl at the site A (478,8 ng l⁻¹). Folpet was the pesticide with the highest concentrations in air from both sites (5,5 ng m⁻³ at the site H and 19,4 ng m⁻³ at the site AA).

High concentrations detected in air were not always followed by corresponding high concentrations in the rain samples (see Figures 51 and 52). Viceversa, high concentrations in rain were not always preceded by high concentrations in air. In some instances, pesticides were detected in the air, but not in the rain samples collected subsequently.

The most evident example was observed for folpet. This fungicide was detected in every air sample collected at the site H and in 69% of the air samples from the site AA, whereas it was sporadically detected in the rain samples from both sites.

These findings suggest that these pesticides were subjected to either atmospheric transport or selective dissipation by chemical processes before scavenging by rain could occur.

The design of the rain sampler and how the samples were collected and processed for analysis may also have played a critical role in the determination of the final results. The sampler used in this study was continuously open to the environment so that the collected samples reflected the dry deposition as well as the rain, the so called bulk deposition. However, once in the laboratory, the rain samples were filtered (through filters with 1,4 µm pore size) and only the aqueous phase was kept for analysis. The particulate material trapped on the filters was not extracted for pesticide analysis. Furthermore, results of the air sampling campaigns showed that the investigated pesticides were predominantly found in the particulate phase. As a consequence, particles loaded with pesticides scavenged by rain may have been trapped on the filters during the filtration process leading to an underestimation of the pesticide content of the rain samples.

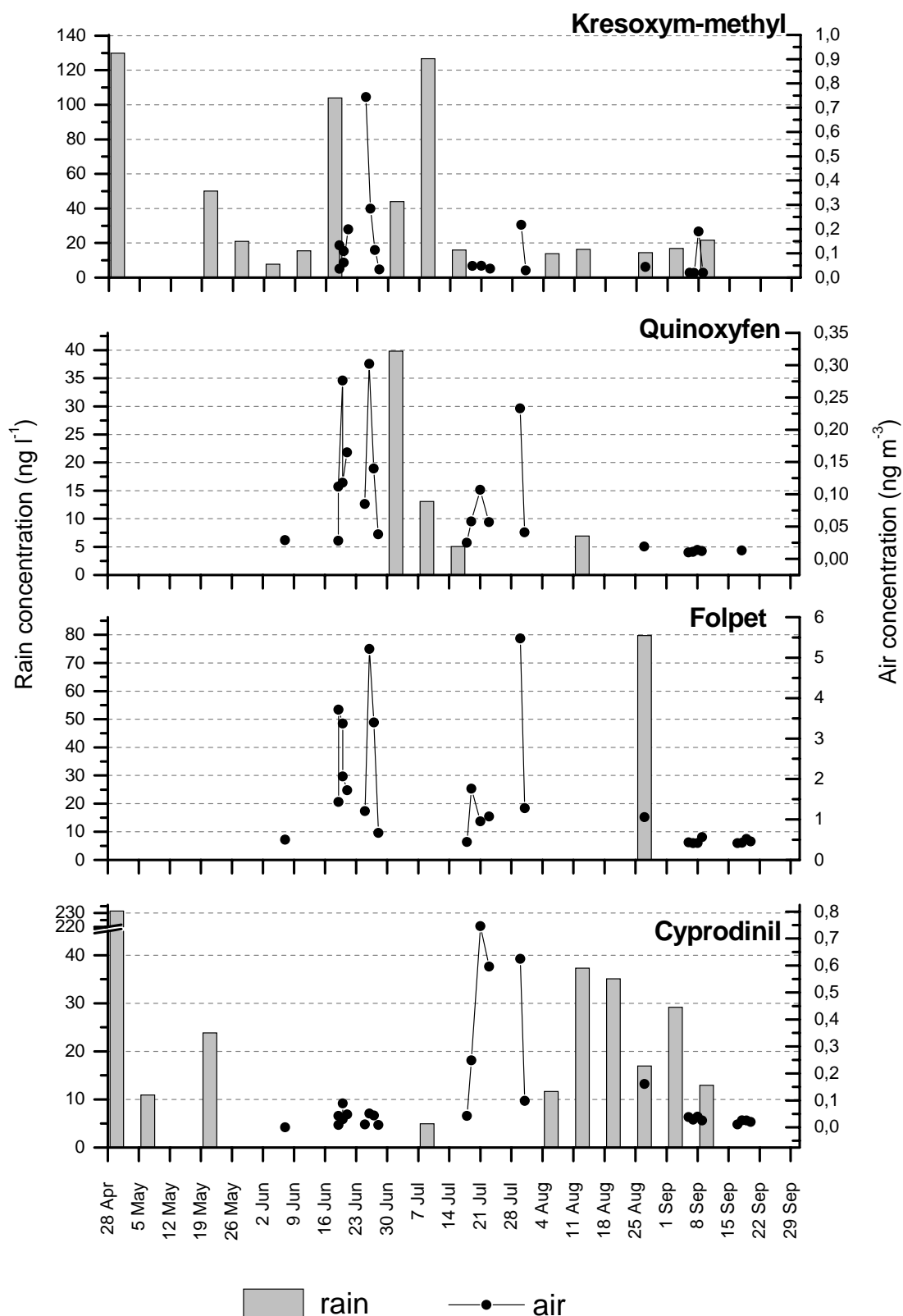


Figure 51: Concentration time series for selected fungicides detected in the rain (bars) and in the air (line with circles) at the sampling site H during the growing season 2002.

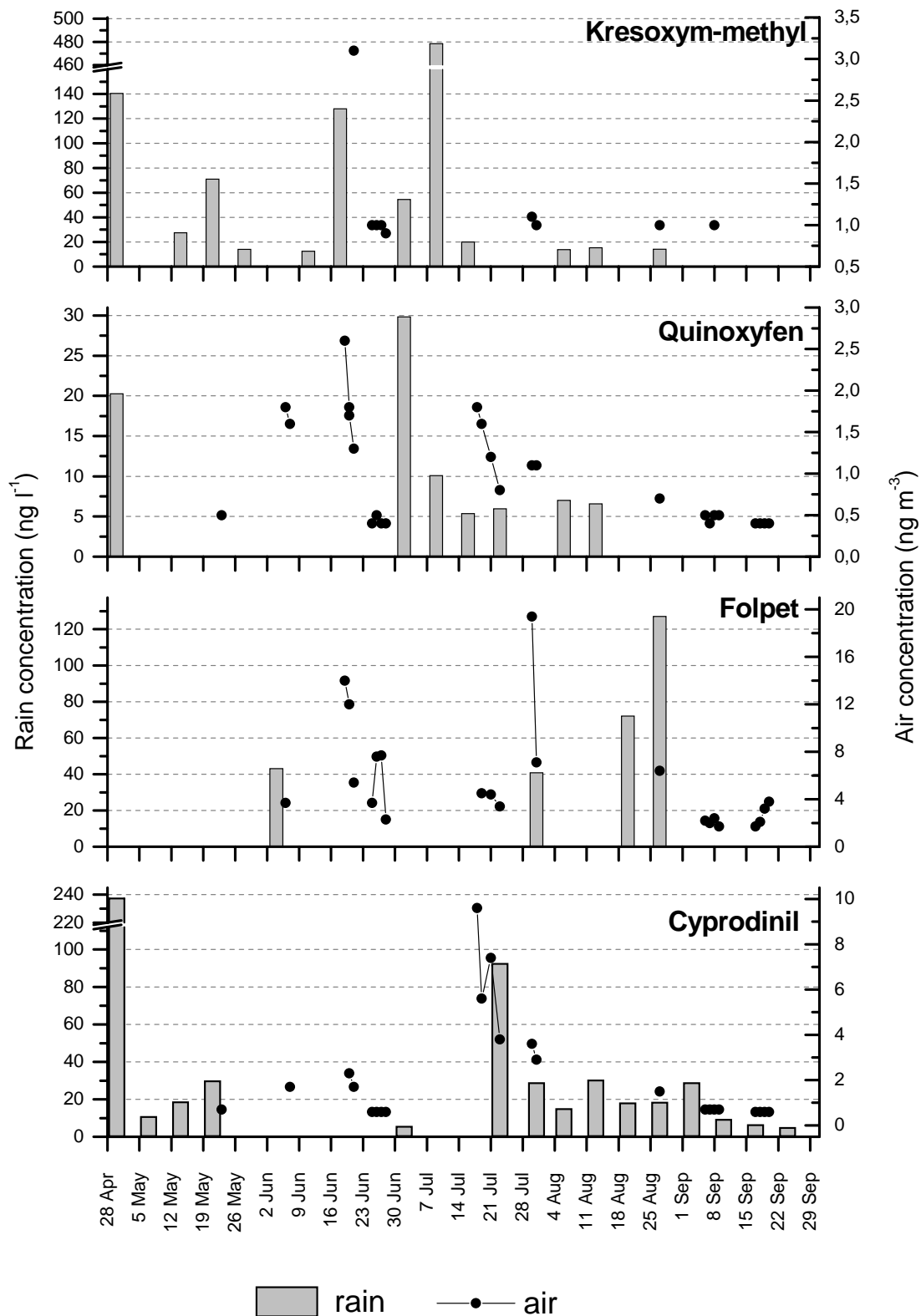


Figure 52: Concentration time series for selected fungicides detected in the rain (bars) and in the air (line with circles) at the sampling site A during the growing season 2002.

4.3.4 Summary and conclusions on air sampling campaigns

During the growing season 2002 seven air sampling campaigns were carried out in the area of study. Different sampling times were used in order to investigate (a) the temporal variations of air concentrations of the applied substances right after end of treatments and (b) the air concentration levels of pesticides after application periods of these substances were terminated (late growing season) or no applications took place at all.

The main results of these campaigns can be summarised as follows:

- Seventeen of the 27 measured pesticides were detected at least once in air.
- The highest detection frequencies and highest concentrations were found for the class of fungicides. The occurrence of these pesticides in the air was related to local application times on grapes. This result shows the typical characteristic of vinicultural areas, where fungicides are the most used class of pesticides.
- The highest concentrations were not always found right after the end of treatment, but, in some cases, after a few days. During a few weeks after application, air concentrations did not decrease continuously with time but showed maxima and minima. Such temporal variations were found to be governed by temperature, atmospheric exchange and atmospheric transport processes. These results are in accordance with those found in other field experiments (SIEBERS & GOTTSCHILD 1998, AKKAN 2003, FERRARI *et al.* 2005 a).
- Overall, at the end of the application period, air concentrations decreased with time showing the typical trend of dissipation processes, where remaining residue concentrations were asymptotic to the time axis. At the end of the sampling campaigns (end of September 2002) only four fungicides could still be detected, but at very low concentrations.
- The investigation of air concentration levels showed the importance of the enrichment factor (EF) as a parameter that can reveal differences among sample compositions and provide fingerprint information for source area identification.

After comparing these results with data from the published literature, it can be concluded that the measured air concentration levels found in this study do not represent a concern for human health in terms of acute risk. Inhalation toxicity studies have shown that an acute potential risk only arises at air concentrations in the range of g m^{-3} (AKKAN 2003). However, it must be kept in mind that only a small number of chemicals that were applied in the area were analysed in this study. In order to gain a better evaluation of the local atmospheric load of pesticides, a wider spectrum of applied substances needs to be investigated.

5 Summary and conclusions

To address the lack of information on the presence of pesticides in the atmosphere of the area of Trier, the Department of Hydrology of the University of Trier conducted a 3-year study to characterize the atmospheric presence, temporal patterns, transport and deposition of a variety of pesticides. This study was developed in the framework of the project "SFB522 - Environment and Region" ("SFB522 - Umwelt und Region") and financed by the German Research Foundation (Deutsche Forschungsgemeinschaft - DFG).

To this purpose, rain samples were weekly collected at eight sites during the growing seasons 2000, 2001 and 2002, and seven air sampling campaigns were carried out at three locations during the growing season 2002. Multiresidue analysis methods were developed to determine multiple classes of pesticides in rain water, particle- and gas-phase samples. Altogether 24 active ingredients and 3 metabolites were chosen as representative substances. Given the fact that fungicide products are the most frequently used pesticides in vinicultural areas, and on the basis of available information on pesticide usage in the investigated area, the study was mainly focussed on fungicides.

The results obtained allowed to achieve the major goal of the project, *i.e.* to characterise the atmospheric presence of a variety of current-use pesticides in the area of Trier, by providing detailed answers to the following questions:

Which pesticides were detected?

Twenty-four of the 27 measured pesticides were detected above limit of determination (LoD) at least once in the rain samples; seventeen pesticides were detected at least once above LoD in the air samples.

The most frequently detected pesticides and at the highest concentrations, both in rain and air, were compounds belonging to the class of *fungicides*, namely cyprodinil, fludioxonil, folpet, kresoxym-methyl, quinoxifen, and tebuconazole. Available information on pesticide applications carried out in the area of study confirmed the local use of pesticide products containing these active ingredients.

The *insecticide* methyl parathion was also detected in several rain samples (detection frequency above 41%) and at concentrations levels similar to those of the fungicides applied in the area. Lower detection frequencies and low concentration levels were found in the air samples.

	<p>Substances that are banned in Germany like the <i>herbicides</i> atrazine and simazine were also detected in several rain samples and in a few air samples. Atrazine was detected in more than 45% of the rain samples and attained maximum concentration levels similar to those of the fungicides applied in the area. Lower detection frequencies and concentration levels were measured for simazine.</p>
When were these substances detected?	<p>Characteristic seasonal trends were observed for the different classes of pesticides, mirroring the main application times of these substances.</p> <p><u>In the rain:</u> <i>herbicides</i> were detected from the beginning of sampling (mid April) through August; <i>insecticides</i> were detected between May and September. Most <i>fungicides</i> were detected between June and September, while a few compounds of this class could be detected from the beginning of sampling (mid April) through October. Of all measured pesticides only the fungicide cyprodinil could be detected at concentrations close to LoD in a few samples collected in November.</p> <p><u>In the air:</u> <i>herbicides</i> were detected in June, while the <i>insecticide</i> methyl parathion in July. <i>Fungicides</i> could be detected from mid May until the last sampling campaign carried out at the end of September.</p>
What concentration levels?	<p>Concentration levels varied during the growing season. The highest concentrations were measured in the late spring and summer months, coinciding with application times and warmer months.</p> <p><u>In the rain:</u> rain concentration levels were in the order of ng l^{-1} and only a few fungicides attained levels in the order of $\mu\text{g l}^{-1}$. These extremely high values were the result of a short-duration heavy rain event occurred shortly after the end of a pesticide application (the realistic "worst case" situation).</p> <p>Two main factors turned out to play a significant role in determining the concentration levels found in the rain water:</p> <ol style="list-style-type: none">Precipitation amount: many substances reached their maximum concentrations at rain events that were less than 20 mm.Timing of the rain event relative to applications: rain events occurred shortly after the end of applications were responsible for

	<p>local high pesticide concentrations in rain water.</p> <p>Average concentrations of the single substances were less than 100 ng l⁻¹, with a few exceptions. However, total concentrations were considerable and in some instances well above the EU drinking water quality standard of 500 ng l⁻¹ for total pesticides.</p> <p><u>In the air:</u> air concentration levels greatly differed from site to site. As expected, the highest values were measured at the sites W and AA, located, respectively, in the vineyards where pesticides were applied and in the close vicinity. At these locations maximum concentrations in the order of tens of ng m⁻³ were measured. Lower values, in the order of pg m⁻³, were detected at the site H, located further away from fields where applications were carried out.</p>
Local sources or atmospheric transport?	<p>The occurrence of <i>triazines</i> in rain for which there are no legal uses in Germany was related to transport through the atmosphere from areas where the use of these active ingredients is still permitted.</p> <p>Local sources were identified as the major contributor to the occurrence of the <i>insecticide</i> methyl parathion and <i>fungicides</i> in rain and air detected during the local application period.</p>
Annual deposition rates: a concern for the area of study?	<p>Compared to the amounts applied for pest control, the amounts deposited are very small: annual deposited amounts resulted between 0,004% and 0,10% of the maximum application rates.</p> <p>This low pesticide input from precipitation to surface-water bodies is not a concern in a vinicultural area where the impact of other sources, such as superficial runoff inputs from the treated areas and cleaning of field crop sprayers, is much more important.</p> <p>However, because of atmospheric dispersion and transport of contaminants, deposition in precipitation affects all parts of the environment and can deliver residues to non-target sites, such as organic crops, and sensitive ecosystems, like protected areas or drinking water reservoir. The potential impacts of these aerial pesticide inputs are as yet uncertain because of little available information on the long-term eco-toxicological effects of pesticides at low concentrations.</p>

Concentration levels in the air after application and duration of detection: a concern for human health?	<p>The highest air concentrations (in the order of ng m^{-3}) were measured right after the end of treatments or after a few days. At the end of the application period, concentration levels continuously decreased with time. During the last air sampling campaign (end of September 2002) only 4 fungicides could still be detected at very low concentrations.</p> <p>The measured air concentration levels found in this study do not represent a concern for human health in terms of acute risk. Inhalation toxicity studies have shown that an acute potential risk only arises at air concentrations in the range of g m^{-3} (AKKAN 2003). However, no conclusions can be drawn on long-term effects of pesticides at low concentrations.</p>
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Finally, it must be kept in mind that only a small number of chemicals that were applied in the area were analysed in this study. In order to gain a better evaluation of the local atmospheric load of pesticides, a wider spectrum of applied substances (including metabolites) needs to be investigated.

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Appendix A

Pesticide applications

Table A 1 – Pesticide applications performed in the Trier-Saarburg district (helicopter applications). Four to five applications were performed with an interval of 12 to 13 days from each other. Details are given only for places of interest for the study. (Source: Mr. Mader, National Institute of Trier for Education and Research "Staatliches Lehr- und Versuchsanstalt Trier")

Place (1 st appl., area)	1 st appl.	2 nd appl.	3 rd appl.	4 th appl.	5 th appl.
2000					
Ruwer valley (25 May, 40 ha)	3 Kg Dithane Ultra WG 9 Kg Sulphur	4 Kg Polyram WG 0,5 Kg Vento	3 Kg Ridomil Gold Combi 300 g Discus	4 Kg Polyram WG 400 g Castellan	3 Kg Ridomil Gold Combi 400 g Castellan
Kenn (31 May, 20 ha)	3 Kg Dithane Ultra WG 9 Kg Sulphur	2,5 Kg Aktuan 0,5 Vento	3 Kg Ridomil Gold Combi 300 g Discus	4 Kg Polyram WG 400 g Castellan	
2001					
Ruwer valley (6 June, 42 ha)	Dithane Ultra WG, Sulphur	Ridomil Gold Combi, Vento	Quadris	Aktuan, Prosper	
Kenn (6 June, 14 ha)	Dithane Ultra WG, Sulphur	Aktuan, Prosper	Ridomil Gold Combi, Flint	Aktuan, Vento	

Table A 2 – Pesticide applications performed in the area of Kasel, Ruwer valley. Pesticides applied by means of fan mist-blowers. (Source: Mr. Kirchen, "Schloss Marienlay" winery)

	2000	2001	2002
Early May	Dithane Ultra WG, Sulphur		
Mid May	Dithane Ultra WG, Sulphur, Dithanon	Dithane, Sulphur	Dithane, Sulphur
Late May		Dithane, Sulphur	Dithane, Sulphur
Early June	Delan, Castellan	Delan, Castellan	
Mid June	Ridomil Gold Combi, Topas, Vento	Forum Star, Strobby	Delan, Flint
Late June	Quadris		Aktuan, Flint
Early July		Forum Star, Discus	Forum Star, Discus
Mid July	Delan, Vento	Quadris	Forum Star, Strobby, Switch, Steward
Late July	Botrylon, Quadris, Mimic, ME605, Forum Star, Prosper	Aktuan, Botrylon, Castellan, Steward	Quadris, Steward
Early August	Forum Star, Castellan, Polyram, Kupfer 83V	Forum Star, Steward, Strobby, Discus, Ridomil	
Mid August	Scala	Delan, Sulphur	Quadris
Late August			Switch
Early September		Switch, Scala	
Late September*		Switch	Switch

Early month: between the 1st and the 10th of the month; Mid month: between the 11th and the 20th of the month; Late month: between the 21st and the 31st of the month.

* Pesticide application exclusively on those vines whose grapes are harvested in November for the production of the "Eiswein", a special sweet and expensive typical wine of the area.

Table A 3 – Pesticide applications performed at the “Schloss Marienlay” winery area, Morscheid. Pesticides applied by means of hand-held spray guns and fan mist-blowers. (Source: Mr. Kirchen, "Schloss Marienlay" winery)

	2001	2002
Mid May	Dithane, Sulphur	Dithane, Sulphur
Late May	Dithane, Sulphur	Dithane, Sulphur
Early June	Delan, Castellan	
Mid June	Forum Star, Stroby	Delan, Flint
Late June		Aktuan, Flint
Early July	Forum Star Discus	Forum Star, Discus
Mid July	Quadris	Forum Star, Stroby, Switch
Late July	Botrylon, Steward	Quadris
Early August	Forum Star, Steward, Ridomil Gold Combi, Prosper	
Mid August		Folicur, Quadris, Ronilan
Late August	Switch	Switch, Scala
Late September*	Switch	Switch

Early month: between the 1st and the 10th of the month; Mid month: between the 11th and the 20th of the month; Late month: between the 21st and the 31st of the month.

* Pesticide application exclusively on those vines whose grapes are harvested in November for the production of the “Eiswein”, a special sweet and expensive typical wine of the area.

Table A 4 – Pesticide applications performed at the Avelsbach wine-growing domain. Pesticides applied by means of fan mist-blowers. (Source: Mr. Permesang, Trier/Mosel national wine-growing domain)

	2001	2002
Mid May	Sulphur, Mancozeb, Delan	Mancozeb, Sulphur
Late May	Sulphur, Mancozeb, Delan, Kiron	Delan, Sulphur, Siapton
Early June		Vento, Melody Multi, Siapton
Mid June	Sulphur, Mancozeb, Delan, Siapton, Apollo	Flint, Forum, Siapton, Melodi Multi
Late June	Forum, Stroby, Teldor	
Early July	Forum, Stroby, Ridomil, Vento	Flint, Melody Multi, Siapton
Mid July		Vento, Switch, Siapton, Equation Pro, Teldor
Late July	Vento, Folpet, Kiron, Switch, Quadris, Steward	Funguran, Systhane
Early August	Funguran, Sulphur, Steward	
Mid August		Funguran, Prosper, Scala
Late August	Funguran	

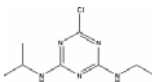
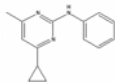
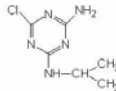

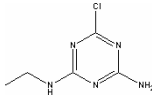

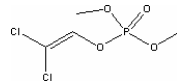
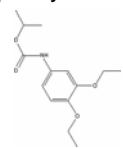
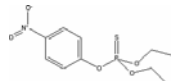
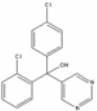
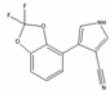
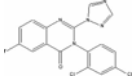
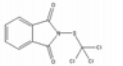
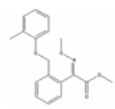
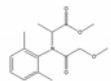
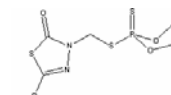
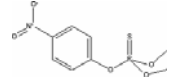
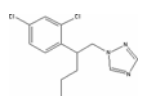
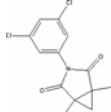
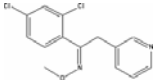
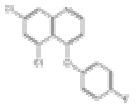
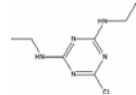
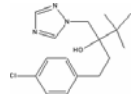
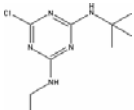
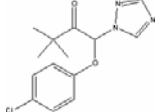
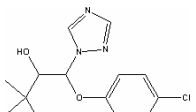
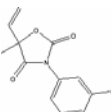
Early month: between the 1st and the 10th day of the month; Mid month: between the 11th and the 20th day of the month; Late month: between the 21st and the 31st day of the month.

Table A 5 – Pesticide products and active ingredients.

Product	Active ingredient	Use
Aktuan	100 g kg ⁻¹ cymoxanil, 250 g kg ⁻¹ dithianon	Fungicide
Bayfidan	250,7 g l ⁻¹ triadimenole	Fungicide
Botrylon	250 g kg ⁻¹ diethofencarb, 250 g kg ⁻¹ carbendazim	Fungicide
Castellan	250 g kg ⁻¹ fluquinconazole	Fungicide
Delan	750 g l ⁻¹ dithianon	Fungicide
Discus	477,6 g kg ⁻¹ kresoxim-methyl	Fungicide
Dithane Ultra WG	750 g kg ⁻¹ mancozeb	Fungicide
Dorado	200 g l ⁻¹ pyrifenox	Fungicide
Equation Pro	300 g kg ⁻¹ cymoxanil, 225,02 g kg ⁻¹ famoxadone	Fungicide
Flint	500 g kg ⁻¹ trifloxystrobin	Fungicide
Folicur	251,2 g l ⁻¹ tebuconazole	Fungicide
Forum	150 g l ⁻¹ dimethomorph	Fungicide
Forum Star	113 g l ⁻¹ dimethomorph, 600 g kg ⁻¹ folpet	Fungicide
Funguran	756 g kg ⁻¹ copper oxychloride	Fungicide
Kiron	51,3 g l ⁻¹ fenpyroximat	Acaricide
Kupfer 83V	424 g kg ⁻¹ copper oxychloride, 153 g kg ⁻¹ sulphur	Fungicide
ME605	405 g kg ⁻¹ methyl parathion	Insecticide
Melody Multi	60 g kg ⁻¹ iprovalicarb, 375 g kg ⁻¹ tolylfluanid	Fungicide
Mimic	240 g kg ⁻¹ tebufenozid	Insecticide
Netzschwefel	796 g kg ⁻¹ sulphur	Fungicide
Polyram WG	700 g kg ⁻¹ metiram	Fungicide
Prosper	499 g l ⁻¹ spiromamine	Fungicide
Quadris	250 g l ⁻¹ azoxystrobin	Fungicide
Ridomil Gold Combi	400 g kg ⁻¹ folpet, 50 g kg ⁻¹ metalaxyl-M	Fungicide
Ronilan	500 g kg ⁻¹ vinclozolin	Fungicide
Scala	400 g l ⁻¹ pyrimethanil	Fungicide
Siapton	Amino acids of animal origin	Fungicide
Steward	300 g kg ⁻¹ indoxacarb	Fungicide
Stroby	500 g kg ⁻¹ kresoxim-methyl	Fungicide
Switch	375 g kg ⁻¹ cyprodinil, 250 g kg ⁻¹ fludioxonil	Fungicide
Systhane	200 g l ⁻¹ myclobutanil	Fungicide
Teldor	510 g kg ⁻¹ fenhexamid	Fungicide
Topas	100 g l ⁻¹ penconazole	Fungicide
Vento	59,8 g l ⁻¹ fenarimol, 196,7 g l ⁻¹ quinoxifen	Fungicide

Chemical structures of the investigated pesticides

Active ingredient, class (A = acaricide, F = fungicide, H = herbicide, I = insecticide, M = metabolite), chemical group, chemical structure

Atrazine H, triazine 	Cyprodinil F, anilinoypyrimidine 	Desethylatrazine M, triazine 	Desethylterbuthylazine M, triazine 
Desisopropylatrazine M, triazine 	Dichlofluanid F, sulphamide 	Dichlorvos I, organophosphorus 	Diethofencarb F, n-phenyl carbamate 
Ethyl parathion I, A, organophosphorus 	Fenarimol F, pyrimidine 	Fludioxonil F, phenylpyrrole 	Fluquinconazole F, triazole 
Folpet F, phthalimide 	Kresoxym-methyl F, strobilurin 	Metalaxyl F, acylalanine 	Methidation I, organophosphorus 
Methyl parathion I, organophosphorus 	Penconazole F, triazole 	Procymidone F, dicarboximide 	Pyrifenox F, pyridine 
Quinoxifen F, quinoline 	Simazine H, triazine 	Tebuconazole F, triazole 	Terbuthylazine H, triazine 
Triadimefon F, triazole 	Triadimenol F, triazole 	Vinclozoline F, dicarboximide 	

Appendix C

Recommended application amounts for selected fungicides

(Source: Federal Office of Consumer Protection and Food Safety – Bundesamt für Verbraucherschutz und Lebensmittelsicherheit BVL).

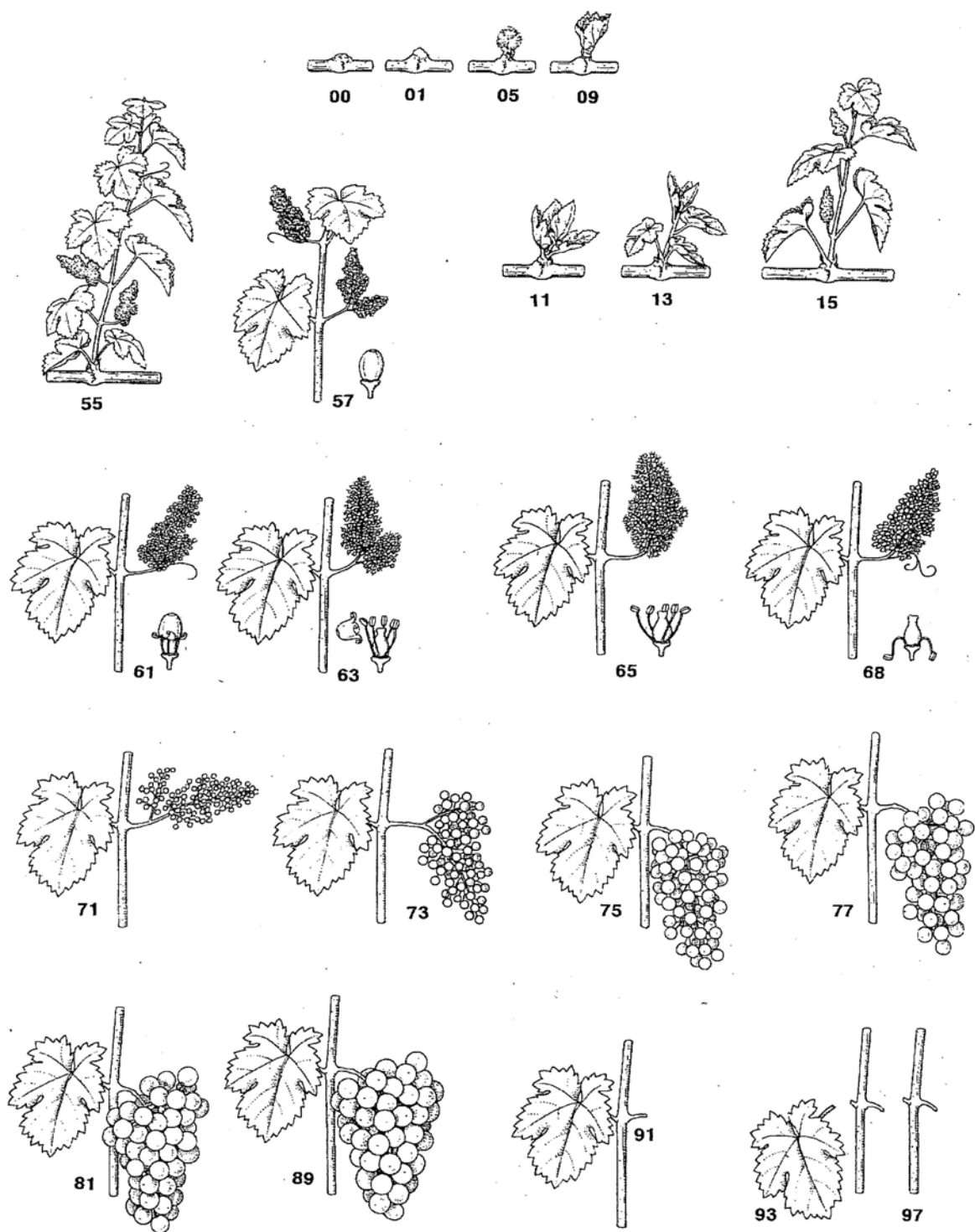
Active ingredient	Product	Max. number of applications per growing season	Growth stage of plants (GS)*	Recommended application amount** of the product	Calculated max. application amount of the active ingredient
Fenarimol	VENTO (59,8 g l ⁻¹ fenarimol)	7	Basic amount	0,1 l ha ⁻¹	41,9-167,4 g ha ⁻¹
			GS 61	0,2 l ha ⁻¹	
			GS 71	0,3 l ha ⁻¹	
			GS 75	0,4 l ha ⁻¹	
Fludioxonil	SWITCH (250 g kg ⁻¹ fludioxonil)	2	Basic amount	0,24 kg ha ⁻¹	120-480 g ha ⁻¹
			GS 61	0,48 kg ha ⁻¹	
			GS 71	0,72 kg ha ⁻¹	
			GS 75	0,96 kg ha ⁻¹	
Fluquinconazole	CASTELLAN (250 g kg ⁻¹ fluquinconazole)	6	Basic amount	80 g ha ⁻¹	120-480 g ha ⁻¹
			GS 61	160 g ha ⁻¹	
			GS 71	240 g ha ⁻¹	
			GS 75	320 g ha ⁻¹	
Kresoxim-methyl	DISCUS (500 g kg ⁻¹ kresoxim-methyl)	3	Basic amount	0,06 kg ha ⁻¹	90-360 g ha ⁻¹
			GS 61	0,12 kg ha ⁻¹	
			GS 71	0,18 kg ha ⁻¹	
			GS 75	0,24 kg ha ⁻¹	
Kresoxim-methyl	COLLIS (100 g l ⁻¹ kresoxim-methyl)	3	Basic amount	0,16 l ha ⁻¹	48-192 g ha ⁻¹
			GS 61	0,32 l ha ⁻¹	
			GS 71	0,48 l ha ⁻¹	
			GS 75	0,64 l ha ⁻¹	
Metalaxyl-M	Ridomil Gold Combi (50 g kg ⁻¹ metalaxyl-M)	3	Basic amount	0,6 kg ha ⁻¹	90-360 g ha ⁻¹
			GS 61	1,2 kg ha ⁻¹	
			GS 71	1,8 kg ha ⁻¹	
			GS 75	2,4 kg ha ⁻¹	
Quinoxifen	VENTO (196,7 g l ⁻¹ quinoxifen)	7	Basic amount	0,1 l ha ⁻¹	138-551 g ha ⁻¹
			GS 61	0,2 l ha ⁻¹	
			GS 71	0,3 l ha ⁻¹	
			GS 75	0,4 l ha ⁻¹	
Tebuconazole	Folicur EM (100 g kg ⁻¹ tebuconazole)	3	Basic amount	1 kg ha ⁻¹	300-1200 g ha ⁻¹
			GS 61	2 kg ha ⁻¹	
			GS 71	3 kg ha ⁻¹	
			GS 75	4 kg ha ⁻¹	

* see Appendix D for further explanation.

** In the steep vineyards this amount can be increased up to 25%.

Appendix D

Growth Stages of Plants (GS)



(MEIER 1997, BBA 1997b)

Appendix E

Details on the air sampling campaigns carried out during the growing season 2002 at the sampling site H.

Sample	H1	H2	H3	H4	H5
Date	6-7 Jun	18-19 Jun	19 Jun	20 Jun	20 Jun
Time	17:18-1:18	17:09-15:51	15:56-20:00	6:00-12:00	13:00-19:00
Duration of sampling	8 h	22,7 h	4,07 h	6 h	6 h
Predominant wind direction	N-NW	N-NE	NE	W	W-NW
Av. wind speed	0,2 m s ⁻¹	1,0 m s ⁻¹	1,2 m s ⁻¹	0,6 m s ⁻¹	1,7 m s ⁻¹
Av. air temperature	16,2 °C	23,4 °C	26,1 °C	21,8 °C	25,5 °C
Sampling flow	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹
Sampled air volume (standard volume)	241,30 m ³	671,24 m ³	120,37 m ³	174,70 m ³	176,94 m ³

Sample	H6	H7	H8	H9	H10
Date	21 Jun	24-25 Jun	25-26 Jun	26-27 Jun	27-28 Jun
Time	8:10-16:00	11:22-11:22	12:05-12:05	12:53-11:55	12:05-12:05
Duration of sampling	7,8 h	24 h	24 h	23,03 h	24 h
Predominant wind direction	W-NW	N	E-NE	W	W-NW
Av. wind speed	0,5 m s ⁻¹	0,8 m s ⁻¹	0,5 m s ⁻¹	0,7 m s ⁻¹	0,9 m s ⁻¹
Av. air temperature	21,6 °C	17,8 °C	19,3 °C	20,5 °C	15,5 °C
Sampling flow	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹
Sampled air volume (standard volume)	232,63 m ³	729,47 m ³	726,31 m ³	685,66 m ³	725,27 m ³

Sample	H11	H12	H13	H14	H15
Date	18 Jul	19 Jul	20-21 Jul	22-23 Jul	29-30 Jul
Time	12:50-20:50	12:34-20:34	12:23-12:23	12:14-12:14	12:11-12:11
Duration of sampling	8 h	8 h	24 h	24 h	24 h
Predominant wind direction	N	W-NW	W-NW	W	E-NE
Av. wind speed	1,1 m s ⁻¹	0,8 m s ⁻¹	0,8 m s ⁻¹	0,5 m s ⁻¹	0,6 m s ⁻¹
Av. air temperature	19,1 °C	23,1 °C	20,1 °C	16,3 °C	25,5 °C
Sampling flow	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹
Sampled air volume (standard volume)	240,95 m ³	236,92 m ³	715,86 m ³	728,59 m ³	705,54 m ³

Sample	H16	H17	H18	H19	H20
Date	30-31 Jul	26-27 Aug	5-6 Sep	6-7 Sep	7-8 Sep
Time	13:25-13:25	10:48-10:48	8:55-8:55	9:06-9:06	9:21-10:26
Duration of sampling	24 h	24 h	24 h	24 h	25,08 h
Predominant wind direction	E-NE	NE	W-NW	W	E-NE, W
Av. wind speed	0,6 m s ⁻¹	0,6 m s ⁻¹	0,3 m s ⁻¹	0,4 m s ⁻¹	0,4 m s ⁻¹
Av. air temperature	21,2 °C	20,6 °C	16,1 °C	16,0 °C	16,5 °C
Sampling flow	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹
Sampled air volume (standard volume)	699,12 m ³	707,64 m ³	718,46 m ³	721,62 m ³	758,40 m ³

Sample	H21	H22	H23	H24	H25
Date	8-9 Sep	16-17 Sep	17-18 Sep	18-19 Sep	19-20 Sep
Time	10:34-8:50	10:57-9:08	9:16-9:33	9:42-9:37	9:44-9:44
Duration of sampling	22,27 h	22,18 h	24,28 h	23,92 h	24 h
Predominant wind direction	E	E-NE	NE	N-NE	N-NE
Av. wind speed	0,5 m s ⁻¹	0,4 m s ⁻¹	0,6 m s ⁻¹	0,8 m s ⁻¹	0,5 m s ⁻¹
Av. air temperature	17,9 °C	11,8 °C	11,7 °C	14,0 °C	16,3 °C
Sampling flow	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹	30 m ³ h ⁻¹
Sampled air volume (standard volume)	654,80 m ³	674,17 m ³	749,64 m ³	716,61 m ³	710,54 m ³