# Recommendations for the experimental determination of volatilization-related deposition of pesticide active ingredients on non-target areas using outdoor wind tunnels

Dr. Ulrike Krug and Dr. Konstantin Kuppe, German Environment Agency Dr. Gunnar Fent, RLP AgroScience

#### 1. Introduction

According to Regulation (EU) No 283/2013 setting out the data requirements for active substances, in accordance with Regulation (EC) No 1107/2009 concerning the placing of plant protection products on the market, the transport of active substances and their volatile metabolites via air needs to be considered in the risk assessment of plant protection products and the EU approval of active substances. If the trigger for volatilization – a vapor pressure of  $\geq 10^{-5}$  Pa (from plant surfaces) or  $\geq 10^{-4}$  Pa (from soil surfaces) at a temperature of 20 °C – is exceeded and (drift) mitigation measures are required, data from confined experiments may be submitted. The type and conditions of the study to be performed shall be discussed with the national competent authorities. If needed, experiments to determine volatilization with subsequent deposition may be provided.

This document provides recommendations for conducting and assessing wind tunnel studies to quantify the volatilization with subsequent deposition of active substances and/or their metabolites.

The purpose of these recommendations is to provide a framework for the experimental conduct of outdoor wind tunnel trials to assess volatilization-induced deposition of substances on adjacent areas as a function of distance from the treated crop. The regulatory result is the volatilization-related deposition to non-target off-field areas as a percentage of the amount of active substances applied as a function of distance from the target area.

The results help to refine the calculated deposition values in the environmental fate models EVA (Exposure Via Air)<sup>[1]</sup> and e.g. SWAN (FOCUS Surface Water Step 4)<sup>[2]</sup> to derive more realistic volatilization/deposition (v/d)-related PEC values for adjacent aquatic or terrestrial non-target areas.

Outdoor wind tunnel trials are semi-field experiments that are independent from environmental parameters like precipitation and fluctuating wind speed and direction as basic requirement to investigate volatilization and subsequent deposition under realistic outdoor conditions. A fan unit produces a constant wind speed over the target and non-target areas during the study phase. In former versions of these recommendations<sup>[5]</sup>, also a test under open field conditions was described. However, due to the great variability of these parameters under field conditions the results of these experiments were hardly reproducible and consequently, this option is no longer supported.

The environmental factors like temperature and humidity of air & soil and solar radiation can lead to uncertainties in the validity of the test results of the wind tunnel trials. To account for these uncertainties, the experiments should be conducted with a reference substance (in a reference formulation) applied simultaneously with the active substance or product to be tested. In the past, lindane was used as a reference substance due to its high potential for volatilization and subsequent deposition. However, because of Lindane's hazardous environmental behaviour and ecotoxicological properties, we now recommend to use fenpropidin as reference substance.

## 2. Experimental design

## 2.1 Wind tunnel test system

## 2.1.1 Wind tunnel set up

The wind tunnel system has been described in detail in Fent  $(2004)^{[3]}$ . A typical wind tunnel consists of a semicircular film greenhouse with a length of 55 m, a width of 7 m and a height of 3 m. The film has a light transmission of 88 % (400 to 700 nm) and is impermeable for UV radiation (320 to 400 nm). The wind engine should be comprised of a sufficient number of fans to achieve a stable air flow of 2 m/s.

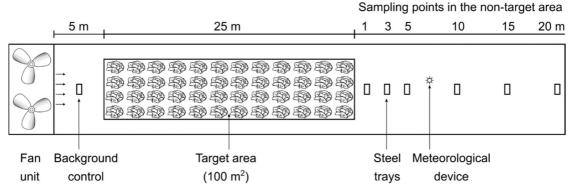
The wind tunnel is divided into three different sections (please refer to Figure 1):

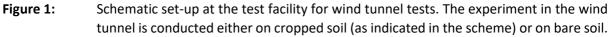
- a 5 m air equilibration zone between the fan and the treatment zone to obtain a roughly laminar airflow,
- a target area of 100 m<sup>2</sup> (25 m length and 4 m width) where the active substance/product to be tested is applied, and
- a non-target area (25 m length and 6 m width).

The non-target area covered with the natural weed vegetation at the site is mowed at regular intervals during the vegetation period (March to October). The vegetation of the non-target area is cut to a few centimeters just before the experiment.

Sampling points are located in the non-target area. For water measurements, stainless-steel trays with a surface area of 0.5 m<sup>2</sup> (1 m length, 0.5 m width and 0.12 m height) are set up 5 min after the beginning of the experiment (according to Fent, 2004) to avoid any contaminations due to spray drift (for details see point 2.5). These trays are positioned in the non-target area at 1, 3, 5, 10, 15 and 20 m downwind direction for sampling. A tray to quantify the background concentration is positioned between the fan unit and the target area with a 2.5 m distance from the fans.

The precise dimensions of the wind tunnel, the position of the stainless-steel trays and the weather station are to be reported.





In special cases, sensitive indicator plants can be placed in the downward direction at 1, 5, 10 and 20 m in the windtunnel to assess phytotoxic damages by exposure of volatilized test item (gaseous or deposited), e.g. bleaching effects of active substances due to v/d (like clomazone). In case of the use of indicator plants background plants are placed in upwind direction. Details on the test design should be specified in close consultation with the regulatory authorities.

### 2.1.2 Soil management

Wind tunnel experiments can be carried out on bare soil or cropped soil. The soil properties are more critical for the volatilization of the pesticides if the active substance or product is applied on bare soils. In this case, reporting the soil properties is of great importance. Sufficient soil moisture should be established by irrigation before the start of the experiment. Initial target value should be about 60 % of the maximum water holding capacity in the top 10 cm layer and decrease during the experimental period of 96 h should be monitored real-time by e.g. TDR probes. Application should be carried out when the soil surface layer is air-dried.

For experiments on cropped soil, freshly harvested lettuce plants<sup>[7]</sup> can be used as a model plant if the application-specific target crop is unavailable on time. It should be noted that the lettuce plants are harvested with roots and laid out, and applied as a target area in the wind tunnel at the latest 12 h after harvest. According to a worst-case approach, the lettuce plants need to cover 100 % of the soil of the treatment area (corresponding to 100 % interception). Photos and related image evaluation should document the degree of coverage.

## 2.2 Reference substance

Due to the high variability of meteorological factors, a stable, easily detectable, and semi-volatile substance with known volatilization/deposition behavior must be applied as a reference substance along with the substance to be tested. The active substance (a.s.) fenpropidin should be used for this purpose (for substance properties see Table 1 below). A specific product in a defined formulation that contains fenpropidin at a concentration of 750 g a.s./L should be used for the reference measurements (for substance properties, see Table 1 below). The product may be requested from RLP AgroScience GmbH (Germany) and should be applied at a dose rate that allows the analytical detection of fenpropidin residues in the samples.

During analysis of the experimental data of the wind tunnel study, the data obtained with the reference substance will be compared to reference datasets measured on cropped or bare soil (details are not part of the recommendations for the experimental procedure provided here).

IUPAC name	(R,S)-1-[3-(4-tert-butylphenyl)-2-methylpropyl]piperidine
CAS No.	67306-00-7
Structural formula	H <sub>3</sub> C H <sub>3</sub> C CH <sub>3</sub>
Molecular formula	C <sub>19</sub> H <sub>31</sub> N
Molecular weight	273.5 g/mol
Water solubility	530 mg/L at 25 °C
Melting point	-64.6 °C
Vapor pressure	1.7 × 10 <sup>-2</sup> Pa at 25 °C
Henry's law constant	10.7 Pa m <sup>3</sup> /mol
log Pow	2.9 at 25 °C
Hydrolysis	Stable under sterile aqueous hydrolysis conditions at 50 °C at pH 3, 7, 9
Photolysis	Stable to UV light under environmental irradiation

Table 1:	Physico-chemical parameters of fenpropidin (EFSA Scientific Report (2007) 124, 1-84).
----------	---

## 2.3 Meteorological conditions

Meteorological conditions are important parameters controlling the soil conditions, particularly soil moisture levels, which is critical in supplying available pesticide at the surface level, and further controls the volatilization rate. Therefore, weather conditions should be recorded with a professional weather station inside the wind tunnel during the experiment. The meteorological sensors should be set up at the center of the non-target area at 2 m height at one single mast.

The following parameters should be monitored inside the wind tunnel:

- air temperature,
- relative air humidity,
- wind speed,
- wind direction.

Optional solar radiation (400 to 700 nm) and leaf wetness can be recorded using devices located in direct neigbourhood to the wind tunnel.

If possible, the accuracy of the sensors should be documented using a nearby official weather station as a reference.

According to the good agricultural practice (GAP) plant protection products should be applied at low wind speeds to minimize spray drift. In the outdoor wind tunnel tests that formed the basis for the empirical approach in EVA, the wind speed was set to 2 m/s. Accordingly, a constant wind speed of 2 m/s should be set for wind tunnel tests.

#### 2.4. Application of the active substance/product to be tested

The application of the active substance/product to be tested should be planned regarding the product's intended use, i.e. the season of application and the maximum recommended application rate. Preparation of the application solution should be reported.

For application, the principles of good agricultural practice should be followed. A suitable sprayer and nozzle should be cleaned and tested before application. The output quantity of the individual nozzles should be checked. Spray pressure, driving speed (ca. 3-4 km/h), and a water application rate of 200-400 L/ha should be adjusted according to the specifics of the sprayer. Technical characteristics of the application technique should be reported in detail.

The day of application should be chosen depending on the local weather forecast, i.e. the sky should preferably be clear to partly cloudy. The application should not be carried out if the expected daily maximum temperature exceeds 25 °C. If the desired maximum temperature exceeds 20 °C, then the application should be carried out no later than 9.00 a.m.

# 2.5 Conduct of the test

The test item is applied to the target area.

Five minutes following the application of the test item to the target area, clean stainless-steel trays are carried into the wind tunnel and placed on the sampling points at 1, 3, 5, 10, 15 and 20 m downwind distance from the target area. They should be filled with 25 L of tap water.

Afterwards, the wind engine will be started with a wind speed of 2 m/s.

To determine the background concentration of the test item, an additional stainless-steel tray filled with 25 L tap water should be placed in the center of the background control area (see figure 1). The

set-up of the background controls should be completed within five minutes after the wind engine has been started.

# 2.6 Sampling

The sampling schedule should be planned considering the characteristics of the substance/product and the application conditions. As volatilization from plant surfaces is significantly faster than from soil surfaces<sup>[4]</sup>, water should be sampled 24 h after treatment. In case of soil applications or testing of compounds with lower volatilization (e.g. capsule formulations), the duration of the experiment should be longer, and water should be sampled up to 96 h after treatment.

At each sampling event, the water in the steel trays at every sampling distance should be homogenized by stirring just before four samples (10 mL per tray) are taken. To quantify evaporation losses, the total remaining volume of the water in the steel trays is determined by weighing after the last sampling event.

The guideline SANTE/2020/12830<sup>[6]</sup> is to be applied for the performance of analytical measurements.

# 2.7 Degradation controls

The possible influence of degradation reactions (hydrolysis or photolysis) on the availability of the active substance to be tested in the test surface waters should be monitored. A fraction of a solution containing the active substance should be incubated in a sealed quartz glass vessel for the same time interval and meteorological conditions as the sampling water in the stainless-steel trays. Aliquots should be taken prior to and at the end of the experiment should be analyzed.

For storage stability measurements, a different portion (about 100 mL) of the solution should be frozen directly after preparation. This control sample should be analysed at a timepoint reflecting the maximum period of frozen study samples.

# 2.8 Reporting

In addition to the above-mentioned conditions of the trial design, all other circumstances that may influence the results, e.g. topographical conditions, pesticide applications in the vicinity of the trial area, application technique and method, and information on the formulation, must be documented. In the case of experiments on bare soil, soil properties need to be reported.

It is recommended to discuss deviations from this test design with the responsible authorities.

The concentrations of the active and reference substances in the water-air samples over the experimental period are to be reported.

The concentrations in the water samples are to be converted to the volume of a standard surface water (1 m<sup>2</sup> area  $\times$  0.3 m depth). In the risk assessment of the terrestrial non-target area, the concentrations in the water samples should be reported as deposition related to the area (1 m<sup>2</sup>).

#### 4. References

- [1] Exposure Via Air (EVA, rev2h, 2017): https://www.bvl.bund.de/EN/Tasks/04\_Plant\_protection\_products/03\_Applicants/04\_Autho risationProcedure/08\_Environment/ppp\_environment\_node.html#doc11010982bodyText2"
- [2] Surface Water Assessment eNabler (SWAN, v. 5.0.1, 2018): https://esdac.jrc.ec.europa.eu/projects/swan
- [3] Fent, G. (2004): Short-range transport and deposition of volatilized Pesticides. Shaker Verlag, Aachen; ISBN 3-8322-3568-X.
- FOCUS (2008). Pesticides in Air: Considerations for Exposure Assessment. Report of the
  FOCUS Working Group on Pesticides in Air, EC Document Reference SANCO/10553/2006 Rev
  2 June 2008. 327 pp.
- [5] Siebers, J. and Fent, G. (2012): Empfehlungen zur experimentellen Bestimmung der verflüchtigungsbedingten Deposition von Pflanzenschutzmittel-Wirkstoffen auf Nichtzielflächen. https://www.bvl.bund.de/SharedDocs/Downloads/04\_Pflanzenschutzmittel/zul\_umwelt\_eva \_empf.html
- [6] SANTE/2020/12830 (2021, Rev.1): Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes
- [7] Fent, G. and Kubiak, R. (2010): Salat als Modellpflanze zur Untersuchung der verflüchtigungsbedingten Deposition von Pflanzenschutzmitteln auf Nichtzielflächen, 57. Deutsche Pflanzenschutztagung 6. - 9. September 2010 Humboldt-Universität zu Berlin -Kurzfassungen der Beiträge, p. 129