## Berichte

aus der Biologischen Bundesanstalt für Land- und Forstwirtschaft

## Reports

from the Federal Biological Research Centre for Agriculture and Forestry

Heft 16 1996

## Assessing Volatilization of Pesticides:

## A Comparison of 18 Laboratory Methods and a Field Method

Bestimmung der Verflüchtigung von Pflanzenschutzmitteln: 18 Labormethoden und eine Freilandmethode im Vergleich

> Compiled by: Bearbeitet von:

Ulrike Walter Garnet Krasel\* Wilfried Pestemer

Institute for Ecological Chemistry GLP Workgroup

> Institut für ökologische Chemie \*Arbeitsgruppe.GLP

> > Contributing Authors:

Burgener, A.; Class, T.; Deas, A.; Haenel, H.-D.; Hausmann, S.; Hellpointner, E.; Jonas, W.;
Krebs, G.; Kubiak, R.; Lembrich, D.; Maestracci, M.; Morgenroth, U.; Müller, T.; Ophoff, H.;
Rüdel, H.; Sandmeier, P.; Sarafin, R.; Scheunert, I.; Skidmore, M.; Stork, A.; Wenzelburger, J.

BBA

Herausgeber Biologische Bundesanstalt für Land- und Forstwirtschaft Braunschweig, Deutschland

Verlag: Eigenverlag

Vertrieb: Saphir-Verlag, Gutsstraße 15, D-38551 Ribbesbüttel Telefon 0 53 74/65 76 Telefax 0 53 74/65 77

ISSN-Nummer: 0947-8809

#### Kontaktadresse:

Ulrike Walter Biologische Bundesanstalt für Land-und Forstwirtschaft Königin-Luise-Str. 19 14195 Berlin Telefon +49/(0) 30 /8304-281 Telefax +49/(0) 30/8304284

© Biologische Bundesanstalt für Land- und Forstwirtschaft

Das Werk ist urheberrechtlich geschützt. Die dadurch begründeten Rechte, insbesondere die der Übersendung, des Nachdrucks, des Vortrages, der Entnahme von Abbildungen, der Funksendung, der Wiedergabe auf fotomechanischem oder ähnlichem Wege und der Speicherung in Datenverarbeitungsanlagen, bleiben, auch bei nur auszugsweiser Verwertung, vorbehalten.

# CONTENTS

TABLES	4
FIGURES	5
ABBREVIATIONS	5
INTRODUCTION	6
Volatilization of Pesticides	6
Terminology	6
Why study Volatilization of Pesticides?	6
The German Guideline on Assessing Pesticide Volatilization	7
Development of Methods for Assessing Volatilization	8
The Interlaboratory Comparison	
METHODS	10
Organization	10
Experiments	
General Methods	
Individual Methods	
RESULTS AND DISCUSSION	22
Volatilization Kinetics	
Active Ingredient A	
Active Ingredients B and C	
24-hour-Volatilization	
Active Ingredient A / Plant Surfaces	
Active Ingredient A / Soil Surfaces	
Active Ingredient B	
Active Ingredient B / Plant Surfaces	
Active Ingredient B / Soil Surfaces	
Active Ingredient C	
Active Ingredient C / Plant Surfaces	
Active Ingredient C / Soil Surfaces	
Overall Comparison of Results in Relation to the German Guideline	40
SUMMARY	41
REFERENCES	41
ACKNOWLEDGEMENTS	44

Table 1: Participating Institutions and Contributing Authors 11	
Table 2: Physicochemical Properties of the Active Ingredients	
Table 3: Properties of Volatilization Chambers	
Table 3b: Properties of Volatilization Chambers, continued         14	
Table 4: Properties of Application Devices	
Table 5a: Analytical Procedures regarding Air	
Table 5b: Analytical Procedures regarding Plants and Soil         17	
Table 6a: Soil Properties	
Table 6b: Soil Properties, continued	
Table 7: Plant Properties	
Table 8: Determination of Reference Value	
Table 9: Description of the Field Experiment by KRE	
Table 10: References describing Methods	
Table 11: Number of Experiments evaluated in the Comparison         22	
Table 11a: Climatic Parameters (active ingredient A / plant surfaces)	,
Table 11b: Additional Information (active ingredient A / plant surfaces)       27	,
Table 12a: Climatic Parameters (active ingredient A / soil surfaces)       28	
Table 12b: Climatic Parameters, continued (active ingredient A / soil surfaces)       29	•
Table 12c: Additional Information (active ingredient A / soil surfaces)	•
Table 13a: Climatic Parameters (active ingredient B /plant surfaces)	I
Table 13b: Additional Information (active ingredient B / plant surfaces)	
Table 14a: Climatic Parameters (active ingredient B / soil surfaces)       34	
Table 14b: Climatic Parameters, continued (active ingredient B / soil surfaces)	
Table 14c: Additional Information (active ingredient B / soil surfaces)       35	l
Table 15a: Climatic Parameters (active ingredient C / plant surfaces)	
Table 15b: Additional Information (active ingredient C / plant surfaces)	,
Table 16a: Climatic Parameters (active ingredient C / soil surfaces)    39	1
Table 16b: Climatic Parameters, continued (active ingredient C / soil surfaces)	)
Table 16c: Additional Information (active ingredient C / soil surfaces)	)

## FIGURES

Figure 1: Cumulative volatilization of active ingredient A from plant surfaces
Figure 2: Cumulative volatilization of active ingredient A from soil surfaces
Figure 3: Cumulative volatilization of active ingredient B from plant surfaces
Figure 4: Cumulative volatilization of active ingredient B from soil surfaces
Figure 5: Cumulative volatilization of active ingredient C from plant surfaces
Figure 6: Cumulative volatilization of active ingredient C from soil surfaces
Figure7: Volatilization of active ingredient A from plant surfaces
Figure 8: Volatilization of active ingredient A from soil surfaces
Figure 9: Volatilization of active ingredient B from plant surfaces
Figure 10: Volatilization of active ingredient B from soil surfaces
Figure 11: Volatilization of active ingredient C from plant surfaces
Figure 12: Volatilization of active ingredient C from soil surfaces

## ABBREVIATIONS

a. i.		active ingredient
BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft	Federal Biological Research Centre for Agriculture and Forestry
CEC		Cation Exchange Capacity
EC		emulsifiable concentrate
ID		identification
IVA	Industrieverband Agrar e. V.	Crop Protection and Fertilizer Association
LSC		Liquid Scintillation Counting
MWC		maximum water holding capacity
n. <b>d</b> .		no data available
n. r.		not relevant
PflSchG	Pflanzenschutzgesetz	Plant Protection Act
PUF		polyurethane foam
UBA	Umweltbundesamt	Federal Environmental Agency
Ø		average

## INTRODUCTION

## Volatilization of Pesticides

#### Terminology

According to the McGraw-Hill Dictionary of Physics [1],

#### volatilization is the

"conversion of a chemical substance from a liquid or solid state to a gaseous or vapor state by the application of heat, by reducing pressure, or by combination of these processes. Also known as vaporization."

#### and evaporation is the

"conversion of a liquid to the vapor state by the addition of latent heat".

Hence, in the case of pesticides, the term volatilization is more appropriate and will be used throughout this report, although some of the older literature uses the term 'evaporation'. However, the way we understand volatilization, it also does occur without the application of heat and reduction of pressure the definition calls for.

Volatility, consequently, can be described as a substance's tendency to volatilize, and:

"Potential volatility is related to vapor pressure of the pesticide, but actual volatilization rate will depend on environmental conditions and all factors that modify or attenuate the effective vapor pressure of the pesticide." [2]

## Why study Volatilization of Pesticides?

Volatilization has been recognized as a process, sometimes major, in the loss of pesticides from the areas where they are applied [2-4]. Hence, volatilization is a means by which some pesticides are widely distributed, contributing to pollution of air, rain, and soil [5-12].

Since the late 1960s, an enormous amount of research on this subject has been conducted (extensive lists of literature are provided in [13] and [14]). While factors influencing volatilization in principle have been understood very early on [2-4], many problems concerning volatilization remain unsolved.

One of the properties influencing a substance's volatility is its vapor pressure. Volatile substances, such as water, ethanol, methanol have comparatively high vapor pressures at room temperature  $(10^3 - 10^4 \text{ Pa})$ . However, pesticides generally have a comparatively low vapor pressure (approx.  $10^{-7} - 10^{-2} \text{ Pa}$ ) and still volatilize at considerable rates (e. g. [15, 16]).

Another property that is important with respect to volatility is the air-water partition coefficient, the Henry's Law constant. The Henry's Law constant usually is calculated by dividing vapor pressure (dimension Pa) by water solubility (dimension mol m<sup>-3</sup>). Consequently, uncertainties in vapor pressure values are reflected by Henry's Law constants as well. A high Henry's Law constant (> 1 Pa m<sup>3</sup> mol<sup>-1</sup>) indicates a high volatility from aqueous solution (e. g., from moist soil). However, a substance with very

low water solubility may have a rather high Henry's law constant even if its vapor pressure is comparatively low. Therefore, while these physicochemical properties may be used to estimate relative volatility, deducing actual volatilization behavior from them may be erroneous.

It is evident that there are other factors beside vapor pressure and Henry's Law constant that influence volatilization, such as climatic parameters (e. g., wind speed, air and soil temperature, humidity) and interactions of the substance with the substrate it is applied to (e. g., adsorption, desorption) to name but a few. In spite of all the work that has been done in this field, up to now, measuring or assessing volatilization is not a simple task. Models simulating or predicting volatilization have been published (e. g., [17-21], for a survey of part of the literature see [13]), but they all can be applied only under certain, usually very restrictive, conditions. Therefore, the search for a better understanding of the volatilization process and for methods accurately assessing pesticide volatility still goes on.

#### The German Guideline on Assessing Pesticide Volatilization

In Germany, the Plant Protection Act (*Pflanzenschutzgesetz*, *PflSchG*) was revised in 1986. The purpose of this law is stated in its first section where it says:

"Zweck dieses Gesetzes ist (…) Gefahren abzuwenden, die durch die Anwendung von Pflanzenschutzmitteln oder durch andere Maßnahmen des Pflanzenschutzes, insbesondere für die Gesundheit von Mensch und Tier und für den Naturhaushalt, entstehen können, (…)"

(The purpose of this Act is (...) to avert risks to the health of man and animals and to the balance of nature which might result from the use of pesticides or other measures of plant protection, (...).)

In section two of the Act, the term 'Naturhaushalt' ('balance of nature') is defined as

"seine Bestandteile Boden, Wasser, Luft, Tier- und Pflanzenarten sowie das Wirkungsgefüge zwischen ihnen;"

(its components soil, water, air, animal and plant species, as well as the network of effects among them).

According to the same law, only registered pesticides (with a few exceptions) may be used in Germany. The authority for registration of pesticides is the Federal Research Centre for Agriculture and Forestry (BBA; *Biologische Bundesanstalt für Land- und Forstwirtschaft*). Registration requires, in addition to other things, details on risks to the balance of nature that might be caused by the substance in question. The BBA issues guidelines according to which substances have to be tested in order to provide all the details necessary for evaluation (*Richtlinien für die Prüfung von Pflanzenschutzmitteln im Zulassungsverfahren*).

The development of the guideline concerning volatilization [22] was prompted not only by the legal demands for protecting the air, but also by increasing public concern over pesticide residues found in precipitation and ground water. A third reason for paying closer attention to volatilization was the observation by the BBA that details in degradation studies done for registration purposes did not account for a certain amount of loss of pesticide during the first hours of the respective experiment. When the guideline was designed, the objectives were twofold, firstly to get a good estimate of a substance's volatility, and secondly to obtain that estimate with as little experimental effort as possible.

However, no method of assessing volatilization was at hand that seemed to meet those requirements. It was therefore decided to design a 'liberal' guideline with only a few specific demands to be met by the method applied. After several years of experience, the methods then in use should be compared and evaluated, and it should be decided whether a more specific guideline would have to be issued.

A study on "Pesticides in the environment - exposition, bioaccumulation, degradation" sponsored by the Federal Environmental Agency (UBA, *Umweltbundesamt*) was completed in 1989. The study focused on volatilization and was carried out in part by the BBA [23] and in part by a major research institution (GSF) [24, 25]. This study provided an extensive review of 'volatilization literature' as well as an experimental section. It was this study, along with research in progress at the BBA at that time [26]. on which the first drafts of the guideline were based.

The BBA-Guideline today [22] contains a graduated three step plan for experiments assessing the fate of pesticides in air. In step one, hydrolysis and photolysis of the substance in water are to be assessed. If and only if the substance's half-life in both processes is found to be more than 4 days, volatilization experiments are required in step two. If the volatilization rate is found to be higher than 20% within 24 hours after application, the third step is to estimate the photochemical-oxidative degradation in air.

The guideline neither requests (nor suggests) a specific method of assessing volatilization. Descriptions of volatilization measurements in the literature are merely referred to. Field as well as laboratory experiments are accepted. However, some requirements have to be met: with a few exceptions. volatilization from plant as well as from soil surfaces has to be assessed. Plants should either be French Bean or the target plant. Soil should have at least 70% sand and not more than 1.5% organic carbon. Experiments must be done using the formulated substance. When field experiments are conducted, details on air temperature, humidity, wind speed, precipitation, sunshine (duration and intensity), and on the general weather situation, must be supplied. Experiments are to be carried out to the greatest possible extent under conditions common to agricultural practice. For laboratory experiments, wind speed should be greater than 1 m/s, humidity should be about 35% (however, this condition has now, due to practical experiments). When volatilization is assessed indirectly (that is, via residues in / on plants and soil, respectively), adsorption, desorption and degradation and non-extractable residues have to be taken into consideration. The amount of volatilized pesticide should be assessed 1, 3, 6, and 24 hours after application.

### **Development of Methods for Assessing Volatilization**

With the 'volatilization guideline' in effect in 1990, whoever wished to apply for the registration of pesticides had to provide details on the volatilization rates of the substance in question. Due to the lack of precision in the guideline, applicants were faced with the task of learning about different existing methods for assessing volatilization and / or developing new ones, suitable to their needs. Since then a number of methods have been developed, ranging from very simple to high-tech designs. The methods can be grouped into 'direct' and 'indirect' ones. 'Direct' in this sense means that the volatilized portion of the pesticide can be directly assessed via sampling the air above the testing area. The 'indirect' approach uses the residues of pesticide on the experimental surface to calculate volatilization. However, there are also methods that present a combination of 'direct' and 'indirect' measurement.

#### The Interlaboratory Comparison

In November 1990, a meeting, initiated by the Crop Protection and Fertilizer Association (IVA; *Industrieverband Agrar e.V.*) and the Chemistry Division of the Department for Plant Protection Products and Application Techniques of the BBA was held at the BBA, Berlin, where representatives of the BBA, the UBA and industry and research laboratories, discussed how that task should be dealt with. Concepts for new volatilization chambers were presented as well as already existing methods. Criteria for 'good' methods were discussed. At that time, there was a tendency to favor 'direct' methods, because it was believed that only they were capable of measuring actual volatilization, whereas 'indirect' methods might overestimate volatilization due to possible failure to identify degradation and other losses. Also, the use of radiolabeled compounds was encouraged. At that time, however, most of the methods discussed existed merely on paper, and those already in operation could not really be compared due to a lack of data.

In July, 1991, a workshop on volatilization was held at Neustadt, where ten methods (or concepts of methods, respectively) and some results obtained with them were presented. The participants of this workshop were basically the same as at the meeting mentioned above. Advantages and disadvantages of different methods were discussed, but with the limited experience and data given at that time, no final conclusions on suitability of methods could be drawn. It was agreed that an interlaboratory comparison of all the methods used for registration purposes at that time would be a good idea and should be initiated as soon as possible.

However, it was not until February, 1994, that the concept of the interlab comparison was developed at a meeting held by the future participants at the BBA, Braunschweig. The following terms were agreed on:

- The three substances to be used.
- Use of EC-formulations with radiolabeled active ingredient; supply of these formulations to all participants from each of the respective manufacturers, respectively.
- The volume applied should be ca. 400 l spray ha<sup>-1</sup>.
- Air temperature should be 20 °C, humidity 50 60 %.
- For plant experiments, French Bean should be used.
- For soil experiments, the guideline requirements concerning soil properties should be met.
- Volatilization should be assessed 1, 3, 6 and 24 hours after application.

Participants were encouraged to perform experiments in the way they had done previously in work submitted to the BBA.

By the end of June, 1994, the radioactive compounds had been delivered to the participants and experiments could be started. In October, 1995, the interlab comparison officially ended with a meeting at the BBA, Braunschweig, where results were discussed extensively. It was agreed that the interlab comparison had yielded results relevant to registration procedures as well as to volatilization research and therefore should be published as soon as possible.

## **METHODS**

#### Organization

The contributing participants in the interlab comparison are listed in Table 1. After the general conditions of the interlab comparison had been agreed on, the test substances were provided to the participants by the manufacturers of those substances within four months.

At the Institute for Ecological Chemistry of the BBA, an Excel spreadsheet was designed and discussed with all participants. In it, the significant information on methods and results was supposed to be entered by the participants. Unfortunately, it turned out later that this spreadsheet could not be used with some methods, so an Access database was designed that offered more flexibility for entering and evaluating data. Participants handed their data in to the BBA when they had finished all their experiments.

The only true field experiment in the comparison was - due to technical problems- finished only after the official ending of the comparison. Since it is regarded as providing important additional information, however, it is included in this report.

The interlab comparison was ended with a meeting of all participants, at which the data gathered was thoroughly discussed.

Institution	Abbreviation in this Paper	Contributing Author(s)
AgrEvo UK Ltd. Saffron Walden, England	AGP (plants) AGS (soil)	A. Deas
BASF AG Limburgerhof, Germany	BAS	R. Sarafin
BAYER AG Monheim, Germany	BAY	E. Hellpointner
Biologische Bundesanstalt für Land- und Forstwirtschaft Berlin, Germany	BBA1, BBA2	U. Walter M. Frost G. Krasel W. Pestemer
Ciba-Geigy Ltd. Basle, Switzerland	CIB	P. Sandmeier
Fraunhofer-Institut für Umweltchennie und Ökotoxikologie Schmallenberg, Germany	FHG	H. Rüdel
GSF-Forschungszentrum für Umwelt und Gesundheit GmbH Oberschleissheim, Germany	GSF	D. Lembrich I. Scheunert
Forschungszentrum Jülich GmbH Jülich, Germany	KFA	H. Ophoff A. Stork
Dr. Gerhard Krebs Analytik <sup>a)</sup> Cologne, Germany	KRE	G. Krebs HD. Haenel
NATEC Institut für naturwissenschaftlich-technische Dienste GmbH Hamburg, Germany	NAT1, NAT2	W. Jonas
ptrl Europe Pharmacology and Toxicology Research Laboratory Ulm, Germany	PTR	T. Class S. Hausmann
RCC Umweltchemie AG Itingen/Basle, Switzerland	RCC	U. Morgenroth A. Burgener
Rhône-Poulenc Agro Lyon, France	RHO	M. Maestracci
Staatliche Lehr-und Forschungsanstalt für Landwirtschaft, Weinbau und Gartenbau Neustadt/Weinstrasse, Germany	SLF	R. Kubiak T. Müller
Zeneca Agrochemicals Bracknell, England	ZEP (plants) ZES (soil)	M. Skidmore

## Table 1: Participating Institutions and Contributing Authors

<sup>a)</sup> field experiment

## Experiments

## General Methods

Except for the one field experiment mentioned above, all experiments were carried out using radioactive labeled compounds. Three active ingredients were provided in EC-formulations to all participants from the same three sources. Physicochemical properties of those substances are given in Table 2.

Table 2: Physicochemical Properties of the Active Ingredie	ents
--	------

Details are according to the suppliers and to [22].

Active Ingredient	A	В	С
Mode of action	insecticide	fungicide	insecticide
State	crystalline solid	liquid	crystalline solid
Water solubility (mg 1 <sup>-1</sup> ; 20°C)	0.25 - 0.001	4.3	55
Vapor pressure (Pa; 20 °C)	2.0 x 10 <sup>-6</sup>	3.5 x 10 <sup>-3</sup>	2.0 x 10 <sup>-4</sup>
Henry's Law constant (Pa m <sup>3</sup> mol <sup>-1</sup> )	4 x 10 <sup>-3</sup> - 1.1	2.7 x 10 <sup>-1</sup>	0.96 x 10 <sup>-3</sup>
Melting point (°C)	100	-	-
Boiling point (°C)	-	120 (at 6.7 Pa)	154 (at 136 Pa)
Partition coefficient (log Pow)	4.6	4.06 (at pH 7, 22 ℃)	3
Formulation and content of active ingredient	EC 025	EC 750	EC 400
Field application rate (g ha <sup>-1</sup> )	10	750	200

According to their physicochemical properties, the active ingredients are expected to differ in their volatilization behavior. Judging from the vapor pressure and Henry's Law constant of substances B and C, one would expect a higher volatility for substance B. The data for substance A is an example of ambiguous data for water solubility and, consequently, Henry's Law constant. The Henry's Law constant of substance A is greater than that of B and C, so one might expect a higher volatility for substances. However, the water solubility of A is decidedly lower than that of B and C, contributing to the high Henry's Law constant. On the other hand, the vapor pressure of substance A is lower than that of B and C, suggesting a lower volatility.

For plant experiments, different varieties of French Bean (*Phaseolus vulgaris*) were used. As participants were following their established procedures, it was not possible for all participants to use the same variety. For soil experiments, sandy soils with a maximum content of 1.5% organic carbon were used. For the foregoing reason, it was not possible for everyone to use the same soil. Details on the respective plants and soils are given in the 'Individual Methods' section below.

## Individual Methods

Essentially with 18 different methods involved, describing and comparing these methods can only be done in tabular form. Thus, some information is invariably lost. Therefore, at the end of this section (Table 10) you will find references describing, where available, the respective methods in greater detail.

The following tables list significant features of the methods. The configuration of the field experiment mentioned above could not easily be fit into these tables; it is therefore described in a table of its own (Table 9).

	Chamber	Experim	iental area	Wind in	Height at	Air
	size (m <sup>3</sup> )	Plant (m²)	Soil (m²)	Chamber generated by	which Wind is Measured	Exchange Rate (h <sup>-1</sup> )
AGP	0.000009	0.0005	n.r.	blowing	calculated for 0-3 cm	36000
AGS	0.00001	п. г.	0.005	blowing	calculated for 0-3 cm	14440
BAS	0.003	n. r.	0.006	blowing	> 10 cm	67
BAY	a)	1	I	field conditions	3 - 10 cm	varying
BBA1	0.432	0.67	0.67	suction	calculated	2300
BBA2	0.1	n. r.	n. r.	blowing	0 - 3 cm	430
CIB	18.2	0.6	n. r.	blowing	3 - 10 cm	1000
FHG	1.5	0.4	0.6	suction & blowing	> 10 cm	1900
GSF	0.00025	n. r.	0.00878	suction	0 - 3 cm	20000
KFA	1.008	0.5	0.5	blowing	3 - 10 cm	900
NAT1	0.32	0.28	0.42	suction	3 - 10 cm	6
NAT2	0.015	0.023	0.013	suction	3 - 10 cm	105
PTR	0.02	0.023	0.023	suction	3 - 10 cm	60
RCC	0.22	0.30	0.30	suction &blowing	0 - 3 cm	800
RHO	0.003	n. r.	0.0225	blowing	0 - 3 cm	3000
SLF	1.024	0.5	0.5	suction & blowing	0 - 3 cm	3750
ZEP	b)	0.00196	n. r.	blowing	0 - 3 cm	n. d.
ZES	b)	n. r.	0.00166	suction	0 - 3 cm	n. d.

Table 3a: Properties of Volatilization Chambers

Details on height of wind measurement above plant / soil surface have been classified as follows: 0-3 cm; 3-10 cm; > 10 cm.

a) No chamber but open field container

.

b) No chamber but single plant / soil vessels

n. r.: not relevant; n. d.: no data available

	Soil Surface (Roughness)	Irrigation	Illumination
AGP	п. г.	none	optional
AGS	smoothed	moisture content maintained continuously via pump	optional
BAS	smoothed	soil experiments: capillary supply	day-night-cycle
BAY	regular sandy soil & crop stand	none	natural light in the daytime
BBA1	smoothed	none in plant experiments	daylight (green house)
BBA2	smoothed	none in plant experiments	daylight (greenhouse)
СІВ	n. r.	none	11 h light, 10 h dark, 3 h light, ca. 160 μΕ
FHG	soil loose-packed, surface roughened	soil experiments: soil supported by moist clay granules (ca. 60 % MWC)	1000 lx. 12 h during experiment
GSF	disturbed soil samples, surface smoothed	water supply via ceramic tile	artificial light
KFA	0.5 - 1 cm	before experiment	day light (without UV-B)
NAT1	smoothed	capillary supply	darkness during 95% of experimental time
NAT2	smoothed	capillary supply	darkness during 95% of experimental time
PTR	smoothed	continuously in soil experiments	continuously in plant experiments, artificial light
RCC	sieved, 2 mm	continuously, via pump	daylight (no direct sunlight). artificial light
RHO	none observed	continuously	daylight
SLF	1 cm	soil experiments only (to 50 % MWC)	none
ZEP	п. г.	continuously via pump	n. d.
ZES	smoothed	continuously via pump	n. d.

#### Table 3b: Properties of Volatilization Chambers, continued

n. r.: not relevant;

n. d.: no data available

With respect to the volatilization chamber properties, the differences in size, experimental area, and air exchange rate are the most apparent. In cases where the size of the experimental area for plants is marked as 'not relevant', either no plant experiments had been conducted, or single plants or isolated parts of plants had been used.

The list of chamber properties included in this table can not be considered comprehensive. Due to the wide variety in experimental designs, a more comprehensive table would have been very complex and was therefore precluded. The present table reflects those features that were considered significant for assessing volatilization by the authors when the interlab comparison was designed.

			Duration	Distanc	ce from		
	Appli-		of	Nozz	le to	Soil covered	Application
	cation as	Type of Nozzle	Appli- cation (s)	Plant (cm)	Soil (cm)	during Application	inside Chamber
AGP	spray	modified TLC applicator	120	1	n. r.	no	no
AGS	spray	modified TLC applicator	120	n. r.	1	no	no
BAS	spray	full cone spray nozzłe TG 0.5	7.5	12.5	28	yes	no
BAY	spray	LU 120-04 Lechler. 3 overl. nozzles	0.6	50	n. r.	no	no
BBA1	spray	TeeJet 95015E	6	30	30	yes	yes
BBA2	spray	TeeJet 8001E	б	35	35	yes	no
CIB	spray	TeeJet 8001E	2.5	30	40	yes	no
FHG	spray	SS EVS 8001	15	25	25	yes	no
GSF	spray	airbrush nozzle	30	n. r.	15	no	по
KFA	spray	TeeJet 8004E	0.6	37	n. r.	no	yes
NAT1	spray	test tube atomizer	25	25	55	yes	yes
NAT2	spray	G-H49-55. hollow cone	25	20	30	yes	no
PTR	droplets	HPLC-syringe	1800	0	0	yes	no
RCC	droplets	Hamilton-syringe	60	0	0.5	no	ю
RHO	spray	micro-spraying system	30	n. r.	7	no	no
SLF	spray	TeeJet 8001E	7	40	40	yes	no
ZEP	droplets	modified TLC- applicator	240	1.5	n. r.	no	no
ZES	droplets	modified TLC- applicator	240	n. r.	1.5	no	no

#### Table 4: Properties of Application Devices

n. r.: not relevant;

n. d.: no details available

Application devices used in the methods compared in this study differed greatly. Everything from nozzles used in agricultural practice to modified TLC applicators to simple Hamilton syringes was used. Depending on the device used, the duration of the application process varied considerably, too.

- 16 -

	Air		Adsorbent	Mode of		Adsorbent
	Sampled	Adsorbent	Extracted	Extraction	Extraction Solvent	Combusted
AGP	yes	PUF	yes	cold	solvent depends on active ingredient	no
AGS	yes	PUF	yes	cold	solvent depends on active ingredient	по
BAS	yes	activated charcoal	no	n. r.	п. г.	yes
BAY	no	n. r.	п. г.	n. <b>r</b> .	n. r.	n. r.
BBA1	yes	PUF	yes	hot	methanol	no
BBA2	no	п. г.	n. r.	п. г.	n. r.	п. г.
CIB	no	n. r.	n. r.	n. r.	n. r.	п. г.
FHG	yes	PUF	yes	cold	toluene	no
GSF	yes	PUF	yes	cold	acetone	no
KFA	yes	PUF / glass fiber filters	yes	cold/hot	solvent depends on active ingredient.	no
NAT1	yes	activated charcoal	no	n. r.	п. г.	yes
NAT2	yes	activated charcoal	no	n. r.	n. r.	yes
PTR	no	n. r.	п. г.	п. г.	п. г.	п. г.
RCC	no	п. г.	n. r.	п. г.	п. г.	n. r.
RHO	yes	XAD2	yes	cold	acetonitrile	yes
SLF	yes	PUF	yes	cold	acetone, methanol	no
ZEP	no	п. г.	п. г.	п. г.	n. r.	по
ZES	no	п. г.	n. r.	n. r.	n. r.	no

#### Table 5a: Analytical Procedures regarding Air

n. r.: not relevant

Features of analytical procedures described here (Table 5a) are confined to whether air was sampled or not, and, if so, which adsorbent was nsed and how it was prepared for analysis. Since for the interlab comparison radiolabeled compounds were used, residues of active ingredient were measured as <sup>14</sup>C-radioactivity; in some cases samples were analyzed for possible metabolites. It can generally be assumed that radioactivity of extracts was detected by LSC, and that combustion of samples also served the preparation of samples for LSC.

	Plants / Soil	Plants / Soil	Mode of		Plants / Soil
	Sampled	Extracted	Extraction	Extraction solvent	Combusted
AGP	yes	yes	cold	solvent depends on active ingredient	yes
AGS	yes	yes	cold	solvent depends on active ingredient	yes
BAS	yes	yes	cold	methanol / phosphoric acid	yes
BAY	yes	yes	cold	methanol	yes
BBA1	yes	yes	hot	methanol	yes
BBA2	yes	по	n. r.	n. <b>r</b> .	yes
CIB	yes	yes	cold	acetonitrile	yes
FHG	yes	yes	cold	soil: acetone; plants: methanol	yes
GSF	yes	yes	hot	acetone	yes
KFA	yes	yes	cold	solvent depends on active ingredient	yes
NAT1	yes	yes	cold	acetone / water, acetone	yes
NAT2	yes	yes	hot	acetone / water; acetone	yes
PTR	yes	no	n. r.	n. <i>r</i> .	yes
RCC	yes	yes	cold	acetonitrile	yes
RHO	yes	yes	cold	acetonitrile, methanol	yes
SLF	yes	yes	cold	acetone, methanol	yes
ZEP	yes	no	n. r.	п. г.	yes
ZES	yes	yes	cold	acetonitrile	yes

#### Table 5b: Analytical Procedures regarding Plants and Soil

n. r.: not relevant

As with analysis of air samples (Table 5a), analytical procedures described for plants and soil (Table 5b) center on the preparation for the actual quantification of radioactivity. Again, liquid scintillation counting was the method for measuring <sup>14</sup>C-radioactivity in extracts and combusted samples.

In the following tables dealing with soil and plant properties, only the relevant methods have been listed, respectively.

	Soil Type	Soil Texture	Sieved (mm)
AGS	standard soil 2.1 LUFA Speyer	sand / loamy sand	-
BAS	standard soil 2.1 LUFA Speyer	loamy sand	2
BAY	brown earth from sand	slightly loamy sand (DIN 19682)	-
FHG	light sand soil	silty sand	2
GSF	sandy soil	slightly loamy sand	2
NAT1	standard soil 2.1 LUFA Speyer	sandy soil	2
NAT2	standard soil 2.1 LUFA Speyer	sandy soil	2
PTR	standard soil 2.1 LUFA Speyer	sandy soil	1
RCC	standard soil 2.1 LUFA Speyer	sand (DIN)	2
RHO	standard soil 2.1 LUFA Speyer	sandy soil	•
SLF	para-brown earth / brownearth	silty sand	5
ZEP	standard soil 2.1 LUFA Speyer	sandy soil	2
ZES	standard soil 2.1 LUFA Speyer	sandy soil	2

#### Table 6a: Soil Properties

#### Table 6b: Soil Properties, continued

	MWC	Soil	CEC	Sand	Silt	Clay	C org.
	(g/100g)	pН	(mval/100g)	(%)	(%)	(%)	(%)
AGS	36	6	5	87	9	4	1.2
BAS	24	6	5	83	7	10	0.5
BAY	29	6	5	76	19	5	1.4
FHG	24	6	10	<b>7</b> 6	19	6	1.5
GSF	31	5	n. d.	89	6	5	1.0
NAT1	31	6	5	88	10	2	0.6
NAT2	31	5.9	5	88	10	2	0.6
PTR	26	5.9	5	87	9	4	0.7
RCC	21	5.7	5	87	9	4	0.7
RHO	26	5.9	5	87	9	4	0.7
SLF	33	5.3	5	80	18	3	0.9
ZEP	n. d.	6.2	3	91	6	3	1.0
ZES	n. d.	6.2	3	91	6	3	1.0

n. d.: no data available

It should be noted that there was some variation in the pH of soils used by different participants. Especially in the case of active ingredient B this may be one reason for a considerable variation among results (see below for more details). Also, MWC varied, even for the same soil type.

Table	7:	Plant	Prop	erties
-------	----	-------	------	--------

	Plant Species and Variety	Stature	Stage of Development	Growing Site	Growing Conditions
AGP	French Bean, ProsGitana	n. d.	6-9 leaf stage, flowering	greenhouse	1 seed per 10cm x 10cm pot
BAS	French Bean, Brasilia or Tuff	small, dwarfed	flower, first fruit	greenhouse	n. d.
BAY	French Bean, Dublette	n. d.	first foliage leaves completely open	field	directly in experimental container
<b>BBA1</b>	French Bean, Saxa	small, self- supporting	two foliage leaves fully developed	greenhouse	continuous light, 18 - 20 °C
BBA2	French Bean, Saxa	small, self- supporting	two foliage leaves fully developed	greenhouse	continuous light, 18 - 20 °C
СІВ	French Bean, Autan	n. d.	flower, first fruit	greenhouse, climatic chamber	Basudin 3 weeks after sowing; plants cut back to six leaves before application
FHG	French Bean, Saxa	n. d.	flower, first fruit	climatic chamber	climatic chamber, 20 °C. 70% rel. humidity, 5000 lx 8 h/d
KFA	French Bean, Sirio, Dublette	dense stand, self - supporting	shortly before first blossom	field	approx400 kg / ha NPK-fertilizer, irrigated when necessary
NAT1	French Bean, Saxa	self- supporting	flower, first fruit	field	n. d.
NAT2	French Bean, Saxa	self- supporting	flower, first fruit	field	n. d.
PTR	French Bean, Delinel	n. d.	flower, first fruit	field / greenhouse	n. d.
SLF	French Bean, Canadian Wonder	high	flower, first fruit	greenhouse	greenhouse conditions
ZEP	French Bean, Prince	n. d.	flower, first fruit	greenhouse	n. d.

n. d.: no data available

The following table gives a brief explanation of how the crucial reference value was determined for each method. The reference value in this case is the initial amount of radioactivity which was applied to plant and soil surfaces in the form of the active ingredient. The amount of radioactivity (active ingredient) volatilized is expressed as a percentage of the reference value.

	Determination of Reference Value
AGP	Usually by reference to the mean of targets of the same size sprayed before and after the actual plant targets.
AGS	Usually by reference to the mean of targets of the same size sprayed before and after the actual soil targets.
BAS	Amount of radioactivity in spray solution less application losses (chamber rinse, loop and nozzle rinse, cryotrap and filter rinse, also: rinse of transfer equipment).
BAY	100 % reference value equals a radioactivity of 20 % (= 0.05 $\text{m}^2$ ) of the testing area. determined via regular sample analysis 3-4 min after application.
BBA1	Amount of radioactivity in spray solution less application losses (remaining radioactivity in vessel, application system and paper covering chamber walls during application).
BBA2	Leaves of four plants are cut eff immediately after application and treated like other sample leaves, radioactivity is measured in an LSC and average radioactivity / g lcaf-weight is calculated.
СІВ	Total residue (ppm) at time $t_0$ (radioactivity relative to leaf mass, ppm calculated from specific activity of active ingredient).
FHG	100%-value equals radioactivity in spray solution less application losses: radioactivity in spray solution is determined from amount removed from stock solution (weight).
GSF	Net amount applied equals radioactivity in spraying solution less radioactivity remaining in nozzle / syringe less radioactivity remaining in application vessel.
KFA	Radioactivity applied equals radioactivity of spray solution less application losses (contamination of application equipment). Since soil is not covered during application, in plant experiments radioactivity residues in soil are subtracted from the reference value.
NAT1	Radioactivity in spray solution less application losses.
NAT2	Radioactivity in spray solution less application losses.
PTR	Application and analysis of a set of soil or plant surface samples at time 0, analogous to experimental samples.
RCC	Extraction of four 0-hour samples $\rightarrow$ LSC, standardization.
RHO	Radioactivity applied equals radioactivity on microscopic covers times area of treated soil divided by area of covers.
SLF	Radioactivity actually applied equals radioactivity of spraying solution less radioactivity of application loss. Application loss equals rinse of nozzle plus extraction of spraying system plus other loss (funnel, vessel) plus wipe test of application chamber plus soil cover (plant experiments) plus cover of inside walls of application chamber.
ZEP	Mean value obtained from combustion of three 0-hour leaves.
ZES	Mean value obtained from summation of activity in the acetonitrile extract and the residual soil debris for three 0-hour soil pots.

## Table 8: Determination of Reference Value (100 % applied)

Component	Information
Active Ingredient / Formulation	B, EC 750, no radioactive labeling
Plants	French Bean, Cantare, dense plant stand, ca. 0.5 m high, application 4 weeks after flowering.
Soil	Sandy loam, C <sub>org</sub> . 1.9 %
Experimental Area	40m x 40m area within a bigger field
Application	AGR-Hardy trailed sprayer, 20 nozzles at 50 cm distances. Nozzle type: TeeJet XR11003VS, distance between nozzles and crop 55 cm; application speed 4.8 km/h.
Air Sampling	0.5 m and 1.5 m above crops, vacuum pumps, adsorption material C18.
Plant Sampling	About 1 kg of plant material from different sites within experimental area
Soil Sampling	None
Analytics	Air: elution of C18 material with methanol, extract concentration addition of toluene, GC-MS. Plants: extraction of plant material with water/acetone, extract concentration, addition of toluene, clean-up on silicagel. GC-MS
Evaluation	Volatilization is calculated based on air samples and meteorological data, as well as based on residues in plants.

Table 9: Description of the Field Experiment by KRE

## Table 10: References describing Methods

Method	Reference
AGP	[27]
AGS	[27]
BAS	not yet published
BAY	[28]
BBA1	not yet published
BBA2	[26], now modified for use with radiolabeled substances
CIB	[29]
FHG	[30]
GSF	[31]
KFA	[32, 33]
KRE	[34], for assessment based on air sampling
NAT1	[35, 36]
NAT2	not published
PTR	[37]
RCC	not published
RHO	[38]
SLF	[39]
ZEP	[40]
ZES	[40]

## **RESULTS AND DISCUSSION**

The volatilization of three pesticides from plant and soil surfaces was assessed using eighteen different laboratory methods and one field method. The results of 102 single experiments were gathered (see Table 11). The aim of the study was to see whether the different methods yielded results that were consistent among the methods. However, there was no definition of 'consistent' in a statistical sense. Since the background of the study was the German guideline requiring information on a substance's volatility prior to its legal authorization as an active ingredient in pesticides, the single experiments have been conducted and evaluated according to that guideline.

		Active Ingredient	
	<u>A</u>	В	С
Plant	9	22	19
Soil	I 1	20	17
Plant & Soil <sup>a)</sup>	-	2	2

Ta	ιb	le	1	1:	N	lum	ıbe	r (	of	Ex	per	rim	ent	s e	va	lua	ited	in	the	Con	iparis	on

<sup>a)</sup> Results are presented and discussed in the respective plant sections.

The German guideline requests details on the percentage of active ingredient volatilized 1, 3, 6, and 24 hours after application, the 24-hour-value being the crucial one for the authorization process. Therefore, results here are given in two sections. The first one depicts some typical kinetics of volatilization, and the second records the 24-hour-values of all the experiments. In both sections, experiments have been grouped by active ingredient / surface - combinations.

Climatic parameters such as temperature, humidity, and wind speed, are known to influence the volatilization process. Therefore, we consider it necessary to present data about those parameters along with the actual results of the experiments. In addition to climatic parameters there is further information available on most of the experiments to aid comparison of results. Climatic parameters and additional information are listed in tables (Tables 12 - 17) following the graphs representing the 24-hour-values (Figures 7 - 12).

## **Volatilization Kinetics**

The following graphs show representative volatilization kinetics for the active ingredient / surface combinations indicated.

### Active Ingredient A

Note that the Y-scales for the graphs dealing with active ingredient A are about ten times smaller than that of the graphs for the other two ingredients.



Figure 1: Cumulative volatilization of active ingredient A from plant surfaces The legend gives abbreviations of methods and identification numbers of experiments.



Figure 2: Cumulative volatilization of active ingredient A from soil surfaces The legend gives abbreviations of methods and identification numbers of experiments.



Figure 3: Cumulative volatilization of active ingredient B from plant surfaces The legend gives abbreviations of methods and identification numbers of experiments.



Figure 4: Cumulative volatilization of active ingredient B from soil surfaces The legend gives abbreviations of methods and identification numbers of experiments.



Figure 5: Cumulative volatilization of active ingredient C from plant surfaces The legend gives abbreviations of methods and identification numbers of experiments.



Figure 6: Cumulative volatilization of active ingredient C from soil surfaces The legend gives abbreviations of methods and identification numbers of experiments.

For active ingredient B and C, considerable variation was observed among the kinetics obtained with different methods. However, as will be seen below, there also was some variation among results obtained using the same method. Furthermore, for reasons of clarity the data presented have been selected by the authors from a larger number of experiments which they represent very well.

Interpreting the kinetics graphs, it generally can be said that the values the German guideline asks for seem to be reasonable: they document the high volatilization rates within the first few hours after application, and the 24-h-value is measured at a time when the volatilization process has considerably slowed down.

## 24-hour-Volatilization

In the German registration procedure, the 24-hour-value is crucial for the judgment of a substance's volatility. The trigger-value here is 20%: if more than that percentage of the active ingredient originally applied volatilizes within 24 hours, additional data on the substance's behavior in air will be required by the BBA.

The following graphs represent the results of all the single experiments evaluated in this study. No mean values are given in order to document the variation among experiments conducted with the same method as well as the variation among results obtained with different methods.

Columns representing percentage of volatilization are labeled with the experiments' identification numbers. Unique identification numbers have been assigned to experiments automatically when they were entered into the Access database used for evaluation of this study. These numbers accordingly can be used to identify the climatic and other information regarding a given experiment in the tables following each graph.

## Active Ingredient A / Plant Surfaces



**Figure 7: Volatilization of active ingredient A from plant surfaces** The figure represents the results from all the a. i. A / plant experiments evaluated in the interlab comparison. Methods missing were not applied to this combination of active ingredient and surface.

All of the 24-hour-values measured for active ingredient A from plant surfaces are significantly below the 20%-trigger-value. Significance of variation among values in this range of measuring cannot be assessed.

- ID	Air T	emperatur	e (°C)	Rel	Humidity	(%)	Wi	Wind Speed (m/s)		
#	Min	Max.	Ø	Min.	Max.	Ø	Min.	Max.	Ø	
5	22.0	27.0	24.5	43.0	51.0	47.0	1.0	2.0	1.5	
9	18.5	21.9	20.2	43.1	53.8	48.6	1.04	1.16	1.07	
10	18.4	21.9	20.1	44.1	63.4	50.1	0.63	1.11	1.06	
39	23.0	29.0	26.0	37.0	58.0	44.0	1.05	1.46	1.39	
60	20.0	24.0	22.0	n. <b>d</b> .	n. <b>d</b> .	n. d.	1.0	2.0	1.5	
71	19.5	31.0	24.2	12.2	35.2	21.4	1.0	1.9	1.5	
97	16.8	20.9	18.5	33.6	47.7	42.7	0.1	2.0	1.0	
110	20.4	22.0	21.0	34.0	45.5	40.5	n. d.	n. d.	1.0	
111	21.0	22.6	21.4	34.5	46.5	40.5	n. <b>d</b> .	n. d.	1.0	

Table 12a: Climatic Parameters (active ingredient A / plant surfaces)

n. d.: no data available

 Table 12b: Additional Information (active ingredient A / plant surfaces)

 Recovery is only given where applicable, that is for methods in which air is sampled. Details on time span between application and start of experiment have been classified in three groups: 'up to 5 min'.

 '5 to 10 min', and 'more than 10 min'.

	Active		Time Span between		
D	Ingredient	Volume applied	Application & Start of	Plants per	Recovery <sup>a</sup>
<del>_7</del>	appned (g na )	<u>(1 na<sup>+</sup>)</u>	Experiment		(70)
5	6.8	148	up to 5 min	50	100.5
9	10.0	400	5 to 10 min	28	95.7
10	10.0	400	5 to 10 min	28	102.9
39	6.6	300	more than 10 min	n. r.	n. r.
60	8.0	184	up to 5 min	50	101.5
71	9.7	255	more than 10 min	n. r.	n. <b>r</b> .
97	10.0	400	up to 5 min	n. <i>r</i> .	n. r.
110	10.6	400	up to 5 min	n. r.	98.7
111	10.6	400	up to 5 min	n. r.	108.2

n. r.: not relevant

a) Recovery rates have been calculated by the database and are deliberately given with one digit following the decimal point. This accuracy may not reflect author's intentions.



Active Ingredient A / Soil Surfaces

Figure 8: Volatilization of active ingredient A from soil surfaces The figure represents the results from all the a. i. A / soil experiments evaluated in the interlab comparison. Methods missing were not applied to this combination of active ingredient and surface.

Volatilization of active ingredient A from soil is apparently even lower than from plant surfaces. Again, in this range of measurements, variation among values need not be significant.

For active ingredient A, all methods compared yielded results in the same order of magnitude, i. e., less than 10 % volatilization of the amount applied within 24 hours after application.

D	Air T	emperatur	e (°C)	Rel.	Humidity (	(%)	Wind Speed (m/s)		
#	Min.	Max.	Ø	Min.	Max.	Ø	Min.	Max.	Ø
4	22.0	24.0	23.0	82.0	84.0	83.0	1.0	2.0	1.5
7	20.1	20.3	20.2	49.0	49.9	49.1	1.15	1.33	1.21
8	18.8	23.2	20.3	48.2	51.1	49.5	1.18	1.31	1.23
12	18.0	19.2	18.5	51.0	54.6	52.1	0.55	0.61	0.59
13	17.8	19.3	18.2	51.6	57.8	54.0	0,55	0.61	0.59
14	18.1	19.4	18.4	50.6	56.2	53.0	0.55	0.61	0.59
34	22.1	24.5	22.5	30.7	37.3	32.6	1.3	1.9	1.6
35	19.4	25.1	23.7	30.4	49.8	32.8	1.3	2.0	1.5
38	22.0	28.0	24.0	44.0	64.0	55.0	1.25	1.53	1.39
59	21.0	24.0	22.5	n. <b>d</b> .	n. d.	n. d.	1.0	2.0	1.5
69	18.5	22.3	20.8	20.5	31.6	24.8	1.3	1.5	1.4

Table 13a: Climatic Parameters (active ingredient A / soil surfaces)

ID ID	Soil Temperature (°C)			Soil Moisture (% MWC)			
#	Min	Max	Ø	Min	Max	Ø	
4	n. d.	n. d.	n. d.	57.0	59.0	58.0	
7	n. d.	n. d.	n. d.	36.0	50.0	n. d.	
8	n. d.	n. d.	n. d.	33.0	50.0	n. d.	
12	17.6	19.8	17.9	36.6	55.9	48.5	
13	16.7	18.6	17.1	16.4	36.0	21.8	
14	17.1	19.2	17.7	38.7	51.4	47.0	
34	18.2	22.8	18.6	55,3	60.0	57.7	
35	16.3	24.7	21.3	50.7	60.0	55.4	
38	19.0	25.0	21.0	n. d.	n. d.	61.5	
59	n. d.	n. <b>d</b> .	n. d.	58.0	60.0	59,0	
69	n. d.	<b>n. d</b> .	n. d.	59.51	60.5	60.3	

n. d.: no data available

#### Table 13c: Additional Information (active ingredient A / soil surfaces)

Recovery is only given where applicable, that is, for methods in which air is sampled. Details on time span between application and start of experiment have been classified into three groups: 'up to 5 min', '5 to 10 min'. and 'more than 10 min'.

	Active		Time Span between	
D	Ingredient applied	Volume applied	Application & Start of	
#	(g ha <sup>-1</sup> )	(l ha <sup>-1</sup> )	Experiment	Recovery <sup>a)</sup> (%)
4	5.7	137	up to 5 min	97.5
7	10.0	400	up to 5 min	103.8
8	10.0	400	5 to 10 min	96.1
12	7.6	450	up to 5 min	102.7
13	23.1	450	up to 5 min	95.2
<b>1</b> 4	22.2	450	up to 5 min	95.8
34	8.5	500	up to 5 min	119.5
35	10.5	500	up to 5 min	100.4
38	3,8	300	more than 10 min	n. r.
59	7.2	198	up to 5 min	101.2
69	10.5	301	up to 5 min	<b>n</b> . r.

n. r.: not relevant

a) Recovery rates have been calculated by the database and are deliberately given with one digit following the decimal point. This accuracy may not reflect author's intentions.

#### Active Ingredient B

Active ingredient B presented participants with an unforeseen challenge: during the synthesis of the <sup>14</sup>C-labeled compound an unexpected reaction occurred, causing a reduction of radiochemical purity of the active ingredient to about 85% only. Since the compound(s) that had been <sup>14</sup>C-labeled besides the active ingredient could not be determined, its / their volatility could not be predicted or estimated.

#### Active Ingredient B / Plant Surfaces

The unfortunate circumstance described in the previous paragraph made evaluating these experiments difficult. Adding to that difficulty was the fact that the only field experiment conducted for this study was carried out using non-radiolabeled active ingredient B. As can be seen in Figure 9, in the field experiment a significantly lower volatilization of active ingredient B was assessed than in all the other experiments. Several reasons may have contributed to this discrepancy, from slight differences in the test substances over variety and developmental stage of the beans to weather conditions. Also, in a field experiment, given the large testing area, determination of the crucial reference value may be difficult. A study to investigate the discrepancy is currently in progress (a laboratory experiment with the SLF-method simulating the conditions of the field experiment); the results will be published elsewhere. Although no statistical evaluation of the comparison has been conducted yet, it is obvious that given the result of one field experiment only, no conclusions can be drawn as to whether results of laboratory experiments can be applied to field conditions.



∃BAS □BBA1 ⊠BBA2 ≡CIB □FHG ⊠KFA ⊗NAT1 □NAT2 ⊞PTR ⊠SLF □ZEP ■BAY ⊗KRE

## **Figure 9: Volatilization of active ingredient B from plant surfaces** The figure represents the results from all the a. i. B / plant experiments evaluated in the interlab

comparison. Methods missing were not applied to this combination of active ingredient and surface. 'F' is the field experiment.

Note that in some cases (experiments 53, 54, 63, 64, 74) the recoveries are very low (Table 14b). In these cases, more pesticide may have volatilized than is indicated by the diagram.

ID	Air T	emperatur	e (°C)	Rel.	Humidity	(%)	Win	nd Speed (1	n/s)
#	Min.	Max.	Ø	Min.	Max.	Ø	Min.	Max.	Ø
6	20.2	21.3	20.5	40.8	43.2	41.7	0.96	0.98	0.97
11	20.2	21.3	20.5	39.8	42.5	41.2	0.97	0.99	0.98
24	19.9	21.5	19.8	41.1	55.6	45.5	1.04	1.14	1.08
25	19.6	21.4	19.9	47.0	52.5	51.6	1.01	1.1	1.07
42	18.0	20.0	19.0	32.0	41.0	37.0	1.41	1.48	1.43
43	19.0	21.0	19.0	42.0	52.0	48.0	1.21	1.46	1.41
45	20.0	21.0	20.0	23.0	29.0	25.0	1.34	1.47	1.36
53	20.0	24.0	22.0	n. d.	n. <b>d</b> .	n. d.	1.0	2.0	1.5
54	20.0	24.0	22.0	n. d.	n. d.	n. d.	1.0	2.0	1.5
63	22.0	24.0	23.0	32.0	42.0	37.0	1.0	2.0	1.5
64	23.0	25.0	24.0	27.0	35.0	31.0	1.0	2.0	1.5
72	12.4	33.0	19.5	23.0	81.7	49.3	1.0	2.0	1.6
73	12.7	22.0	17.3	33.0	53,6	44.3	0.9	1.1	1.0
74	18.1	22.1	19.3	26.5	33.9	30.5	0.9	1.1	1.0
79	19.1	21.0	19.7	43.0	51.0	47.0	0.97	1.07	1.0
81	21.0	22.0	21.5	56,0	69,0	62.5	1.0	1.0	1.0
82	22.0	22.0	22.0	48.0	59.0	53.0	1.0	1.0	1.0
85	17.9	31.9	24.8	57.0	96.0	75.5	1.0	1.0	1.0
86	11.7	21.4	17.3	36.9	69.3	53.2	0.9	1.0	1.0
94	11.7	19.7	15.7	45.8	96.5	70.4	0.0	2.1	0.9
96	13.3	24.8	22.2	42.9	91.5	72.0	0.0	2.3	1.3
98	17.7	22.8	19.3	41.2	62.6	56.1	0.44	2.18	1.41
101	17.8	20.8	19.0	43.7	58.2	51.1	0.65	2.04	1.45
F	10.9	23.5	17.6	60.3	96.1	76.6	1.08	3.50	2.24

Table 14a: Climatic Parameters (active ingredient B /plant surfaces)

.

\_

Table 14b: Additional Information (active ingredient B / plant surfaces)
Recovery is only given where applicable, that is, for methods in which air is sampled. Details on time span
between application and start of experiment have been classified into three groups: 'np to 5 min'. '5 to 10 min'.
and 'more than 10 min'.

т	Active	Volume applied	Time Span between		
#	(g ha <sup>-1</sup> )	(I ha <sup>-1</sup> )	Experiment	Plants per m <sup>2</sup>	Recovery <sup>a)</sup> (%)
6	640	200.0	5 to 10 min	40	n. r.
11	880	200.0	5 to 10 min	40	n. r.
24	750	400.0	5 to 10 min	28	109.8
25	750	400.0	5 to 10 min	28	93.8
42	493	300.0	more than 10 min	n. r.	n. r.
43	585	300.0	more than 10 min	n. r.	n. r.
45	432	300.0	more than 10 min	n. r.	n. r.
53	431	144.0	up to 5 min	50	84.1
54	308	111.0	up to 5 min	50	82.3
63	662	220.0	up to 5 min	50	80.4
64	618	207.6	up to 5 min	50	80.6
72	663	255.0	more than 10 min	п. г.	n. r.
73	750	400.0	5 to 10 min	300	93.7
74	750	400.0	5 to 10 min	300	84.2
79	750	400.0	up to 5 min	90	89.9
81	750	440.0	5 to 10 min	п. г.	105.0
82	750	440.0	5 to 10 min	n. r.	92.3
85	750	450.0	5 to 10 min	90	96.5
86	750	450.0	5 to 10 min	90	98.4
94	700	320.0	up to 5 min	280	n. r.
96	750	320.0	up to 5 min	280	п. г.
98	750	400.0	up to 5 min	n, r.	n. r.
101	750	400.0	up to 5 min	n. r.	<b>n</b> . r.
F	741	296.3	more than 10 min	n. d.	n. r.

n. r.: not relevant

n. d.: no data available

a) Recovery rates have been calculated by the database and are deliberately given with one digit following the decimal point. This accuracy may not reflect author's intentions.



#### Active Ingredient B / Soil Surfaces



There is considerable variation among results from different methods for assessing the volatilization of active ingredient B from soil surfaces. However, in addition to the problems with active ingredient B in general, soil pH might be another cause for that variation. The SLF-results (ID numbers 21 - 23) from experiments carried out with different values for soil pH suggest that in this case there is a strong dependency of volatilization on that parameter. That assumption is also supported by the chemical nature of active ingredient B.

Results of experiments with active ingredient B exhibited a far greater variation among different methods than did the results of active ingredient A experiments. Some possible reasons for that have been discussed above.

D	Air T	emperatur	e (°C)	Rel	Rel. Humidity (%)		Wind Speed (m/s)		
#	Min.	Max.	Ø	Min.	Max.	Ø	Min.	Max.	Ø
15	17.8	19.9	18.4	50.5	58.0	53.2	0.51	0.58	0.55
16	17.9	19.3	18.6	50.7	58,2	52.9	0.51	0.58	0.55
17	17.9	19.4	18.4	51.0	56.2	53.0	0.51	0.58	0.55
21	19.9	21.5	20.0	44.6	52.2	49.3	1.16	1.29	1.22
22	19.7	21.4	20.0	44.7	53.1	50.6	1.21	1.33	1.24
23	19.6	21.4	20.0	49.2	56.7	53.4	1.11	1.25	1.21
32	20.0	22.2	21.8	33.1	41.0	36.0	1.1	1.5	1.3
33	20.6	21.5	21.0	33.8	36.8	35.4	1.0	1.4	1.2
37	20.3	21.8	21.2	46.5	52,4	48.3	0.5	1.4	1.02
40	20.0	24.0	21.0	54.0	67.0	59.0	1.08	1.38	1.28
41	19.0	20.0	20.0	31.0	37.0	33.0	1.2	1.49	1.25
51	21.0	24.0	22.5	n. d.	n. d.	n. d.	1.0	2.0	1.5
52	20.0	24.0	22.0	n. d.	n. d.	n. d.	1.0	2.0	1.5
61	21.0	23.0	22.0	52.0	57.0	54.5	1.0	2.0	1.5
62	21.0	23.0	22.0	51.0	54.0	52.5	1.0	2.0	1.5
70	16.3	21.6	19.6	40.4	60.0	46.4	1.3	1.5	1.4
77	19.2	21.3	19.8	40.0	46.0	44.0	0,95	1.11	1.0
78	19.4	21.4	20.1	40.0	46.0	45.0	0.93	1.11	1.0
83	21.0	22.0	21.5	74.0	82.0	78.0	1.0	1.0	1.0
84	20.0	22.0	21.0	82.0	90.0	86.0	1.0	1.0	1.0

Table 15a: Climatic Parameters (active ingredient B / soil surfaces)

n. d.: no data available

## Table 15b: Climatic Parameters, continued (active ingredient B / soil surfaces)

D	Soil	Soil Temperature (°C)			Soil Moisture (% MWC)			
#	Min	Max	Ø	Min	Max	Ø		
15	16.9	19.8	17.4	16.6	31.2	21.0		
16	17.0	19.5	17.2	32.7	50,9	41.6		
17	17.1	19.6	17.2	35.7	51.4	44.5		
21	n. <b>d</b> .	n. d.	n. d.	38.0	50.0	n. <b>d</b> .		
22	n. <b>d</b> .	n. <b>d</b> .	n. d.	43.0	50.0	n. <b>d</b> .		
23	n. d.	n. d.	n. d.	42.0	50.0	n. <b>d</b> .		
32	17.3	19.4	19.1	60.0	86.1	73.1		
33	17.9	18.6	18.3	51.0	60.0	55.0		
37	17.4	24.3	18.7	n. d.	n. d.	60.0		
40	17.0	19.0	18.0	n. d.	n. d.	61.5		
41	15.0	15.0	15.0	n. d.	n. d.	59.2		
51	n. <b>d</b> .	n. <b>d</b> .	n. d.	58.0	59.0	58.5		
52	n. <b>d</b> .	n. d.	n. d.	57.0	59.0	58.0		
61	n. <b>d</b> .	n. <b>d.</b>	n. d.	58.0	60.0	59.0		
62	n. <b>d</b> .	n. d.	n. d.	59.0	60.0	59.5		
70	n. d.	n. d.	n. d.	59.36	61.68	60,33		
77	n. d.	n. d.	17.0	58.0	60.0	n. d.		
78	n. d.	n. d.	16.8	60.0	61.0	n. <b>d</b> .		
83	n. d.	n. d.	n. d.	59.0	60.0	59.5		
84	n. d.	n. <b>d</b> .	n. d.	58.0	63.0	60.5		

n. d.: no data available

<b>Table 15c: Additional Information</b>	(active ingredient B / soil surfaces)
--	---------------------------------------

Recovery is only given where applicable, that is, for methods in which air is sampled. Details on time span between application and start of experiment have been classified into three groups: 'up to 5 min'. '5 to 10min' and 'more than 10 min'.

	Active		Time Span between	
ID	Ingredient applied	Volume applied	Application & Start of	,
#	$(g ha^{-1})$	<u>(i ha <sup>-1</sup>)</u>	Experiment	Recovery <sup>11</sup> (%)
15	449.0	450	up to 5 min	97.7
16	817.7	450	up to 5 min	98.5
17	695.8	450	up to 5 min	95.1
21	750.0	400	up to 5 min	102.4
22	750.0	400	5 to 10 min	105.2
23	750,0	400	up to 5 min	98.6
32	598.0	500	up to 5 nún	101.2
33	795.0	500	up to 5 min	99.0
37	750.0	594	5 to 10 min	п. г.
40	411.0	300	more than 10 min	n. r.
41	479.0	500	more than 10 min	п. г.
51	630.0	255	up to 5 min	98.2
52	715.0	271	up to 5 min	93.6
61	992.0	428	up to 5 min	95.9
62	1300.0	505	up to 5 min	100.9
70	765.0	271	up to 5 min	<b>n</b> . r.
77	750.0	400	up to 5 min	97.9
78	750.0	400	up to 5 min	91.2
83	750.0	440	5 to 10 min	101.9
84	750.0	440	5 to 10 min	101.6

n. r.: not relevant

u. d.: no data available

 a) Recovery rates have been calculated by the database and are deliberately given with one digit following the decimal point. This accuracy may not reflect author's intentions.

## Active Ingredient C

Active ingredient C may be degraded to some extent within a couple of hours, yielding two known degradation products. Since for this study a radiolabeled form of active ingredient C was used, that fact is only of minor importance because the degradation products should be detected as well as the original substance. However, in this way volatilization of the degradation products may be mistaken for volatilization of the active ingredient.



## Active Ingredient C / Plant Surfaces



Results from experiments assessing volatilization of active ingredient C from plant surfaces exhibited considerable variation among values obtained with the same method as well as among values from different methods. However, all results showed volatilization to be more than the crucial 20% within 24 hours after application and would be treated alike within the registration process.

ID	Air T	emperature	e (°C)	Rel	Humidity	(%)	Wi	nd Speed (r	n/s)
#	Min.	Max.	Ø	Min.	Max.	Ø	Min.	Max.	Ø
28	18.3	21.7	19.9	50.4	56.0	51.2	1.06	1.17	1.09
29	19.8	20.3	19.9	50.7	52.3	51.2	1.05	1.12	1.08
48	18.0	20.0	19.0	32.0	41.0	37.0	1.41	1.48	1.43
49	19.0	21.0	19.0	42.0	52.0	48.0	1.21	1.46	1.41
50	19.0	21.0	20.0	38.0	44.0	41.0	1.24	1.47	1.29
57	26.0	30.0	28.0	n. d.	n. d.	n. <b>d</b> .	1.0	2.0	1.5
58	21.0	27.0	24.0	n. d.	n. d.	n. <b>d</b> .	1.0	2.0	1.5
67	27.0	35.0	31.0	36.0	58.0	47.0	1.0	2.0	1.5
68	24.0	30.0	27.0	33.0	38.0	35.5	1.0	2.0	1.5
75	17.3	19.9	18.5	15.6	37.5	23.2	0.9	1.1	1.0
76	19,0	21.0	20.0	n. d.	n. d.	40.0	0.9	1.1	1.0
87	9.3	17.6	12.3	71.0	99.0	89.0	1.0	1.2	1.1
88	18.8	32.4	26.9	33.7	83.1	54.5	1.0	1.0	1.0
90	19.1	31.3	25.7	31.1	78.0	48.6	0.0	2.2	1.0
92	19.6	30.9	27.1	28.6	86.6	49.6	0.0	2,6	1.1
99	15.7	22.7	20.6	36.9	56.0	48.3	0.2	2.6	1.1
100	17.6	25.1	20.5	35.9	57.2	50.3	0.2	1.3	1.2
104	21.0	22.0	21.2	34.0	38.5	37.0	n. d.	п. <b>d</b> .	1.0
105	20.8	21.4	21.0	29.0	33.5	30.5	n. <b>d</b> .	п. <b>d</b> .	1.0
106	20.0	21.4	20.2	32.5	37.5	35.0	n. d.	n. d.	1.0
109	19.4	20.5	20.1	43.0	49.0	47.0	0.93	1.07	1.1

Table 16a: Climatic Parameters (active ingredient C / plant surfaces)

n. d.: no data available

#### Table 16b: Additional Information (active ingredient C / plant surfaces)

Recovery is only given where applicable, that is, for methods in which air is sampled. Details on time span between application and start of experiment have been classified into three groups: 'up to 5 min', '5 to 10 min', and 'more than 10 min'.

	Active	Volume	Time Span between		
ID	Ingredient applied	applied	Application & Start of	_	
#	(g ha <sup>-1</sup> )	(l ha <sup>-1</sup> )	Experiment	Plants per m <sup>2</sup>	Recovery <sup>a)</sup> (%)
28	200.0	400	5 to 10 min	28	93.4
29	200.0	400	5 to 10 min	28	93.9
48	243.0	300	more than 10 min	n. r.	п. г.
49	254.0	300	more than 10 min	n. r.	п. г.
50	193.0	400	more than 10 min	п. г.	n. r.
57	60.0	174	up to 5 min	50	92.4
58	104.0	261	up to 5 min	50	77.4
67	100.0	260	up to 5 min	50	78.7
68	74.1	200	up to 5 min	50	99.1
75	200.0	400	5 to 10 min	300	109.2
76	200.0 ·	400	5 to 10 min	300	91.1
87	200.0	450	5 to 10 min	90	99.0
88	200.0	450	5 to 10 min	90	99.6
90	200.0	320	up to 5 min	280	n. r.
92	200.0	320	up to 5 min	280	<b>n</b> . r.
99	200.0	400	up to 5 min	п. г.	п. г.
100	200.0	400	up to 5 min	п. г.	п. г.
104	200.0	400	up to 5 min	п. г.	100.4
105	200.0	400	up to 5 min	n. r.	99.7
106	200.0	400	up to 5 min	n. r.	92.5
109	200.0	400	up to 5 min	90	90.9

n. r.: not relevant, n. d.: no data available; a) Recovery rates have been calculated by the database and are deliberately given with one digit following the decimal point. This accuracy may not reflect author's intentions.



#### Active Ingredient C / Soil Surfaces



Less volatilization of active ingredient C occurs from soil surfaces than from plant surfaces. However, like the results from the plant experiments, results from the soil experiments exhibit a considerable variation. With respect to the registration guideline, the results presented in Figure 12 are problematic, some of them are below the 20%-trigger-value, some are higher than that. With respect to the trigger-value, there is no difference in assessing volatilization via air sampling and via soil sampling.

Active ingredient C exhibited the highest volatility of the substances tested in this study. Among the results of plant as well as soil experiments considerable amount of variation occurred among the methods compared. For this substance, however, there also is a notable amount of variation among the results obtained with the same method, especially in the plant experiments.

D	Air Temperature (°C)		re (°C)	Rel. Humidity (%)			Wind Speed (m/s)		
#	Min.	Max.	Ø	Min.	Max.	Ø	Min.	Max.	Ø
18	16.8	20.4	18.7	48.6	55.8	52.8	0.55	0.6	0.57
19	17.6	19.5	18.3	51.0	58.5	53.3	0.55	0.6	0.57
20	17.5	19.6	18.4	51.0	56.2	53.0	0.55	0.6	0.57
26	18.6	21.1	19.9	50.6	54.7	51.5	1.19	1.28	1.22
27	19.6	21.4	20.0	47.5	52.9	51.9	1.17	1.32	1.24
30	22.2	26.3	24.3	27.6	47.5	32.4	0.9	1.4	1.2
31	21.6	22.6	22.2	38.1	40.8	39.41	1.0	1.2	1.1
36	20.1	22.3	20.8	47.9	62.2	52.8	0.5	1.5	1.34
46	17.0	22.0	20.0	50.0	66.0	56.0	1.26	1.37	1.33
47	19.0	20.0	20.0	31.0	37.0	33.0	1.2	1.49	1.25
55	20.0	23.0	21.5	n. d.	n. d.	n. <b>d</b> .	1.0	2.0	1.5
56	20.0	24.0	22.0	n. d.	n. <b>d</b> .	n. <b>d</b> .	1.0	2.0	1.5
65	19.0	21.0	20.0	44.0	58.0	51.0	1.0	2.0	1.5
66	20,0	24.0	22.0	n. d.	n. d.	n. <b>d</b> .	1.0	2.0	1.5
102	21.2	22.4	21.6	32.0	34.0	33.0	n. d.	n. d.	1.0
103	20,8	21.6	21.0	33.5	36,0	34.5	n. d.	n. d.	1.0
108	18.2	21.5	20.1	31.0	47.0	44.0	0,96	1.06	1.0

Table 17a: Climatic Parameters (active ingredient C / soil surfaces)

n. d.: no data available

Table 17b: Climatic Parameters, continu	ed (active ingredient C / soil surfaces)
---	--

ID	Soi	I Temperature	(°C)	Soil	Moisture (% M	WC)
#	Min	Max	Ø	Min	Max	Ø
18	16.1	19.7	17.4	43.0	54.7	48.5
19	16.9	18.6	17.2	39.3	51.2	43.7
20	16.6	19.5	17.2	38.7	49.7	44.5
26	n. d.	n. d.	n. d.	30.0	50.0	n. d.
27	n. d.	n. d.	n. d.	32.0	50.0	n. <b>d</b> .
30	19.5	24.6	22.1	49.2	60.0	54.6
31	18.3	19.1	18.7	60.0	73.1	66.6
36	15.7	22.1	18.1	n. d.	n. d.	60.0
46	14.0	19.0	17.0	n. d.	n. d.	62.3
47	15.0	15.0	15.0	n. d.	n. d.	59.2
55	n. d.	n. d.	n. d.	59.0	61.0	60.0
56	n. d.	n. d.	n. d.	57.0	60.0	58.5
65	n. d.	n. d.	n. d.	60.0	61.0	60.5
66	n. d.	n. d.	n. d.	59.0	61.0	60.0
102	n. d.	n. d.	n. d.	n. d.	n. <b>d</b> .	n. d.
103	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
108	n. d.	n. d.	17.1	60.0	62.0	n. d.

n. d.: no data available

Table 17c: Additional Information (active ingredient C / soil surfaces) Recovery is only given where applicable, that is, for methods in which air is sampled. Details on time span between application and start of experiment have been classified into three groups: 'up to 5 min', '5 to 10 min', and 'more than 10 min'.

	Active		Time Span between	
D	Ingredient applied	Volume applied	Application & Start of	Recovery <sup>a)</sup> (%)
#	(g ha ')	(l ha <sup>-1</sup> )	Experiment	
18	220.9	450	up to 5 min	101.4
19	176.5	450	up to 5 min	94.2
20	181.0	450	up to 5 min	98.6
26	200.0	400	5 to 10 min	101.6
27	200.0	400	up to 5 min	99.0
30	135.0	500	up to 5 min	95.1
31	363.0	500	up to 5 min	106.2
36	200.0	390	5 to 10 min	n. r.
46	140.0	300	more than 10 min	п. г.
47	228.0	500	more than 10 min	п. г.
55	175.0	144	up to 5 min	99.4
56	171.0	141	up to 5 min	92.7
65	331.0	309	up to 5 min	101.3
66	323.0	301	np to 5 min	85.4
102	195.7	400	up to 5 min	95.4
103	196.4	400	up to 5 min	96.7
108	200.0	400	up to 5 min	95.1

n. r.: not relevant

n. d.: no data available

a) Recovery rates have been calculated by the database and are deliberately given with one digit following the decimal point. This accuracy may not reflect author's intentions.

## Overall Comparison of Results in Relation to the German Guideline

- In the case of active ingredient A, variation among results from different methods seemed to be of no importance. With every method applied, the volatility was assessed to be extremely low, with less than 10% volatilization within 24 hours of application, regardless whether plant or soil surfaces were involved. In spite of its Henry's Law constant, active ingredient A volatilized considerably less than the other two compounds.
- In the case of active ingredient B, there was considerable variation among the results obtained with different methods. For plant experiments conducted with the laboratory methods, with respect to the guideline's trigger-value no differences between the methods were observed. Some experiments yielding low estimates of volatilization in this category showed poor recoveries, suggesting a problem with analysis of air samples. This may be accounted for by the low radiochemical purity of the test substance used. The field experiment yielded a clearly lower volatilization rate than the other experiments. Possible reasons for this difference are discussed above, it is to be investigated further. For soil experiments, differences with respect to the guideline's trigger value occur. However, the trigger value in no case is exceeded very far. Strong dependence of volatilization on soil pH may provide an explanation for variation of results in this case.

- In the case of active ingredient C plant experiments, variation among results from different methods didn't exceed variation among results obtained with the same method. With the exception of one single method, all the experiments compared yielded results between 50% and 90% volatilization within 24 hours after application, thus clearly exceeding the guideline's trigger-value. In the case of *soil experiments*, the situation is similar to that of active ingredient B. The volatility of active ingredient C was assessed to be high compared with that of the other two substances.
- With respect to the guideline and the *registration procedure* in Germany, all the methods compared here seem to be suitable, even if considerable variation among the results obtained with them occurs.
- In the frame of this report it is not possible to evaluate the influences of *climatic and other parameters* on the results. The main difficulty associated with an evaluation like that is the heterogeneity of the data available. However, the reader is encouraged to take a close look at the tables provided in order to gain more insight into possible causes of variation in results. A detailed analysis of the data gained in the interlab comparison will be performed and published later.
- From the scientific point of view, the interlaboratory comparison once more made it obvious that the problems of assessing pesticide volatilization have not been solved yet, and that great care has to be taken when comparing volatilization rates assessed with different methods.

## SUMMARY

The main objective of the interlaboratory comparison presented in this report was to see whether different methods of assessing volatilization of pesticides yield comparable results. For this purpose, experiments employing 18 laboratory and one field method were conducted. Three active ingredients were used as test substances, with French Bean and sandy soil as test substrates. The test substances had been selected so as to provide examples for different volatility. The active ingredients were <sup>14</sup>C-radiolabeled.

The methods compared in this study are described in tabular form, references for more details on methods are given.

Experiments were conducted and results were evaluated in view of the German guideline for assessing the volatilization of pesticides [22]. The results presented in this report include volatilization kinetics, volatilization within 24 hours after application, and information on climatic and other parameters potentially affecting volatilization.

With all three substances tested, a considerable amount of variation among results obtained with the different methods was observed. In the described cases the differences were not considered to be important with respect to the trigger value required by the guideline. However, with other substances or a different trigger value another conclusion might be reached.

The considerable amount of data available in the comparison provides further scope for statistical examination of the variables involved.

#### REFERENCES

[1] S. P. Parker, "McGraw-Hill Dictionary of Physics," New York: McGraw-Hill Book Company, 1984.

[2] W. F. Spencer, W. J. Farmer, and M. M. Cliath, "Pesticide volatilization," *Residue Reviews*, vol. 49, pp. 1-47, 1973.

[3] G. S. Hartley, "Evaporation of Pesticides," Pesticidal Formulations Research - Physical and Colloidal Chemical Abstracts, Miami Beach, Florida, USA, 1969.

[4] J. R. Plimmer, "Volatility," in *Herbicides - Chemistry, Degradation and Mode of Action*, vol. 2, P. C. Kearney and D. D. Kaufman, Eds., 2 ed. New York, Basel: Marcel Dekker, Inc., 1976, pp. 891-933.

[5] H. R. Buser, "Atrazine and Other s-Triazine Herbicides in Lakes and in Rain in Switzerland." *Environmental Science & Technology*, vol. 24, pp. 1049-1058, 1990.

[6] B. Gath, W. Jaeschke, I. Ricker, and E. Zietz, "Depositionsmonitoring von Pflanzenschutzmitteln auf dem Kleinen Feldberg. Erste Ergebnisse," *Nachrichtenblatt des Deutschen Pflanzenschutzdienstes*, vol. 44, pp. 57-66, 1992.

[7] B. Gath, W. Jaeschke, R. Kubiak, I. Ricker, F. Schmider, and E. Zietz, "Depositionsmonitoring von Pflanzenschutzmitteln: Teil 2 Süddeutscher Raum," *Nachrichtenblatt des Deutschen Pflanzenschutzdienstes*, vol. 45, pp. 134-143, 1993.

[8] J. Siebers, D. Gottschild, and H.-G. Nolting, "Pesticides in Precipitation in Northern Germany,", vol. 28, pp. 1559-1570, 1994.

[9] D. E. Glotfelty, M. S. Majewsky, and J. N. Seiber, "Distribution of Several Organophosphorus Insecticides and Their Oxygen Analogues in a Foggy Atmosphere," *Environmental Science & Technology*, vol. 24, pp. 353-357, 1990.

 [10] C. J. Schomburg, D. E. Glotfelty, and J. N. Seiber, "Pesticide Occurence and Distribution in Fog Collected near Monterey, California," *Environmental Science & Technology*, vol. 25, pp. 155-160, 1991.

[11] B. K. Nations and G. R. Hallberg, "Pesticides in Iowa Precipitation," *Journal of Environmental Quality*, vol. 21, pp. 486-492, 1992.

[12] J. Scharf and K. Bächmann, "Verteilung von Pflanzenschutzmitteln in der Atmosphäre. Nahund Ferntransportmessungen," *Nachrichtenblatt des Deutschen Pflanzenschutzdienstes*, vol. 45, pp. 82-87, 1993.

[13] H.-G. Nolting, A. Boehnke, and W. Storzer, "Zum Eintrag, Verhalten und Verbleib von Pflanzenschutzmitteln in Luft," Biologische Bundesanstalt für Land- und Forstwirtschaft, Abteilung für Pflanzenschutzmittel und Anwendungstechnik, Braunschweig, Literaturstudie 1988.

[14] D. Gottschild, J. Siebers, and H.-G. Nolting, *The volatilization and deposition of plant protection products*. Strasbourg Cedex: Publishing and Documentation Service council of Europe, 1995.

[15] G. Krasel and W. Pestemer, "Pflanzenschutzmittel-Verflüchtigung von Oberflächen," Proceedings of the 8th EWRS Symposium "Quantitative approaches in weed and herbicide research and their practical application", Braunschweig, pp. 399-406, 1993.

[16] A. Boehnke, J. Siebers, and H.-G. Nolting, "Investigation of the Evaporation of Selected Pesticides from Natural an Model Surfaces in Field and Laboratory," *Chemosphere*, vol. 21, pp. 1109-1124, 1990.

[17] C. Chen, R. E. Green, D. E. Thomas, and J. A. Knuteson, "Modeling 1,3-Dichloropropene Funigant Volatilization with Vapor-Phase Advection in the Soil Profile," *Environmental Science* & *Technology*, vol. 29, pp. 1816-1821, 1995.

[18] B. Lindhardt, T. H. Christensen, and A. Brun, "Volatilisation of *o*-Xylene from Sandy Soil.," *Chemosphere*, vol. 29, pp. 2625-2637, 1994.

[19] B. Lindhardt and T. H. Christensen, "Measured and Estimated Volatilisation of Naphthalene from a Sandy Soil," *Chemosphere*, vol. 29, pp. 1407-1419, 1994.

[20] R. Mayer, J. Letey, and W. J. Farmer, "Models for Predicting Volatilization of Soil-Incorporated Pesticides," *Soil Science Society of America: Proceedings*, vol. 38, pp. 563-568, 1974.

[21] W. A. Jury, R. Grover, W. F. Spencer, and W. J. Farmer, "Modeling vapor losses of soilincorporated triallate.," *Soil Science Society of America: Proceedings*, vol. 44, pp. 445-450, 1980.

[22] H.-G. Nolting, J. Siebers, W. Storzer, A. Wilkening, M. Herrmann, and C. Schlüter, "Teil IV 6-1 Prüfung des Verflüchtigungsverhaltens und des Verbleibs von Pflanzenschutzmitteln in der Luft." in *Richtlinien für die Prüfung von Pflanzenschutzmitteln im Zulassungsverfahren*, Abteilung für Pflanzenschutzmittel und Anwendungstechnik der Biologischen Bundesanstalt Braunschweig, Ed. Ribbesbüttel: Saphir-Verlag, 1990.

[23] A. Boehnke, J. Siebers, and H.-G. Nolting, "Verbleib von Pflanzenschutzmitteln in der Umwelt- Exposition, Bioakkumulation, Abbau - Teil B," Biologische Bundesanstalt für Land- und Forstwirtschaft, Braunschweig, Forschungsbericht im Auftrag des Umweltbundesamtes UFOPLAN - Nr. 89-12605008/02, 1989.

[24] I. Scheunert and U. Dörfler, "Verbleib von Pflanzenschutzmitteln in der Umwelt - Exposition, Bioakkumulation, Abbau - Teil A," Gesellschaft für Strahlen- und Umweltforschung mbH, München, Forschungsbericht im Auftrag des Umweltbundesamtes UFOPLAN-Nr. 10609008/01, 1989.

[25] U. Dörfler, R. Adler-Köhler, P. Schneider, I. Scheunert, and F. Korte, "A Laboratory Model
 System for Determining the Volatility of Pesticides from Soil and Plant Surfaces," *Chemosphere*, vol. 23, pp. 485-496, 1991.

[26] G. Krasel, G. Maas, and W. Pestemer, "Versuchsapparatur zur Messung der Verflüchtigung von Pflanzenschutzmitteln von Oberflächen," *Nachrichtenblatt des Deutschen Pflanzenschutzdienstes*, vol. 44, pp. 1-5, 1992.

[27] A. Deas, M. J. Phillips, G. N. Jackson, and D. Moore-Vale, "Laboratory-scale Apparatus for the Study of Pesticide Volatility from Soil and Plant Surfaces," Proceedings of the Brighton Crop Protection Conference - Pests and Diseases, Brighton, pp. 847-853, 1992.

[28] R. Fritz, "Pflanzenschutzmittel in der Atmosphäre," *Pflanzenschutz-Nachrichten Bayer*, vol. 46, pp. 229-264, 1993.

[29] P. Sandmeier, "Volatilization of C 570 (Phosphamidon) from Bean Leaves under Indoor Conditions after Spray Application of 14C labelled Material," CIBA GEIGY Ltd., Basle, Metabolism Report 14/93, June 16 1993.

[30] H. Ruedel and B. Waymann, "Volatility Testing of Pesticides in a Wind Tunnel," Proceedings of the Brighton Crop Protection Conference- Pests and Diseases, Brighton, pp. 841-846, 1992.

[31] D. Lembrich, "Charakterisierung von Boden- und Umweltparametern als Einflußgrößen auf die Volatilität von Pflanzenschutzmitteln aus Ackerböden anhand eines Labormodells," München: Technische Universität, 1996 (in press).

[32] A. Stork, "Windkanalanlage zur Bestimmung gasförmiger Verluste von Umweltchemikalien aus dem System Boden/Pflanze unter praxisgerechten Bedingungen mit direkten luftanalytischen Methoden unter Nutzung der <sup>14</sup>C-Tracertechnik," Landwirtschaftliche Fakultät.der Universität Bonn:. 1995, pp. 402.

[33] A. Stork, R. Witte, and F. Führ, "A Wind Tunnel for Measuring the Gaseous Losses of Environmental Chemicals from the Soil/Plant System under Field-Like conditions." *Environmental Science & Pollution Research*, vol. 1, pp. 234-245, 1994.

[34] H.-D. Haenel, and J. Siebers, "Lindane volatilization under field conditions: Estimation from residue disappearances and concentration measurements in air," *Agircultural and Forest Meteorology*, vol. 76, pp. 237-257, 1995.

[35] K. Figge, J. Klahn, and J. Koch, "Testing of Chemicals by Evaluation of Their Distribution and Degradation Patterns in an Environmental Standard System," *Regulatory Toxicology and Pharmacology*, vol. 3, pp. 199-215, 1983.

[36] K. Figge, J. Klahn, and J. Koch, *Chemische Stoffe in Ökosystemen*, Stuttgart, New York: Gustav Fischer Verlag, 1985.

[37] S. Hausmann, "Methodenentwicklung zur Untersuchung des Verflüchtigungsverhaltens von Pflanzenschutzmitteln von Boden- und Pflanzenoberflächen im Modellversuch," Diploma thesis (Diplomarbeit) Fachbereich Chemie der Fachhochschule Reutlingen: 1995.

[38] M. Maestracci, P. Adrian, N. Jendrzejczak, and G. Turier, "A Laboratory System for Measuring the Volatilization of Pesticides from Soil," presented at the Eighth IUPAC International Congress of Pesticide Chemistry, Washington, DC (USA), 1994.

[39] R. Kubiak, T. Maurer, and K. W. Eichhorn, "A new laboratory model for studying the volatilization of pesticides under controlled conditions," *The Science of the Total Environment*, vol. 132, pp. 115-123, 1993.

[40] J. Heath, A. Ahmad, and J. P. Leahey, "A simple procedure to measure the volatility of agrochemicals from soil and leaf surfaces," Proceedings of the Brighton Crop Protection Conference - Pests and Diseases, Brighton, pp. 835-840, 1992.

## ACKNOWLEDGEMENTS

The authors thank R. Campana for his extensive help with the design and use of the Access database, and P. Lipow for proof-reading the manuscript and valuable suggestions for improvement.

Die Berichte aus der Biologischen Bundesanstalt für Land- und Forstwirtschaft erscheinen seit 1995 in zwangloser Folge.

Bisher erschienene Berichte:

Heft 1, 1995	Sachverständigengutachten zur Genehmigung von Weihnachtsbaumkulturen (in Landschaftsschutzgebieten) unter Berücksichtigung von Herbizideinsätzen bzw. mechanischen oder kulturtechnischen Verfahren zur Unkrautbekämpfung und deren Folgewirkungen au den Naturhaushalt. Dr. Gerd Heidler 100 S.
Heft 2, 1995:	Liste der zugelassenen Pflanzenschutzmittel (Stand: 1.Januar 1995). Bearbeitet von Dr. Achim Holzmann und Andreas Spinti, 63 S.
Heft 3, 1995:	Rechtliche Regelungen der Europäischen Union zur Prüfung und Zulassung von Pflanzenschutzmitteln und Wirkstoffen (Richtlinien, Verordnungen, Entscheidungen und Protokolle) (Stand: 1. Juni 1995). Bearbeitet von Dr. Jörg-Rainer Lundehn, 233 S.
Heft 4, 1995:	Verzeichnis der Wirkstoffe in zugelassenen Pflanzenschutzmitteln (ehemals Merkblatt Nr. 20) (Stand: November 1994). Bearbeitet von Dr. Günter Hoffmann, 86 S.
Heft 5, 1995:	Spritz- und Sprühgeräte für Flächenkulturen Auszug aus der BESCHREIBENDEN PFLANZENSCHUTZLISTE -Teil Geräte Bearbeitet von DrIng. Heinz Ganzelmeier, Sabine Gebauer,
	Hans-Joachim Wehmann und Siegfried Rietz, 170 S.
Heft 6, 1995:	Information Exchange and Prior Informed Consent (PIC) Procedure in the Export and Import of Pesticides in the Framework of the FAO Code of Conduct. Bearbeitet von Dr. Achim Holzmann, 111 S.
Heft 7, 1995:	Workshop Integrated Pest Management November 2nd 1995, Kleinmachnow. Bearbeitet von Dr. Holger Beer, 39 S.
Heft 8, 1995:	Art und Menge der in der Bundesrepublik Deutschland abgegebenen und der ex- portierten Wirkstoffe in Pflanzenschutzmitteln (1987-1994) Ergebnisse aus dem Meldeverfahren nach § 19 des Pflanzenschutzgesetzes. Bearbeitet von Dr. Hans-Hermann Schmidt, Dr. Achim Holzmann und Edel- gard Adam, 65 S.
Heft 9, 1995:	Arbeitsschutz und Arbeitssicherheit im öffentlichen Dienst (Stand: Juni 1995). Dirk Altewein, 16 S.
Heft 10, 1996:	Zur Umsetzung biometrischer Verfahren in SAS mit Beispielen aus dem Pflanzenschutz. Eckard Moll, 185 S.
Heft 11, 1996:	Liste der zugelassenen Pflanzenschutzmittel (Stand: 1. Januar 1996) Bearbeitet von Dr. Achim Holzmann und Andreas Spinti, 63 S.
Heft 12, 1996:	Methodische Anleitung zur Bewertung der partiellen Resistenz und die SAS - Anwendung RESI. Eckart Moll, 60 S.
Heft 13, 1996:	Saatgutbehandlung von Getreide und Beschreibende Liste - Beizgeräte (Stand: Dezember 1995). Bearbeitet von Dr. Helmut Ehle, Dr. Günter Menschel, Dr. Wolfgang Radtke, Siegfried Rietz, Friedrich-Otto Ripke, 48 S. Die SAS-Anwendung FELD, VA-konstruktion des Lagenlages und der varianz-
Hell 14, 1990.	analytischen Auswertung ein- bis dreifaktorieller Feldversuche. Dr. Eckart Moll, 43 S.
Heft 15, 1996:	Dokumentation der Forschungsvorhaben - Forschungsaufgaben der BBA unter be- sonderer Berücksichtigung ihrer "Drittmittelforschung" - laufende Vorhaben der BBA, Stand Januar 1996. Dr. Holger Beer Dr. Heinrich Brammeier, 145 S.