Chemosphere 145 (2016) 163–173

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

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

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HIGHLIGHTS

- Boscalid residues found in a sandy soil three years after last application.
- Boscalid concentrations were lower as expected from literature *DT₅₀* values.
- Field derived boscalid *DT₅₀* values are smaller as laboratory *DT₅₀* values.

ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form
5 November 2015
Accepted 7 November 2015
Available online 10 December 2015

Handling Editor: Klaus Kümmerer

Keywords:
Pesticide
Dissipation
Field experiment
Batch experiment
Boscalid

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 297–337 compared to the 345 days taken from literature. However, this DT_{50} value is still considerably larger compared to the 104–224 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.

1. 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 et 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 dissipation / 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

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http://dx.doi.org/10.1016/j.chemosphere.2015.11.026
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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 and 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 and 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 $\mu g\ kg^{-1}$ with a median of 2.1 $\mu g\ kg^{-1}$ and 33 $\mu g\ kg^{-1}$ in the suspended fraction (median 4.1 $\mu g\ kg^{-1}$). 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 and Orlando (2011) found large amounts of boscalid with up to 36 $\mu g\ L^{-1}$ 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 $\mu g\ L^{-1}$ (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 dissipation 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 additional dissipation data from a short term incubation experiment using the same soil.

2. Materials and methods

2.1. Study site

The study was conducted at an agricultural field in Kaldenkirchen in North Rhine-Westphalia, Germany (51.306687N, 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 Table 1. It has to be noted that the field was planted with leek during the sampling campaign.

2.2. 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 Table 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; Valleé 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 8–10 cm.

2.3. Soil sampling

Soil samples were taken at the nodes of a regular grid with spacings of 10 × 20 m among the nods on the 20th of April 2014. In total, four transects were sampled using a Humax auger (n = 65

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	Silt	Sand	C_{org}		
(<2 μm)	(2–63 μm)	(63–2000 μm)			
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).