Field scale boscalid residues and degradation half-life estimation in a sandy soil

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Abstract

The aim of this study was to analyze the environmental fate of the fungicide boscalid in a sandy soil. Boscalid was applied in spring 2010/11 to a cropland site in western Germany. Three years after second application 65 undisturbed soil samples were taken. Boscalid was extracted using accelerated solvent extraction (ASE). Boscalid contents in the plough horizon ranged between 0.12 and 0.53 with a field mean of 0.20 ± 0.09 µg kg^{-1}. These contents were considerably lower compared to calculation using literature DT_{50} values, whereby a concentration of 16.89 µg kg^{-1} was expected assuming a literature DT_{50} value of 345 days. Therefore, the measured field boscalid concentration only yields 1.2 % of the expected value. To test whether the unknown extraction efficiency, losses from spray drift and interception can explain the mismatch between calculated and measured concentrations all these uncertainties were taken into account into calculations, but field concentrations and DT_{50} were still lower as expected. Leaching to deeper horizons was also studied but could not explain the discrepancy either. Moreover, a short-term incubation experiment using ^{14}C labelled boscalid revealed also shorter DT_{50} values of 297 to 337 compared to the 345 days taken from literature. However, this DT_{50} value is still considerably larger compared to the 104 to 224 days that were calculated based on the field experiment. Our results indicate that boscalid dissipation under field conditions is much faster at agricultural sites with sandy soil type as expected from laboratory incubation experiments.

Introduction

During the last decades several studies showed that over the globe various water bodies are contaminated with pesticides (e.g., Leistra and Boesten, 1989, Kolpin et al., 1998; Tappe et al., 2002, Kuster at al. 2010, Vonberg et al., 2013) and that pesticide residues can be still found in soils several years or even decades after the last application (e.g., Jablonowski et al., 2009; Farlin et al., 2013, Vonberg et al., 2014). Despite of the ecological relevance of these findings, most pesticide degradation and sorption studies were based on short-term laboratory and/or field experiments. Long-term field studies over several drainage periods are only mandatory for the estimation of the risk of potential groundwater contamination in the second tier of the European pesticide registration procedure (Verschoor et al., 2002). The data obtained from these field experiments are then used to model the long-term environmental behavior of the substances by pesticide fate assessment models (Sarmah and Close, 2009). As stated by Jablonowski et al. (2009) and Farlin et al. (2013) these short-term trials only have limited predictive power for the long-term environmental fate of pesticides, as the long-term residue concentration and spatial distribution might not be described appropriately.

Moreover, only pesticides, which are widely found in the environment, are key subject of scientific research. This is particularly the case for well-established pesticides such as atrazine (introduced in 1958) and glyphosate (introduced in 1974) with more than 20.000 search results each, in ISI Web of Science. In contrast, reports of the long-term environmental fate of newly introduced pesticides, e.g. the fungicide boscalid are less frequent (552 ISI listed articles on the fate of boscalid in the environment; verified in May 2014).

Because boscalid has not been subject to much soil scientific research, DT_{50} values are mainly reported in governmental reports or in industry publications, which often lack in full details of the data necessary to judge the DT_{50} reported. For example, soils are often only rudimentary classified in terms of location, soil type, C_{org} content etc. Boscalid DT_{50} values for loam, clay, and silt loam are reported to range between 1000 to 2553 days (EPA, 2010) and for German soils, without any given texture between 87 and 6600 days (APVMA, 2004). Unfortunately, only few data are available on the DT_{50} in loamy sands. The APVMA (2004) listed DT_{50} values ranging from 133 to 348 days, whereby the type of measurement used for the DT_{50} determination was not provided. Ebert & Harder (2000) determined the half-life to be 348, 365, and 322 days, respectively, whereby mineralization was not measured directly, which means that these data represent boscalid dissipation.

Irrespectively of the low number of studies analyzing boscalid fate in the environment, there are indications that boscalid is already widely detectable in different environmental compartments. Smalling et al. (2013a) analyzed boscalid residues in river bed sediments and colloidal suspensions of US-American streams. They found boscalid being the second most detected pesticide that occurred in 53% of the samples of both environmental compartments. The maximum concentration in river bed sediment was 44.5 µg kg^{-1} with a median of 2.1 µg kg^{-1} and 33 µg kg^{-1} in the suspended fraction (median 4.1 µg kg^{-1}). Reilly et al. (2012) found boscalid with 72% being the most frequent pesticide in ground- and surface-water of selected regions in the USA. Smalling & Orlando (2011) found large amounts of boscalid with up to 36 µg L^{-1} in water samples from 12 coastal watersheds of California, USA and Smalling et al. (2013b) could identify boscalid in all water, fish and sand crab samples, and in 89% of the sediment samples, which they took at the Californian estuary. Moreover, boscalid could be detected in 12 out of a total of 24 surface water samples from streams of Rhineland-Palatinate (Germany) studied in 2008 and 2009, whereby water samples of two rivers even exceeded the threshold value for drinking water for pesticides of 0.1 µg L^{-1} (LUWG, 2010).

The detection of boscalid residues in many surface and groundwater bodies is contradictory to reported physic-chemical properties of boscalid from laboratory incubation and short term field experiments, i.e. the strong sorption of boscalid to the soil matrix as reported by e.g., Seher (1998) and Valleé et al. (2013) but in-line with the GUS leaching potential index of 2.66 (PPDB, 2014), which classifies boscalid as a potential leaching substance. Even if the GUS leaching potential index classifies boscalid as a potential leacher, it could be questioned if the reported surface water contamination is caused by deep leaching, especially with respect to the relatively short time period since market placing, or mainly caused by other processes such as spray drift, erosion, or spillage. On the other hand, boscalid is reported to be fairly stable with dissipation half-lifes between 348, 365, and 322 days (Ebert and Harder, 2000). These contradictory findings underline the need for studies on the long-term environmental fate of boscalid in soil to prevent the pollution of surface- and ground water bodies.

Therefore, the objectives of this study were i) to measure the amount of boscalid residues within the sandy textured plough layer of an agricultural field site three years after the last boscalid application, ii) to calculate the bulk boscalid half-life for this site from the obtained long-term data, iii) to compare the calculated half-life to half-life data from literature, and iv) to interpret the obtained field data in consideration of an additional dissipation data from a short term incubation experiment using the same soil.

Materials and Methods

Study site

The study was conducted at an agricultural field in Kaldenkirchen in North Rhine-Westphalia, Germany (51.306687 N, 6.201907E). The field was mainly cultivated by vegetables (leek) and winter wheat over the last four years. The climate is warm-temperate, with a mean annual temperature of 10.8°C and mean annual precipitation of 730 mm. The soil at the site is formed of floodplain loam and terrace sands and can be described as Endogleyic Cambisol (IUSS Working Group Reference Base, 2007). Soil texture is loamy sand (FAO, 2006) and varies within the Ap-horizon (0-30 cm) between 68.5 and 75.2% sand and between 21.6 and 26.7% silt. Clay content of the Ap-horizon is less than 5.5% and soil organic carbon content varies around 1%. Basic soil properties are provided in Tab. 1. It has to be noted that the field was planted with leek during the sampling campaign.

Field application of boscalid

An overview of the chemical properties of boscalid and reported K_d, K_{OC}, K_{FOC}, and K_{OW} values are listed in Tab. 2. In general, the high K_d, K_{OC}, K_{FOC}, and K_{OW} values of boscalid point to a relatively low mobility and a high adsorption affinity of boscalid to the soil matrix (e.g., Long et al., 2005; Vallée et al., 2013). It has to be noted that no major metabolites are reported for boscalid (EPA, 2003).

Boscalid was applied as the product Signum® (BASF, The Chemical Company, GmbH) at the Kaldenkirchen site containing 267 g kg^{-1} boscalid and 67 g kg^{-1} pyraclostrobin in the years 2010 and 2011 with a total amount of 0.4 kg ha^{-1} boscalid in spring 2010 and 2011 onto leek (*Allium porrum*) using a conventional field sprayer. The leek was already in maturity stage at application and planted in rows of 70 cm distance with leek plants every 8 to 10 cm.

Soil Sampling

Soil samples were taken at the nodes of a regular grid with spacings of 10 x 20 m among the nods on the 20th of April 2014. In total, four transects were sampled using a Humax auger (n = 65 samples) to extract undisturbed samples from a depth of 0 to 30 cm (Fig. 1). Along transect 1 the sampling was denser with 10 m intervals. Because the field inclines gently to south east a trend in the soil characteristics could be expected. Pürckhauer augers were drilled down to a depth of 1 m at each sampling point along the northern transect (transect 1) to describe and distinguish the Ap-horizon and any other detectable horizons underlying.

Sample Preparation

All samples were stored field moist at +4°C until further analysis. The undisturbed field moist samples were weighed for bulk density (BD) and water content (SWC) determination. In a second step, the soil from each core was homogenized and subsamples were taken and the weight loss after drying at 105°C for 48 h was determined. Based on the weight loss of the subsample, the theoretical weight loss of the entire core can be calculated, and the bulk density [g cm^{-3}] and volumetric water content [cm^3 cm^{-3}] of the entire core can be estimated. Additionally, one part of the homogenized field fresh subsample was taken for organic carbon content (C_{org}) analysis.

Soil organic carbon (C_{org}) content was determined by dry combustion on a Leco RC 612 multiphase carbon analyzer (Co. LECO Instruments GmbH, Germany) at the central chemical laboratory ZEA-3 of the Forschungszentrum Jülich GmbH.

For the Accelerated Solvent Extraction (ASE) of boscalid residues, sieved and homogenized subsamples were used and the actual gravimetric water content (g g^{-1}) was determined at time of extraction using a Moisture Analyzer HB43-S (Mettler-Toledo AG, Greifensee, Switzerland).

Extraction of boscalid from soil samples

Extraction of boscalid from soil samples was performed using a Dionex™ ASE™ 350 Accelerated Solvent Extractor (Co. Thermo Fisher Scientific Inc., Germany). Briefly, 4 g of moist, sieved soil was mixed with 1 g of infusorial earth (Co. Thermo Fisher Scientific Inc., Germany), and filled into 10 ml stainless steel cells. The cells were then filled up to the brim with infusorial earth to allow constant pressure and solvent flow. Extraction was carried out at a pressure of 100 bar and a temperature of 120 °C using 50% water and 50% methanol as solvent. All reported boscalid concentrations are reported on soil dry weight basis.

Ultra performance liquid chromatography and detection

Boscalid in the extracts was identified and quantified with an Acquity Xevo TQ-S an UPLC-MS/MS (Ultra Performance Liquid Chromatography, Tandem Quadrupole Mass Spectometry) (Co. Waters, USA), equipped with a SecurityGuard Guard-Column, Kinetex PFP CoreShell (Main-Column, reversed phase) of 2.6 µm particle size and 100A pore size (Co. Phenomenex, Germany) running the following program:

The initial settings were a linear gradient using 66% Water, 34% MeOH, and 0.1% formic acid (for 1.7 min), thereafter 100% MeOH (for 2.9 min) returning to the initial gradient (flow rate 0.6 mL, 10 µl column, 10L injection volume). A calibration curve was created with concentrations of Pyrimethanil. An internal standard of Pyrimethanil (D5) was used for quantification. Pyrimethanil was found accurate to quantify boscalid, by comparison of measurement between internal standard use and standard addition.

The limit of quantification (LOQ) of the UPLC-MS/MS was 10 µg L^{-1} or based on the amount of soil used for the extraction 0.006 µg kg^{-1}.

Short term incubation study

To check whether the estimated field derived DT_{50} values can be reproduced, a short term incubation study (120 days) according to the OECD guidelines (OECD, 2000) was performed. For this study ^{14}C labelled boscalid (BASF the Chemical Company, SE Limburger Hof, Germany) with 99 % radiochemical purity was blended with non-labelled boscalid (Sigma-Aldrich Chemie GmbH, Steinheim, Germany). 150 g of the Kaldenkirchen soil taken from a plough horizon bulk sample close to the road (see Fig. 1) was filled into a Scott Duran flask and the pesticide was added in a concentration of 1.33 mg kg^{-1} soil. The soil water content was set to 50 % maximum water holding capacity (WHC_{max}). Pesticide mineralization from the incubation flasks was measured by trapping evolved $^{14}CO_2$ in 1.50 ml 2 M NaOH solution, whereby the NaOH traps were replaced after 0, 3, 8, 14, 23, and 30 days after application, and thereafter twice a month.

To get information about the extractable and non-extractable fractions of the pesticides the incubated soil was sampled at day 0, 8, 30, 60, 90, and 120 after application. Therefore, approx. 5 g (dry mass equivalents) of the soil was taken and extracted using methanol and Millipore water in a ratio of 50:50 (v/v) as solvent. Quantification of trapped $^{14}CO_2$ from the traps and ^{14}C-boscalid from extraction was done via Liquid Scintillation Counting (LSC) using

Instant Scint-Gel Plus as scintillation cocktail (Perkin-Elmer). The recovery (or ^{14}C mass balance) for the short-term incubation experiment was 98.5%.

Statistics

All reported mean values are expressed as arithmetic mean with standard deviation. For the linear correlation between soil characteristics (BD, SWC, and C_{org}) the R^2 as the square of the Pearson product-moment correlation coefficient was used and the root mean square error (RMSE) was calculated. For the correlation a significance level was set to be $p < 0.05$ for all tests. On the other hand, if the correlation is not significant it is indicated by (*ns*).

F-test

An ANOVA was used to test for significant differences between the four transects of the site. Therefore, the total variance was divided into the variance between the samples and between the transects. The significance of differences was tested with an *F-test* at a confidence level of 5%.

DT_{50} and degradation kinetics

The DT_{50} is defined as the *dissipation time*, which is the time needed for 50% of the pesticide to dissipate. Hereby, different main processes can be identified: i) transfer processes by plant uptake, volatilization, leaching, runoff or erosion, ii) full mineralization of the pesticide, and ii) strong sorption to the soil matrix in form of bound or non-extractable residues (FOCUS, 2006).

In general, there are various models reported in literature to describe the degradation kinetics. The simplest model is the single first-order model (SFO) as described in Equation [1] but more different models exist to express the degradation kinetics such as the Gustafson & Holden model, the Hockey-Stick model, and the bi-exponential model or Double-First-Order-in Parallel model. A useful overview of the models and their application is provided in FOCUS (2006).

As already mentioned, the simplest form to estimate the rate constant and the half-life of a pesticide is to fit a single first order (SFO) or exponential decay to the observed data (FOCUS, 2006).

$$C_t = C_0(1-\exp^{(-k*t)}) \qquad [1]$$

where C_t is the mass of the pesticide dissipated [µg] at time t [day], t is the time after pesticide application, and C_0 is the initial mass of applied pesticide at time $t = 0$. From the knowledge of the rate constant the DT_{50} value can be calculated by equation [2] (FOCUS, 2006; Karanasios et al., 2010):

$$DT_{50} = \frac{\ln(2)}{k} \qquad [2]$$

For determination of the half-life of boscalid in our study the SFO model was used based on two constrains: i) this model is corresponding with literature information describing boscalid as a degrading substance which can be fitted appropriately by a single first-order function (e.g. EPA, 2003; Ebert and Harder, 2000) and ii) due to the data available, no higher order or models with larger complexity can be fitted to the data without strong constrains or large uncertainties.

Results and Discussion

Soil Parameters

Because the amount of pesticide residues in field soils is often correlated with the soil states especially soil organic carbon content (e.g., Lima et al., 2010) and clay content (e.g., Weber, 1970) both parameters were measured from the homogenized Humax cores. Because soil textural analysis are tedious and cost expensive for large sampling quantities we used the proxies actual soil water content (SWC) and soil bulk density instead. Additionally, soil horizons were delineated along transect 1.

The results showed that the depth of the Ap-horizon slightly differs between points, which might be caused by the uneven surface due to the leek plantation or correctness of the method used for Ap-horizon delineation (push-in resistance). Average Ap-horizon depth was 28.7cm (min = 20, max = 37 cm). The underlying Bv horizons showed larger differences and also the *C*-horizon could only be delineated at few points along transect 1, mainly in the downslope position of the transect. The data showed that the field is fairly homogenous within the uppermost 40 cm, but rather heterogeneous at larger depths. Nevertheless, no clear trend in horizon depth along the slope could be detected.

The bulk density (BD) varied between 1.11 and 1.47 g cm^{-3} with a mean of 1.29 ± 0.10 g cm^{-3}. In general, BD was slightly higher at the downslope position of the field (>100 meters) and highest BD was generally found in the first transect, with a maximum of 1.47 g cm^{-3} at the center of the transect. On the other hand, lowest BDs were measured for the second and third transects at single points with 1.11 g cm^{-3}.

Mean volumetric soil water content (SWC) was 0.16 ± 0.04 cm^3 cm^{-3}, ranging from 0.09 to 0.36 cm^3 cm^{-3} indicating a large variability over the field. Again a slight tendency of increased water content to the end of the transects (>150m) could be found, which correspond to an increasing slope of the terrain. The reasons for the slightly higher SWC at the downslope position of the field can be explained by the lower position of the sampling points but also by shading of the trees at the south eastern part of the field (especially for the last sampling points along each transect).

Mean soil organic content (C_{org}) was 0.92 ± 0.19 % and varies along the different transects. In general, C_{org} was higher at both ends of the field (0 – 20 m and 200 – 250 m), which is characterized as the foreland. The reason for this higher C_{org} content might be the larger amounts of fertilizer (mainly champost or manure) applied during turning activities of the tractor. The higher contents at the end of the field (220 m) can be also explained with additional diffuse litter input from the nearby glade or by the higher water contents at the same location.

Theoretical boscalid residues

Based on reported DT_{50} literature values and the boscalid application history, the actual expected mean boscalid concentration at the field site Kaldenkirchen was calculated. Therefore, literature was screened for the boscalid DT_{50} values in loamy sand, but respective publications are scarce and the reported DT_{50} values vary largely (see Introduction and Tab. 2). Based on these spare information and reported span a DT_{50} of 345 days was assumed for our loamy sand, which lies in the middle of reported values.

Based on this DT_{50} value, the rate constant r for boscalid at our site and finally the expected concentration of boscalid residues two years after the last application was calculated. The calculation was based on the following assumptions: i) no boscalid was translocated below the plough horizon, ii) no other losses such as spray drift and interception losses occurred during application, and iii) boscalid residues have been homogeneously mixed into the plough horizon due to tillage in the years after application.

It has to be noted that field boscalid concentration was estimated from Humax cores, which sampled the top 30 cm of the soil profile. At certain points this sampling depth does not fully correspond to the ploughing depth as can be seen for the Ap-horizon depth along transect 1. Due to the fact that the ploughing depth was not measured at the other transects and that the plough horizon cannot be easily delineated in the Humax cores, a constant 30 cm plough depth was therefore assumed for all further analysis.

Using the above mentioned DT_{50} value of 345 days, a measured mean bulk density of 1.29 g cm^{-3}, and a constant plough layer thickness of 30 cm would result in a boscalid residue pattern over time as plotted in Fig. 3. Even if the assumption of full mixing into the plough layer directly after the first application does not reflect the management practice, the plot already shows a general feature with decreasing boscalid concentrations within the first year after application and a second peak caused by the second application. After that, a general decrease of boscalid concentration can be observed. For the sampling in spring 2014 (1460 days after 1st application, and 1095 days after 2nd application) it can be expected that only 16.89 µg kg^{-1} or 11.1 % of the total mass available after the second application still remains in the plough layer.

Field boscalid residues

Field boscalid concentration obtained from ASE extraction of the 30 cm Humax cores ranged between 0.12 and 0.53 µg kg^{-1} with a field mean value of 0.20 ± 0.09 µg kg^{-1} (see Tab. 3). The measured residue concentrations are much lower compared to the calculated boscalid residue concentration of 16.89 µg kg^{-1} based on the literature derived DT_{50} value of 345 days. Generally, the measured field boscalid concentrations yield only 1.2 % of the calculated concentrations.

In a next step, measured bulk density for each single point was accounted in the calculation of the field-wide boscalid concentration, whereby again a mean ploughing depth of 30 cm was assumed. The results in g ha^{-1} are depicted in Fig. 4b. The minimum and maximum concentrations are 0.05 - 1.8 g ha^{-1} with a mean of 0.75 ± 0.34 g ha^{-1}, respectively. Both foreland patches of the field site show remarkably higher boscalid residues compared to the patches in the center of the field site. Moreover, boscalid concentrations also differ between transects. Highest amounts were detected in transect 1 with 1.83 g ha^{-1} (sampling point (SP) 0), followed by transect 2 with 1.81 g ha^{-1} at SP 26, and transect 3 with 1.80 g ha^{-1} at SP 52. All these sampling points are located close to the road at the beginning of the transects. On the other hand, lowest concentrations were found in transect 4 with 0.05 and 0.14 g ha^{-1} at the center of the field. The statistical evaluation by ANOVA, with the null hypothesis that the residue variability is higher in the transects than between the transects was confirmed, F-value of 0.31 $\alpha = 0.01$ (F-values below the critical F-value of 25.36).

Because the amount of pesticide residues in a homogeneously managed and sprayed field are often correlated with soil physicochemical states, such as soil organic carbon content, soil bulk density, and soil water content, the influence of these states on the boscalid residues was analyzed separately. In a first step, soil water content and bulk densities were correlated with boscalid residues, whereby both correlations did not show a significant relationship. Only the correlation between C_{org} and boscalid residues indicate a low positive relationship with a R^2 of 0.23 ($p = 0.05$) and a RMSE of 0.33 g ha^{-1}. This low correlation is in contradiction to previous findings of Bollag (1992), Pignatello (1998), and Spark and Swift (2002) who stated that soil organic carbon might act as a sorbent for the pesticides preventing leaching but also degradation. On the other hand, overall C_{org} content does not provide insight into the carbon quality that can be essential for pesticide sorption (Spark and Swift, 2002). Additionally, the formation of soil aggregates might lead to protection of soil organic matter, which becomes inaccessible for the pesticide to sorb, leading to a lower effective amount of active organics in the soil (Barriuso and Koskinen, 1996; Skjemstad et al., 1996). Nevertheless, boscalid concentration cannot be successfully described using C_{org} as a predictor only. One reason for the weak correlation might be a potentially higher application rate at the foreland while spraying equipment is turned. Therefore, points located in the foreland were excluded from the dataset to test whether the correlation increases or not in the area not affected by this possible source of error. Omitting the points not located in the foreland (n = 41) showed no improvement in the correlation with and R^2 of only 0.007 (*ns*) and a RMSE of 0.194 g ha^{-1}. On the other hand, correlation for the points located in the foreland (n = 24) is slightly larger with an R^2 of 0.27 (p = 0.05) and a RMSE of 0.42 g ha^{-1}.

For a more detailed analysis of the entire field, and the analysis of variability between transects, the single transect data (transect 1 to 4) were correlated as well. Best correlation between C_{org} and boscalid residues was found for transect 1 with a moderate R^2 of 0.43 (p = 0.05) and a comparable low RMSE of 0.267 g ha^{-1}, followed by transect 2 with a R^2 of 0.42 (p = 0.05) and a RMSE of 0.29 g ha^{-1}. In comparison, transect 3 and 4 show a much lower correlation with a R^2 of 0.29 (*ns*) (RMSE = 0.29 g ha^{-1}) and 0.37 (p = 0.05) (RMSE = 0.27 g ha^{-1}), respectively. Unfortunately, the plough horizon at the site is characterized by a single grain structure without larger aggregates. Therefore, the theory of inaccessible carbon cannot hold, at least for the plough horizon.

A possible explanation for the better fit of transect 1 data might be the large number of observations associated with a relatively large data spread. Additionally, data scattering for the pesticide residues is larger in transect 2 and 3 compared to those in transect 1 and 4, resulting also in a larger RMSE.

Besides the soil organic carbon content, other site specific parameters or states might be important for the quantity of boscalid residues. One option is the variation in soil texture; especially in the highly sorbing clay fraction. As Spark & Swift (2002) suggested, pesticide sorption in soils with low organic carbon content (<5%) will be mainly controlled by soil texture. Unfortunately, soil texture was not determined for the soil samples. Therefore, it was tested if soil water content (SWC) and bulk density (BD) information can be used as a proxy for soil textural changes and if including this information would improve the predictive power. A multiple regression analysis was performed with SWC, BD, and C_{org} as predicting variables for boscalid residues with n = 65. The regression result showed that boscalid residues can be predicted by:

$$Boscalid_{residues} = -0.7598 + 1.0475C_{org} + 0.8464SWC + 0.3406BD \quad [3]$$

whereby the R^2 is again fairly low with 0.33 (p = 0.05). Due to the larger number of predicting variables (m = 3) the corresponding R^2_{adj} was also calculated to be 0.29. Compared to the R^2 for the regression between residues and C_{org} (n = 65) with a R^2 of 0.23 the multiple regression was only slightly improved. Additionally, a test on significance also showed that only C_{org} significantly contributed to the prediction (p = 0.05).

Leaching to deeper soil depths

Translocation of boscalid into deeper soil horizons could be another explanation for the observed relatively low boscalid residues in the plough layer. In general, boscalid can be considered as a potentially leaching compound in a sandy soil, based on the GUS value of 2.66 (PPDB, 2014). To get information of the leaching potential of boscalid in our soil an additional batch sorption experiment according to OECD guideline 106 (OECD, 2000) was performed, resulting in a K_d and K_{oc} value of 19.2 and 2337 cm^3 g^{-1}, respectively, indicating high sorption potential. Based on the K_d / K_{oc} values only small fractions of the boscalid should be translocated below the plough layer. Nevertheless, translocation of boscalid can occur also in the sorbed state as co-transport via dissolved organic matter (DOM) or particulate organic matter (POM) (Imache et al. 2012; Seol and Lee, 2000; Said-Pullicino et al., 2004).

To check whether boscalid was translocated into deeper soil horizons, selected auger samples from below the plough horizon (30 – 60 cm depth) were analyzed for boscalid residues along transect 1. Selection of subsoil samples along transect 1 was based on boscalid concentrations in the overlying Ap-horizon and samples were chosen to cover a wide range of boscalid concentrations in the topsoil. However, the boscalid concentrations in all obtained subsoil samples were below the limit of quantification (10 pg mL^{-1}; corresponding to 0.06 µg kg^{-1} dry soil), irrespective of the concentration of boscalid in the overlying topsoil. If the leaching from the upper horizon follows a vertical pathway, without interference of interflow or man-made manipulation, this amount was calculated to be 16 to 47% of the residues found in the upper horizon. Even if this is a worst case calculation due to the uncertainty in quantification, which can be easily reduced by half, residues in the subsoil (30 to 60 cm) would make up 8 to 23.5% of the residues found in the plough layer.

Application and Interception Losses

Because some of the boscalid might have been drifted by wind during the application or intercepted by the plants leading to application losses, these two processes have to be quantified for exact calculation of the total boscalid mass entering the soil and the final calculation of the DT_{50} values. Unfortunately, wind drift and interception losses were not quantified in the field. With respect to the location of the field, which is nicely protected by large trees in the (main) north-western wind direction (see Fig. 1) and the small field size, with respect to the wind barrier (tree plantation and small forest) height, wind drift losses should be minimal if not even negligible (Ucar and Hall, 2001). Nevertheless, for the worst case calculations wind drift losses were assumed to be 5% of total applied mass. Interception losses greatly depend on the plant type and development stage. Because there are no reported interception losses for leek, we used the proposed interception losses for onion reported in FOCUS (2011) of maximal 50% of applied mass. Based on these assumptions the total applied mass was corrected to be 180 g ha^{-1} for each application. The corresponding boscalid concentrations in the plough horizon for the literature derived DT_{50} value of 345 days would be 7.73 µg kg^{-1} or 29.5 g ha^{-1}. Compared to the mean field boscalid concentrations (0.20 µg kg^{-1}) this value is still much higher.

Simulation of extractability

Another possible explanation for the low boscalid concentrations found in the field might be a low extraction efficiency of the applied ASE method. Even if ASE extraction was optimized for maximum yields, the total extractability of boscalid by ASE 1095 days after application remains unknown. An additional short term aging experiment with boscalid and the same soil showed extraction efficiencies >86 % after 123 days. Nevertheless, extraction efficiency might further decrease due to aging. Literature data indicate that extraction efficiencies for long-term aged soil vary greatly depending on the pesticide, soil type, time after application, and extraction method (e.g., Boivin et al., 2004; Doick et al., 2005, Jablonowski et al., 2009). To account for this uncertainty, measured residue concentrations were scaled by different assumed extraction efficiencies of 100, 80, 60, 40, and 20%, respectively.

The mean concentration at 100% extractability was measured to 0.78 ± 0.32 g ha^{-1} (ranging from 0.41 to 1.83 g ha^{-1}). For 80% efficiency, the mean value increased to 0.97 ± 0.41 g ha^{-1} (0.52 – 2.29 g ha^{-1}), for 60% extraction efficiency to 1.30 ± 0.55 g ha^{-1} (0.69 – 3.06 g ha^{-1}), for 40% efficiency to 1.94 ± 0.82 g ha^{-1} (1.04 – 4.59 g ha^{-1}), and for 20% efficiency even to 3.88 ± 1.64 g ha^{-1} (2.07 – 9.17 g ha^{-1}) (see Tab. 4).

Assuming the efficiency of the ASE being only 20%, the highest measured boscalid concentration in the plough horizon would be 9.17 g ha^{-1} instead of 1.83 g ha^{-1}. The lowest concentration would be 2 g ha^{-1}, compared to the measured 0.41 g ha^{-1}, Therefore, highest boscalid concentration at 60% efficiency would be 3.06 g ha^{-1}, which corresponds to 0.51% of the applied 590 g ha^{-1} boscalid at t_0 and the lowest concentration would be 0.69 g ha^{-1}, which corresponds to 0.12% of the applied 590 g ha^{-1} boscalid at t_0, respectively.

Calculation of DT_{50} from field samples

Based on the measured field boscalid concentrations shown in Fig. 4b DT_{50} values were calculated using Eq. [1] and [2] with an application dosage of 590 g ha^{-1} boscalid at t_0 (second application at day 365) an elapsed time since last application of 1095 days for the case that all boscalid applied entered the soil and an application dosage of 270 g ha^{-1} for the case where 55% of the applied mass was assumed to be lost due to spray drift and interception. DT_{50} values were calculated in the same way using the simulated extraction efficiencies and corresponding mean, minimum, and maximum boscalid concentrations as listed in Tab 4. The corresponding half-life times are displayed in Tab. 4. The measured values from the ASE extraction are presented as 100% expressed as mean, minimum and maximum value.

The boscalid half-life of the field soils without assuming any losses and 100 % extraction efficiency resulted in a DT_{50} values of 104 to 132 days with a field mean of 115 days. On the other hand, assuming an extraction efficiency of only 20% yields a maximum DT_{50} of 182 days and assuming a moderate extraction efficiency of 60% shows intermediate DT_{50} values of 112 and 144 days (*mean* 124 days), respectively. As mentioned, the losses due to spray drift and interception were not quantified in our experiment but assumed to be in a worst case 55% of the application. The corresponding DT_{50} for this scenario are also listed in Tab. 4 and showed that the DT_{50} increased by 15 days to 130 days assuming 100% extraction efficiency. For the smallest assumed extraction efficiency of only 20% the DT_{50} f was 179 over all points and 224 days for the highest concentration found. Half-life times of boscalid reported in literature are considerably higher as those calculated with and without losses with 307 to 365 days for loamy sand compared. The reasons for these differences are still unclear. To check whether the estimated field derived DT_{50} values can be reproduced, a short term incubation study (120 days) was performed. It has to be noted that the extraction of boscalid was performed using methanol/water in a ratio of 50/50 with shaking only. The results showed that only a minor part of boscalid was mineralized over the 120 days (~4%) but that ~45 % of the added boscalid were non-extractable. The corresponding DT_{50} value calculated from mineralization + non-extractable from a single first-order model was 297 and for the extractable fraction 337 days, which is again shorter as most reported ones but still larger as the field estimates.

Deviations of DT_{50} from field dissipation studies and laboratory incubation experiments have been already reported and the reasons for the observed differences are manifold. The European Food Safety Authority (2014) listed different processes explaining the observed differences such as volatilization losses, soil surface photolysis (or photodegradation), leaching out of the sampled soil layers. Winton (2002) added also runoff and differences in pH, as well as substantial differences in soil water content and soil temperature to the list and stated that in laboratory incubation it is likely that some populations of aerobic and anaerobic soil microbes will accelerate pesticide mineralization. Based on this list and the physico-chemical properties of boscalid listed in Tab. 2 and field observations some of the processes can be defined either as being important or as being not important for the observed deviation in the DT_{50} values.

Based on the reported Henry's law constant (HLC) of 5.178 x 10^{-5} Pa m^3 mol^{-1} and vapor pressure of 7.2 x 10^{-7} Pa boscalid can be defined as essentially non-volatile and it is reported to resist photodegradation on soils (EPA, 2003). Because pH of the sandy soil was 6.1, chemical stability of boscalid is also ensured. Runoff from the field after application seems also to play a minor role due to two facts: i) the slope of the field is fairly low, which does not favor runoff, ii) due to the sandy character of the soil saturated hydraulic conductivity of the Ap-horizon is generally high (> 100 cm d^{-1}), and iii) the aggregation potential is low due to the small percentage of silt and clay content. Leaching as a potential source of loss from the plough horizon could be also excluded by the sampling deeper zones and the additional sorption batch experiment indicating high sorption tendencies of boscalid to our soil. Therefore, only the differences and also the dynamics in soil temperature and soil water content might be considered as possible major drivers for the difference observed. In general, it is known from various investigations that the microbial activity is non-linear related to soil temperature and soil water content (e.g. Bauer et al., 2008), whereby soil temperature regulates microbial activity by a larger extend as soil water content at least in temperate - humid climate. Even if the laboratory incubation experiment was performed at fairly high constant ambient temperature (25°C) variation in temperature under natural conditions might stimulate microbial activity (Weihermüller et al., 2011) and have turned over more boscalid. The mineralization rate during the laboratory incubation experiment showed that only ~4 % of boscalid was mineralized over 120 days and that mineralization already slowed down after eight days of incubation. Therefore, accelerated mineralization under field conditions seems not to explain the difference either. A hint of an additional influencing factor can be found in Tsochatzis et al (2013) who stated that the pesticide Tricyclazole might be faster dissipated under field conditions due to the presence of plants which might have promoted the dissipation through the stimulation of microbial degradation in the plant rhizosphere or through direct plant uptake. Unfortunately, plant uptake cannot be reconstructed anymore, but future field dissipation studies should take into account these pathways and should design their experiments accordingly.

Another reason for the differences observed can be found in the DT_{50} fitting procedure itself. While for laboratory studies fitting of the initial mass (M_0) is recommended to ensure better fitting results (FOCUS, 2006), M_0 was set to the initial mass applied to the field in the field experiment. The procedure of fitting M_0 for the laboratory study resulted in a M_0 of ~67% of initial mass due to instantaneous sorption (derived from non-extractable residues) of boscalid even at short time after pesticide application (~t_0). As a consequence, less boscalid had to be dissipated over the course of the incubation study yielding larger DT_{50} values.

Summary and Conclusion

In the study presented, boscalid concentrations were estimated from a field scale survey three years after last boscalid application. Additionally, actual soil water content (SWC), soil bulk density (BD), and soil organic carbon (C_{org}) was determined at the same samples used for boscalid residue determination to analyze if there is any correlation between boscalid residue concentration and soil states.

The analyzes of the soil samples showed that the field is not homogeneous in nature, whereby soil water content (SWC) and bulk density (BD) showed a slight trend along the long site of the field (corresponding to the slope or transects) with slightly larger values at lower terrain positions. In contrast, soil organic carbon (C_{org}) seemed to be higher at both sites of the field within the foreland.

The ASE-extraction of boscalid from field samples showed that there are still detectable amounts of the pesticide within the plough horizon three years after application with 0.78 ± 0.32 g ha^{-1} (ranging from 0.41 to 1.83 g ha^{-1}). It could also be shown that higher boscalid concentrations were detectable in the foreland of the field, whereby either higher boscalid applications due to the turning of the spray equipment or lower boscalid dissipation might be responsible for this pattern. To check if higher boscalid concentrations are associated with the soil states measured (C_{org}, SWC, or BD) correlations were performed but only a weak correlation with C_{org} could be found. To exclude that the loss of boscalid into deeper soil layers contributed to the low concentrations found in the plough layer deeper soil samples were also analyzed from selected points but no significant boscalid residues could be found and an additional sorption batch experiment revealed strong sorption of boscalid to the soils. Finally, DT_{50} values were calculated based on the measured boscalid concentrations and the uncertainty in the extractability 1095 days after application was simulated assuming different extraction efficiencies and also accounted for potential application losses due to spray drift and interception. The obtained DT_{50} values ranged between 104 to 182 days assuming no losses to 130 to 224 days assuming 55% application losses, which are generally smaller as reported values for same soil types. An additional short-term incubation study using the same soil also revealed larger DT_{50} value of 297 to 337 days. The differences between laboratory and field experiment derived DT_{50} could not be explained by volatilization, runoff, spray drift, and interception losses. Leaching losses could not be determined by sampling the field but they could not be fully excluded. A possible explanation for higher dissipation can be the differences and dynamics in soil temperature and soil water content but more feasible are losses by plant uptake and stimulated mineralization in the root zone due to rhizosphere processes. Therefore, we encourage future surveys for the estimation of field DT_{50} to take into account all plant mediated processes by using appropriate experimental designs.

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Figure 4: Field boscalid residues in a) [µg kg^{-1}] and b) [g ha^{-1}] taking point bulk densities into account (Fig. 2b) and assuming a mean plough horizon depth of 30 cm.

Tables

Table 1: Physicochemical soil characteristics of the Kaldenkirchen soil with soil texture, C_{org}, pH ($CaCl_2$), and cation exchange capacity (CEC).

%				**pH** **[$CaCl_2$]**	**CEC** **[$cmol_c$/kg]**
Clay (<2µm)	**Silt** (2-63µm)	**Sand** (63-2000µm)	**C_{org}**		
3.2	21.6	75.2	0.99	5.35	-
4.9	26.7	68.5	1.07	6.80	7.8
5.5	22.2	72.7	-	-	-
3.3	22.0	75.0	0.99	6.00	7.8
4.4	26.2	69.5	1.01	5.35	-

taken from: Koestel et al. (2009) and Förster et al. (2008)

Table 2: Selected properties of boscalid.

Chemical name		Boscalid (Nicobifen)
IUPAC		2-chloro-N-(4'-chlorobiphenyl-2-yl) nicotinamide
Molecular formula		$C_{18}H_{12}Cl_2N_2O$
Molecular mass		343.2 g mol^{-1}
Vapor pressure (20°C)		7.2 x 10^{-7} Pa
Henry's Law Constant		5.178 x 10^{-5} Pa m^3 mol^{-1}
Solubility	Water	4.64 mg L^{-1}
	Methanol	40-50 g L-1
	Acetone	160-200 g L-1
	Acetonitrile	40-50 g L-1
pH stability		pH 4-9
K_d		3.3 - 28 cm^3 g^{-1} (EPA, 2010) 37.3* cm^3 g^{-1} (Seher, 1998) 17.9* cm^3 g^{-1} (Seher, 1998) 8.9* cm^3 g^{-1} (Seher, 1998) 15.5 - 37.2** cm^3 g^{-1} (Seher, 1998)
K_{OC}		1492* cm^3 g^{-1} (Seher, 1998) 1623* cm^3 g^{-1} (Seher, 1998) 2229* cm^3 g^{-1} (Seher, 1998) 507 - 1110* cm^3 g^{-1} (BVL, 2002) 672 - 1760* cm^3 g^{-1} (FSC, 2004) 809** cm^3 g^{-1} (Vallée et al., 2013)
K_f		3.3 - 27.8 cm^3 g^{-1} (BVL, 2002) 12.6 cm^3 g^{-1} (PPDB, 2014) 4.8** cm^3 g^{-1} (Vallée et al., 2013) 4.4 - 8.4* cm^3 g^{-1} (Vallée et al., 2013)
K_{OW}		507 - 1110 cm^3 g^{-1} (BVL, 2002) 772 cm^3 g^{-1} (PPDB, 2014) 386.1* cm^3 g^{-1} (Vallée et al., 2013)

taken from: BVL (2002); EPA (2003 & 2010); Smalling et al. (2013a)

* was derived from desorption and ** from adsorption experiments

Table 3: Volumetric water content [cm^3 cm^{-3}], bulk density [g cm^{-3}], organic carbon content (C_{org}) [%], and field boscalid concentrations in µg kg^{-1} soil or g ha^{-1}. All concentrations based on soil dry weight. For the calculation of g ha^{-1} the measured point bulk densities and a mean ploughing depth of 30 cm were taken into account.

point No.	transect #	Coordinates		Water content	Bulk density	C_{org}	Concentration	
		x	y	[cm^3 cm^{-3}]	[g cm^{-3}]	[%]	[µg kg^{-1}]	[g ha^{-1}]
1	1	0	0	0.16	1.37	0.99	0.446	1.834
2	1	0	10	0.16	1.32	0.90	0.216	0.852
3	1	0	20	0.15	1.25	0.88	0.209	0.783
4	1	0	30	0.16	1.41	0.85	0.211	0.981
5	1	0	40	0.22	1.24	1.10	0.218	0.810
6	1	0	50	0.15	1.42	0.90	0.163	0.691
7	1	0	60	0.17	1.40	0.87	0.226	0.951
8	1	0	70	0.14	1.36	0.94	0.277	1.131
9	1	0	80	0.14	1.37	0.80	0.219	0.896
10	1	0	90	0.13	1.40	0.67	0.174	0.732
11	1	0	100	0.17	1.44	0.74	0.211	0.908
12	1	0	110	0.15	1.45	0.79	0.151	0.655
13	1	0	120	0.19	1.35	0.74	0.149	0.607
14	1	0	130	0.16	1.47	0.76	0.158	0.695
15	1	0	140	0.15	1.44	0.81	0.188	0.812
16	1	0	150	0.15	1.46	0.76	0.142	0.619
17	1	0	160	0.15	1.43	0.79	0.129	0.553
18	1	0	170	0.16	1.38	0.89	0.142	0.587
19	1	0	180	0.15	1.43	0.80	0.134	0.575
20	1	0	190	0.16	1.38	0.80	0.168	0.697
21	1	0	200	0.17	1.43	0.94	0.154	0.660
22	1	0	210	0.23	1.40	0.85	0.125	0.523
23	1	0	220	0.20	1.39	1.09	0.345	1.440
24	1	0	230	0.19	1.40	0.96	0.283	1.188
25	1	0	240	0.21	1.30	1.20	0.277	1.1079
26	1	0	250	0.21	1.38	1.35	0.263	1.087
27	2	-10	0	0.13	1.14	1.18	0.530	1.807
28	2	-10	20	0.16	1.11	0.87	0.154	0.512
29	2	-10	40	0.09	1.20	0.97	0.155	0.556
30	2	-10	60	0.10	1.17	1.03	0.152	0.535
31	2	-10	80	0.11	1.25	0.82	0.174	0.652
32	2	-10	100	0.10	1.22	0.77	0.191	0.698
33	2	-10	120	0.09	1.19	0.81	0.136	0.485
34	2	-10	140	0.10	1.28	0.80	0.172	0.660
35	2	-10	160	0.12	1.18	1.10	0.159	0.565
36	2	-10	180	0.11	1.19	0.93	0.116	0.414
37	2	-10	200	0.13	1.23	0.95	0.174	0.646
38	2	-10	220	0.13	1.13	1.24	0.293	0.991
39	2	-10	250	0.18	1.33	1.27	0.308	1.229
40	3	-20	0	0.14	1.20	1.12	0.499	1.802
41	3	-20	20	0.09	1.12	0.72	0.155	0.519
42	3	-20	40	0.09	1.14	0.82	0.217	0.741
43	3	-20	60	0.09	1.22	0.72	0.196	0.717
44	3	-20	80	0.12	1.11	0.85	0.222	0.738
45	3	-20	100	0.12	1.26	0.75	0.155	0.587
46	3	-20	120	0.10	1.25	0.81	0.132	0.498
47	3	-20	140	0.11	1.24	0.80	0.145	0.538
48	3	-20	160	0.14	1.23	0.92	0.125	0.462
49	3	-20	180	0.12	1.20	0.96	0.191	0.685
50	3	-20	200	0.11	1.28	0.98	0.154	0.591
51	3	-20	220	0.13	1.20	0.93	0.142	0.510
52	3	-20	250	0.17	1.17	1.54	0.298	1.040
53	4	-30	0	0.13	1.15	1.15	0.416	1.439
54	4	-30	20	0.12	1.34	0.81	0.130	0.525
55	4	-30	40	0.10	1.18	0.83	0.125	0.442
56	4	-30	60	0.10	1.25	0.78	0.155	0.579
57	4	-30	80	0.10	1.24	0.90	0.123	0.461
58	4	-30	100	0.12	1.24	0.79	0.130	0.486
59	4	-30	120	0.10	1.26	0.96	0.129	0.488
60	4	-30	140	0.10	1.25	0.96	0.211	0.792
61	4	-30	160	0.12	1.27	1.03	0.176	0.669
62	4	-30	180	0.13	1.32	0.97	0.152	0.605
63	4	-30	200	0.24	NA	0.94	0.154	0.145
64	4	-30	220	0.11	NA	0.92	0.139	0.050
65	4	-30	250	0.17	1.34	1.14	0.212	0.855

Table 4: Calculated half-life's (DT_{50}) of boscalid according to measured residues (100%) and simulated extraction efficiencies (80, 60, 40, and 20%) assuming no spray drift and interception losses and 55% losses.

Extraction Efficiency [%]	**Field concentration [g ha^{-1}]**			**DT_{50} [days] no losses**			**DT_{50} [days] 55% losses**		
	mean	min	max	*mean*	min	max	*mean*	min	max
100	0.78	0.41	1.83	115	104	132	130	117	152
80	0.97	0.52	2.29	118	108	137	135	121	159
60	1.30	0.69	3.06	124	112	144	142	127	169
40	1.94	1.04	4.59	133	120	156	154	137	186
20	3.88	2.07	9.17	151	134	182	179	156	224

Figures

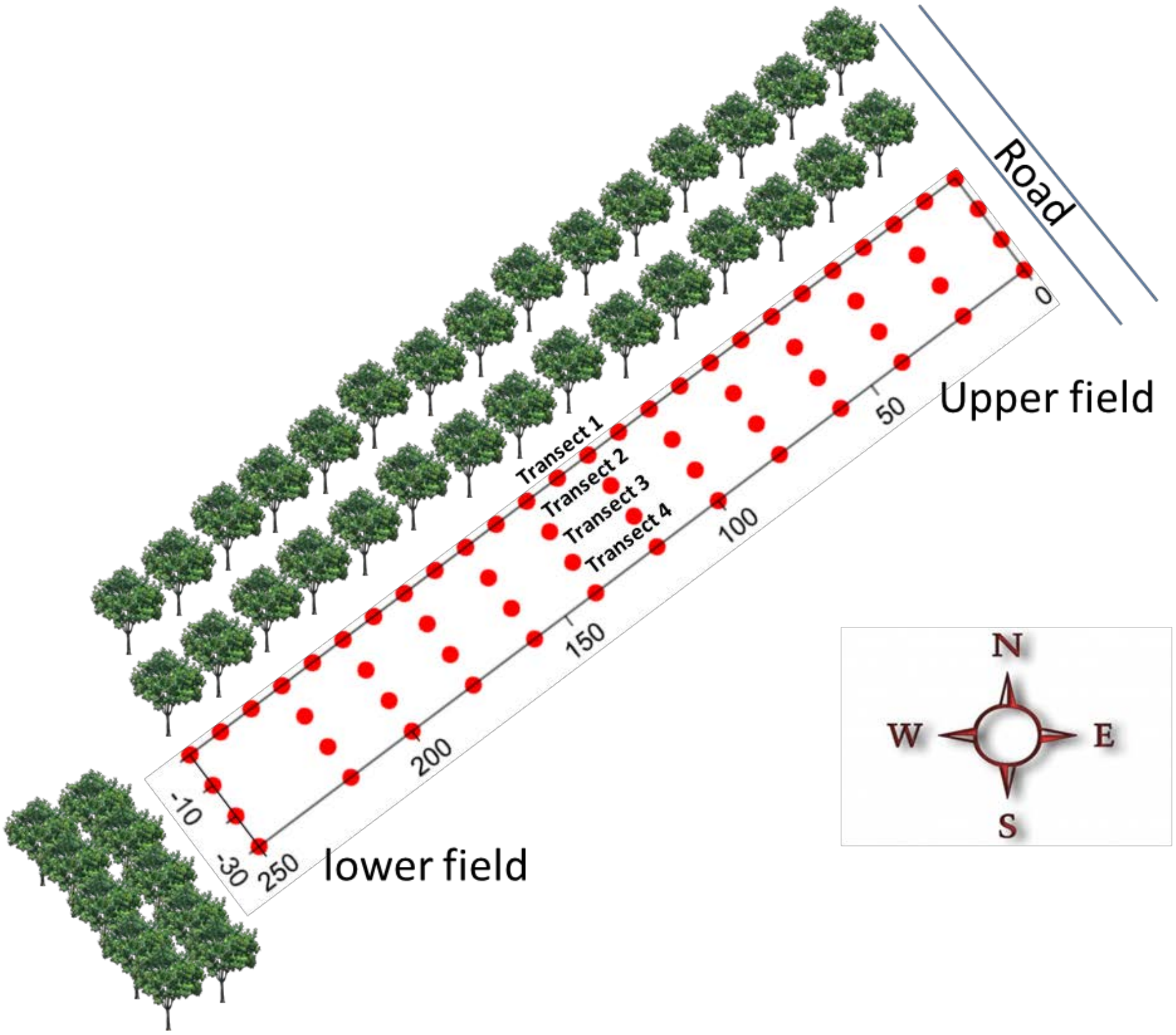

Figure 1: Transect points (red dots) and transect numbers for the soil sampling at the site Kaldenkirchen in the year 2014. Transect 1 in the North with higher sampling density (10 m).

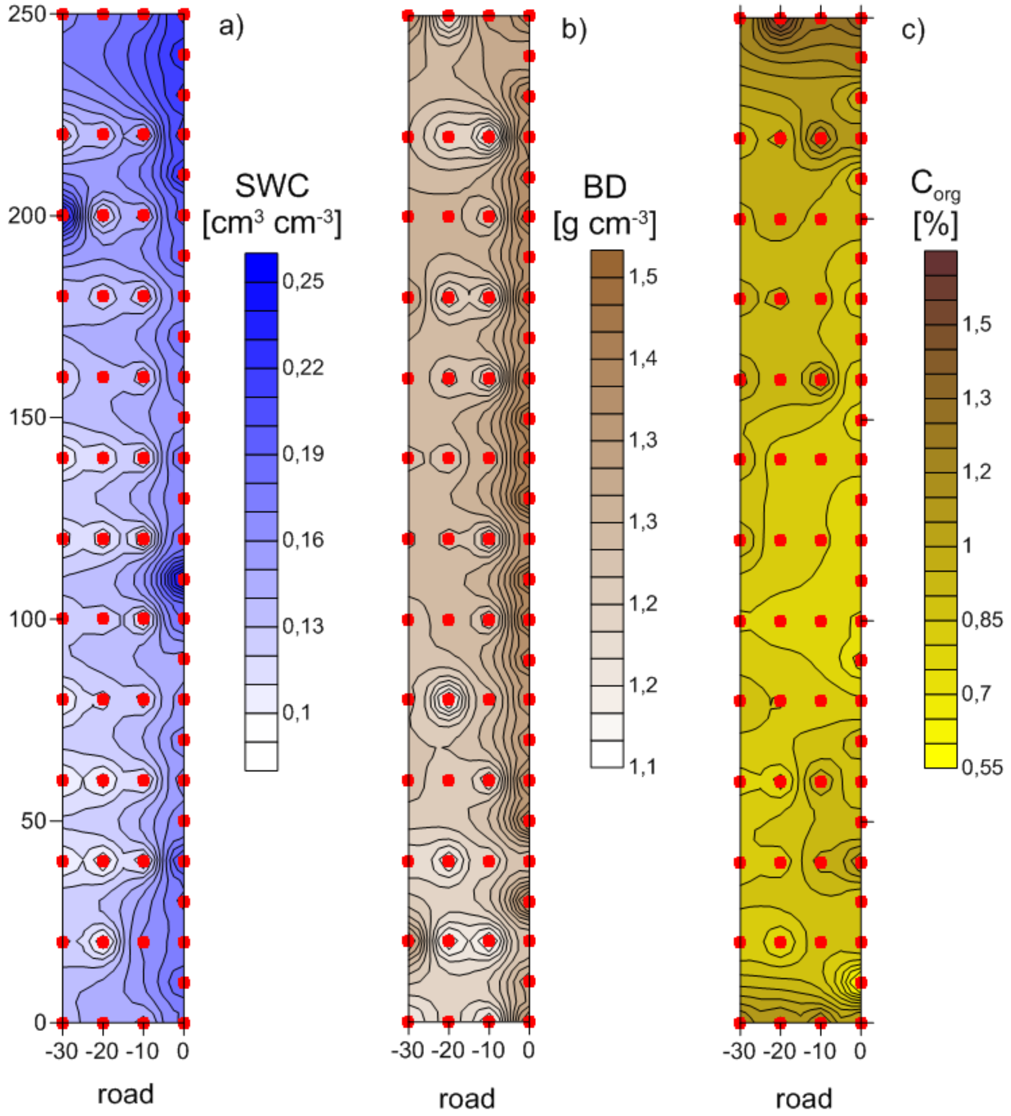

Figure 2: Plough horizon a) volumetric soil water content [cm^3 cm^{-3}], b) soil bulk density [g cm^{-3}], and c) soil organic carbon [%] derived from 30cm Humax augers.

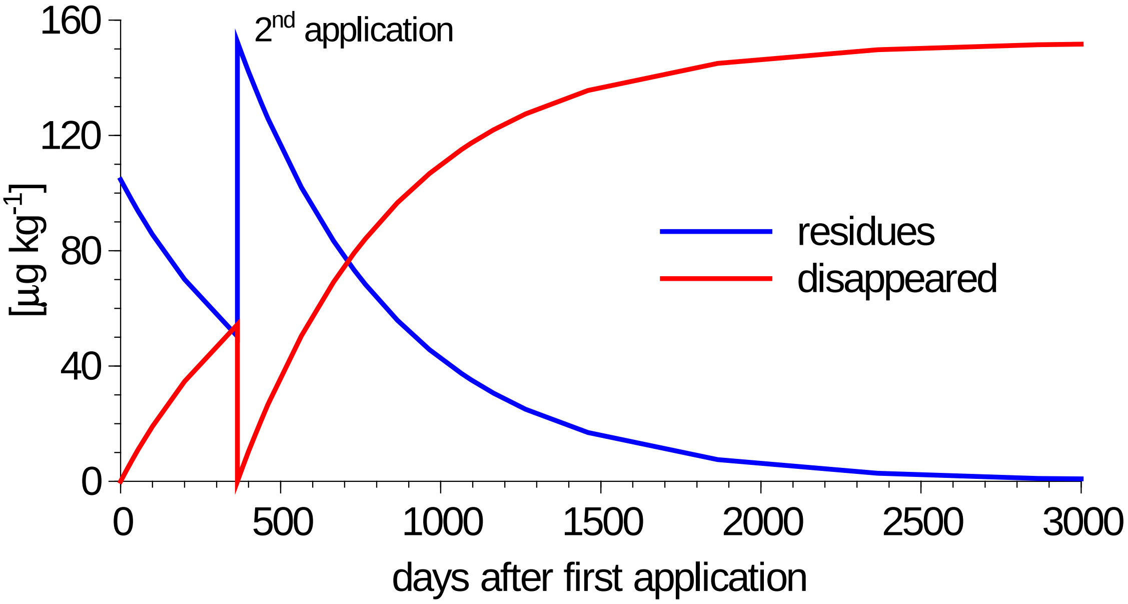

Figure 3: Residues and disappeared fraction [µg kg^{-1}] of boscalid after 1st application at day 0 and 2nd application at day 365. Calculation based on a *mean* DT_{50} of 345 days, a mean bulk density of 1.29 g cm^{-3}, and a mean ploughing depth of 28.7 cm.

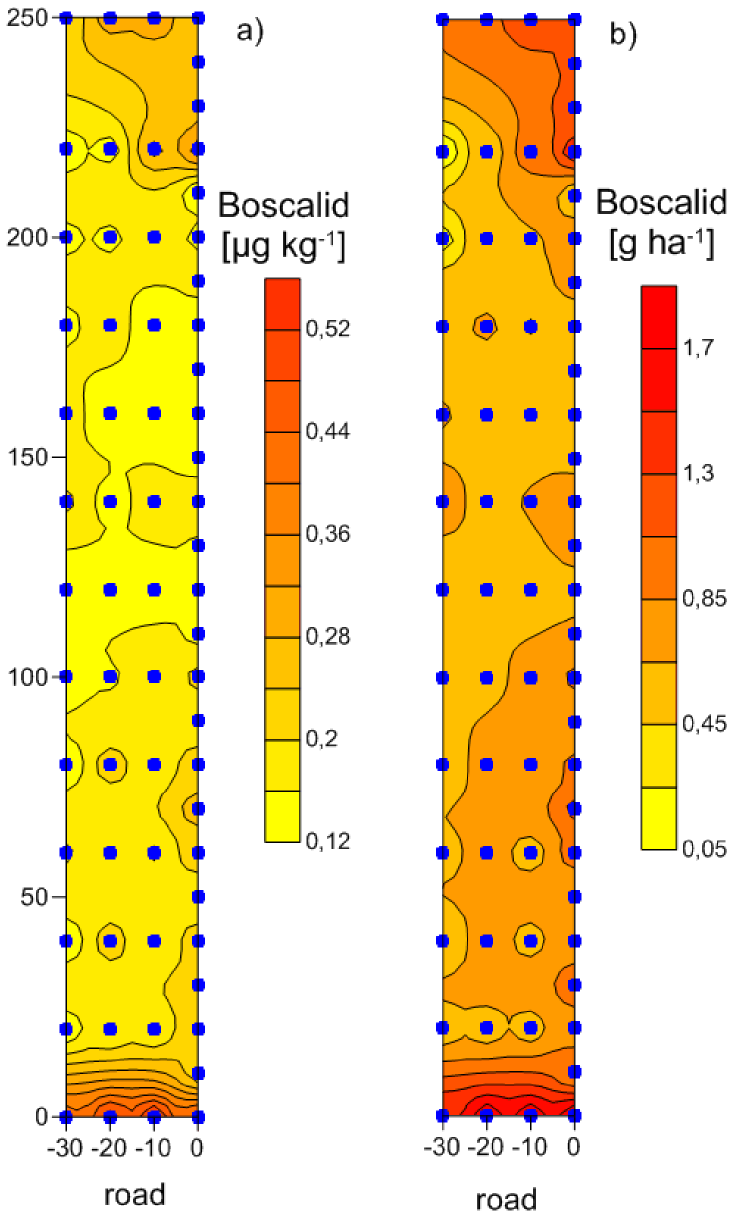

Figure 4: Field boscalid residues in a) [µg kg^{-1}] and b) [g ha^{-1}] taking point bulk densities into account (Fig. 2b) and assuming a mean plough horizon depth of 30 cm.