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Deposition and residues of azoxystrobin and imidacloprid on greenhouse lettuce with implications for human consumption

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Abstract

Lettuce greenhouse experiments were carried out from March to June 2011 in order to analyze how pesticides behave from the time of application until their intake via human consumption taking into account the primary distribution of pesticides, field dissipation, and post-harvest processing. In addition, experimental conditions were used to evaluate a new dynamic plant uptake model comparing its results with the experimentally derived residues. One application of imidacloprid and two of azoxystrobin were conducted.

For evaluating primary pesticide distribution, two approaches based on leaf area index and vegetation cover were used and results were compared with those obtained from a tracer test. High influence of lettuce density, growth stage and type of sprayer was observed in primary distribution showing that low densities or early growth stages implied high losses of pesticides on soil. Washed and unwashed samples of lettuce were taken and analyzed from application to harvest to evaluate removal of pesticides by food processing. Results show that residues found on the Spanish preharvest interval days were in all cases below officially set maximum residue limits, although it was observed that time between application and harvest is as important for residues as application amounts. An overall reduction of 40–60% of pesticides residues was obtained from washing lettuce. Experimentally derived residues were compared with modeled residues and deviate from 1.2 to 1.4 for imidacloprid and azoxystrobin, respectively, presenting good model predictions. Resulting human intake fractions range from 0:045 kg_{intake} $kg^{-1}{}_{applied}$ for imidacloprid to 0,14 kg_{intake} $kg^{-1}{}_{applied}$ for azoxystrobin

Keywords: lettuce, leaf area index, vegetation cover, pesticide residues, food processing, human intake fraction

1. Introduction

With a global production of about 23 million tons in 2009 and an increase of 33% between 2000 and 2009, lettuce is one of the most important leafy vegetable crops in regard to human consumption (FAOSTAT, 2011). Today lettuce is grown almost everywhere around the world, with China, United States and Spain being the three largest producers (FAOSTAT, 2011). A European person for instance consumes on average 16.5 kg of lettuce per year representing 12% of the total vegetable diet (WHO, 2003). At the same time, lettuce was shown to be a crop with relatively high detection frequencies of pesticide residues compared to other crop types like fruits, cereals, or tubers (Cho et al., 2009). This trend was also observed in a study assessing six different crop types (Fantke et al., 2011b) in which lettuce, on average, was shown to have the highest human intake fractions of pesticides. Furthermore, in 2007, the German pesticide monitoring program detected pesticides in 69.4% of all analyzed lettuce samples ($n = 828$) and a total of 2% exceeding the maximum residue limit (MRL) allowed (BVL, 2007). Regarding the importance of lettuce consumption and the high pesticides residues reported, there is a need to evaluate how pesticides behave from the time of application until their intake via human consumption taking into account (i) the primary distribution of pesticides, (ii) field dissipation, and (iii) post-harvest processing.

Directly after application, pesticides are deposited on soil or on crops. The resulting deposition fractions are determined predominantly by crop species and growth stage. The more extensive the foliage, the larger is the deposited fraction intercepted by the crop (Hauschild, 2000). Leaf growth stage can be described by the leaf area index (LAI) defined as the sum of leaf area per unit ground area (m^2_{leaves} m^{-2}_{soil}). In previous studies, LAI has been measured to predict the deposition fractions on tomato crops and was shown to perform well in this regard (e.g. Antón et al., 2004; Juraske et al., 2007). However, in the case of lettuce, during medium and later growth stages intra- and inter-plant leaf overlapping occurs. This can lead to relatively high LAI values and to subsequent overestimation of deposition fractions on lettuce foliage. An alternative measure to estimate leaf growth stage and deposition fractions is the vegetative cover (VC) defined as the proportion of soil area covered by leaves (%) (Vaesen et al., 2001). This approach has already been used to evaluate both, growth stages and radiation light interception in lettuce canopies (Beccafichi et al., 2003; Tei et al., 1996; Archila et al., 1998).

After primary distribution, dissipation processes dominate the evolution of residues in crops until harvest. These processes depend on several factors including weather conditions, doses applied, chemical formulation, application method; and chemical phenomena as thermodegradation and photodegradation (Garau et al., 2002). Using MRLs as a measure to ensure product safety, governmental and international organizations like national environmental protection agencies, Codex Alimentarius Commission, World Health Organization (WHO), and Food and Agriculture Organisation of the United Nations (FAO) have regulated the use of pesticides by fixing MRLs for commercial purposes (Gupta et al., 2008). Another value which is usually fixed in order to comply with MRL is the pre-harvest interval (PHI). This value is usually fixed on country level and can be described as the time period (in days) between the last pesticide application and a safe harvest of the treated crop (Stephenson et al., 2006). Several studies have been conducted on pesticides dissipation on lettuce (Chen et al., 2004; Fenoll et al., 2008; Fenoll et al., 2009) with the majority of them focusing on testing if the established PHI ensures that residue levels are below MRL (Fenoll et al., 2008). The magnitude of residues in/on crops finally depends on post-harvest food processing steps which in most cases decrease residues (Cengiz et al., 2007). In the case of lettuce, which is usually directly consumed after washing, this step needs to be evaluated as it might influence the magnitude residues between harvest and consumption.

In this paper we therefore analyze pesticide fate dynamics on greenhouse lettuce treated by spray application from primary distribution to residues in lettuce ready for consumption. We determine LAI and VC curves as a function of time in order to predict and compare deposition fractions at any growth stage, we discuss initial mass distribution and residues in harvested lettuce, we determine field dissipation half-lives of applied pesticides, we further discuss influence of post-harvest food processing (washing), and their implications on human intake via consumption, and finally we compare experimentally derived residues in lettuce to results of a dynamic plant uptake model.

2. Materials and Methods

2.1. Field trial design

Lettuce plants, cultivar *Maravilla*, were cultivated from March to June 2011 in two similar (230 m^2) greenhouses located in the Institute of Agriculture and Food Research and Technology (IRTA), in Cabrils (Barcelona). Three different experiments (named A, B and C) with differences in crop density, crop duration and pesticide formulation applied, were carried out. Main crop features collected during the experiments are presented in Table 1.

Table 1

Characteristics of the three experiments carried out with lettuce plants.

	experiment A	experiment B	experiment C
pesticide applied	imidacloprid	azoxystrobin	azoxystrobin
date of planting (dd/mm/yy)	07/03/11	26/04/11	17/05/11
date of application (dd/mm/yy)	14/04/11	19/05/11	16/06/11
date of harvest (dd/mm/yy)	28/04/11	02/06/11	30/06/11
LAI/VC at planting day (m^2 m^{-2})/(%)	0.02/3.31	0.03/1.65	0.03/3.9
LAI/VC at application day (m^2 m^{-2})/(%)	4.05/60.2	1.40/14.5	5.59/60.4
LAI/VC at harvest day (m^2 m^{-2})/(%)	7.16/77.6	3.78/26.9	8.74/94.4
dry weight at application day (kg plant^{-1})	0.02	0.01	0.02
fresh weight at application day (kg plant^{-1})	0.33	0.24	0.47
water content at application day (%)	95	94	96
dry yield at harvest day (kg plant^{-1})	0.022	0.037	0.045
fresh yield at harvest day (kg plant^{-1})	0.73	0.96	1.04
density at harvest day (plants m^2)	7.6	3.2	7.6

For experiments A and C the plant area spacing considered was 0.40 m × 0.33 m while for experiment B it was 0.35 m × 0.90 m, which implies crop densities of 7.6 and 3.2 plants m^{-2}, respectively. Experiments A and C were carried out on soil, while experiment B was conducted in hydroponic culture. Treatments were carried out on 14th April, 19th May, and 16th June 2011 using a portable motor sprayer and the following commercial formulations: CONFIDOR® 20 LS (20% of imidacloprid) in experiment A; and ORTIVA® (25% of azoxystrobin) in experiments B and C. Spraying was carried out according to the Spanish recommended dose of 0.075% (imidacloprid) and 1 g L^{-1} (azoxystrobin) (MARM, 2011). A total consumption of 4, 3, and 3 L of pesticide solution were applied in experiment A, B and C, respectively. Lettuce samples were taken one hour after treatment and repeated after 1, 4, 7, and 14 days after application. After sampling, unwashed and washed lettuce samples were kept at -20ºC and stored until analysis. The analysis of pesticide residues were carried out at laboratory Applus+ in Lleida, Spain (Accredited by ENAC: register number 563/LE1047). A liquid chromatography device (HPLC), Varian, equipped with a triple quadrupole detector and C18 column 100 mm × 2.0 mm Pursuit XRs 3 (Varian) were used to detect imidacloprid and azoxystrobin.

2.2. Initial pesticide distribution

After application, the total pesticide amount undergoes initial distribution, namely a fraction lost from the sprayed area via wind drift, f_{drift}, and fractions depositing on lettuce leaves, f_{lettuce}, and on soil, f_{soil}. Drift fractions primarily depend on application technique and weather conditions. For greenhouse conditions, Antón et al. (2004) report a generic value of $f_{\mathrm{drift}} = 0.05$. In contrast, deposition fractions mainly depend on crop growth stage and species-specific canopy density (Linders et al., 2000). Deposition fractions onto soil over time can be estimated from both LAI and VC development. When LAI curves are available, f_{soil} as a function of time t is calculated as follows (Hauschild, 2000):

$$f_{\mathrm{soil}}(t) = (1 - f_{\mathrm{drift}}) \times \mathrm{e}^{-\mathrm{CCS} \times \mathrm{LAI}(t)} \qquad (1)$$

where CCS [-] is the substance capture coefficient, for which a value of 0.35 is suggested for pesticides sprayed as formulation according to Gyldenkaerne et al. (1999). When VC curves are available, f_{soil} for any point in time is calculated as follows:

$$f_{\mathrm{soil}}(t) = (1 - f_{\mathrm{drift}}) \times (1 - \mathrm{VC}(t)) \qquad (2)$$

From f_{drift} and $f_{\mathrm{soil}}(t)$ we finally derive f_{lettuce} as a function of time, i.e.

$f_{\mathrm{lettuce}}(t) = 1 - \left(f_{\mathrm{drift}} + f_{\mathrm{soil}}(t)\right)$, since all three fractions must sum up to 100%.

2.3. Leaf area index and vegetation cover

In order to calculate LAI and VC as a function of time, measurements have been carried out along the whole cultivation period of all three experiments. Lettuce samples were taken every two weeks. Measurements were done using a LI-COR (LI-3100) Area Meter device, capable of measuring the area of leaves (cm^2). VC calculations were done using the software GreenPix 0.3® (Casadesús et al., 2007) which counts the number of green pixels representing plant material from a photograph. Digital photographs, taken in zenithal orientation, were always taken at the day of analysis.

Several authors studied LAI and VC in relation to lettuce crop density. Their results for maximum achieved LAI and VC values at the day of harvest are presented in Table 2.

Table 2

Maximum LAI ($\mathrm{m}^2\ \mathrm{m}^{-2}$) and VC (%) as a function of lettuce plant density per m^2 at day of harvest as reported in different experimental studies.

plants m^{-2}	$\mathrm{LAI}_{\mathrm{max}}$	$\mathrm{VC}_{\mathrm{max}}$	reference
5.0	4.4	60.3	Beccafichi et al. (2003)
6.0	-	-	MARM (2006)
6.2	-	-	MARM (2006)
8.3	6.8	-	Carranza et al. (2009)

plants m^{-2}	LAI$_{max}$	VC$_{max}$	reference
10.0	6.1	84.6	Beccafichi et al. (2003)
12.5	-	-	MARM (2006)
13.3	13.5	-	Archila et al. (1998)
15.0	7.8	94.9	Beccafichi et al. (2003)
17.6	12.7	-	Tei et al. (1996)
24.5	-	-	Santos Filho et al. (2009)
30.0	12.9	99.3	Beccafichi et al. (2003)

2.4. Tracer test

In order to obtain data on the magnitude of pesticide deposited on lettuce foliage at different plant growth stages, experimental tracer tests were conducted. Several methods have been developed and presented in the literature to objectively asses the quality of distribution of pesticides on the plant surface including analytical methods, fluorimetric methods, colorimetric methods or artificial methods based on digital imaging (Gyldenkaerne et al., 1999; Sánchez-Hermosilla et al., 2007; Cabello García et al., 2007). Here, we use a tracer test which is detected and evaluated digitally as performed in the calculation of VC. The tracer experiment was carried out during experiments B and C from April to June of 2011 involving the application of water with an indicator (methylene blue) in various applications. The use of this indicator allows for the detection of the total quantity deposited on lettuce leaves and of that deposited on soil by measuring the blue pixels using the software GreenPix 0.3®. In order to collect and detect the tracer on the ground, the soil around lettuce heads was covered with white plastic foil stripes (35 × 90 cm^2). (Fig. 1). Several tracer applications (n = ???) were conducted in each cultivation row of the plot at the same days the samples and photographs were taken for LAI and VC calculations.

< Fig. 1 >

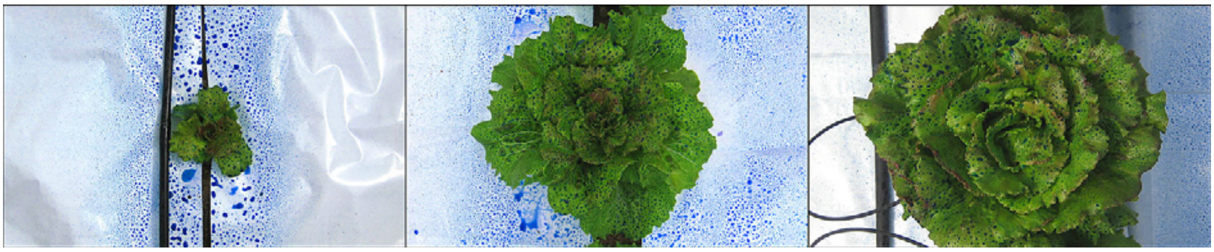

Fig. 1. Distribution of tracer on lettuce at days of planting (left), pesticide application (center) and harvest (right).

2.5. Post-harvest processing and human intake

The fraction of total applied pesticide amount that human population takes in via food ingestion is defined as intake fraction iF ($\text{kg}_{\text{intake}}\ \text{kg}_{\text{applied}}^{-1}$). We calculate intake fractions from pesticide residues on harvested lettuce leaves m_{residue} ($\text{kg}_{\text{residue}}\ \text{ha}^{-1}$) at harvest time t, the applied pesticide mass m_{applied} ($\text{kg}_{\text{applied}}\ \text{ha}^{-1}$) and the factor fp ($\text{kg}_{\text{intake}}\ \text{kg}_{\text{residue}}^{-1}$) reducing the pesticide residues in lettuce due to food processing for human intake:

$$\text{iF}(t) = \frac{m_{\text{residue}}(t)}{m_{\text{applied}}} \times fp \qquad (3)$$

Washing has been considered the exclusive food processing step for lettuce, for which samples of washed lettuce were analyzed as part of the experimental study to evaluate the reduction of pesticide residues.

2.6. Model setup for evaluation

A dynamic assessment model (dynamiCROP) for uptake of pesticides into cereals and subsequent human intake has been developed by Fantke et al. (2011a) based on a transparent matrix algebra framework. This model was extended to include six mayor crop types covering a large fraction of the worldwide human consumption of vegetal origin, thereby representing the most important crop archetypes with lettuce as representative of leafy vegetables (Fantke et al., 2011b). We applied this model for lettuce to evaluate experimentally derived initial mass conditions and residues in harvest for the two assessed pesticides. As measure to estimate model prediction quality compared with experiments we applied the standard error of the log of residuals, between measured and modeled residues. A standard error of e.g. 0.1 implies a deviation between measured and modeled residues of approximately a factor 1.5 (Hamburg and Young, 1994).

3. Results and discussion

3.1. Development of leaf area index and vegetation cover

Experimentally derived LAI and VC values as a function of time measured during experiments A, B, and C are presented in Fig. 2.

< Fig. 2 >

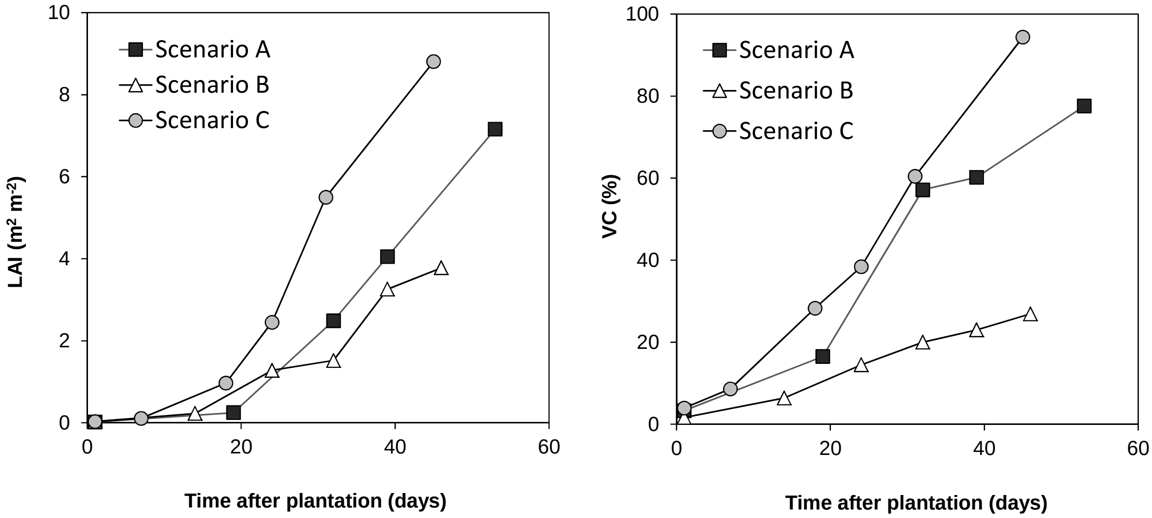

Fig. 2. LAI (m^2 m^{-2}) and VC (%) as a function of time measured during experiments A, B and C.

On average, LAI values range from 0.02 (experiment A) at the day on planting to 8.81 (experiment C) at the day of harvest. VC values range from 2% (experiment B) to 94% (experiment C) for planting and harvest day, respectively. LAI and VC values measured during experiment B are always lower than those observed in experiments A and C in which plant density was twice as higher. Herewith it can be concluded that higher plant densities directly imply higher LAI and VC values. Differences in LAI and VC values obtained with the same plant density (experiments A and C) were due to varying weather conditions (higher temperatures leading to faster growth and higher LAI and VC values). Maximum LAI during experiments A, B, and C were 7.16, 3.78, and 8.81 while corresponding VC values were 78%, 27%, and 94%. On average, LAI was shown to be a factor 2.1 higher between experiments B and C, while for CV the corresponding factor was 2.5. At the day of harvest, this factor was shown to be 2.3 and 3.5, respectively.

The linear relationship between plant growth indicators like LAI and VC and plant density shown in this study was also observed in earlier studies (see Table 2). Beccafichi et al. (2003) evaluated the relationship between crop density and LAI and VC parameters and concluded that there is a linear increase of LAI and VC with increasing plant density. Their studies were conducted during winter and maximum LAI reported are similar to those obtained in experiment A of this study. On the other hand, results reported by Carranza et al. (2009) are lower than in the current study although the lettuce density was higher. This can be explained by the fact that plants were grown in poor saline soil leading to lower growth rates. Studies by Tei et al. (1996) and Archila et al. (1998) reported higher lettuce densities and subsequently also higher LAI values.

In order to calculate general dynamic LAI and VC equations, data from experiments A and C (i.e. crop density of 7.6 plants per m^2) were fitted using a logistic growth function, resulting in the following equations:

$$\mathrm{LAI}(t) = \frac{8.5}{1 + \mathrm{e}^{6.20 - 0.19 \times t}}; \ \mathrm{R}^2 = 0.99 \qquad (4)$$

$$\mathrm{VC}(t) = \frac{0.9}{1 + \mathrm{e}^{3.46 - 0.13 \times t}}; \ \mathrm{R}^2 = 0.99 \qquad (5)$$

Results obtained in experiment B were rejected from the analysis as they do not represent conventional production practices for lettuce.

3.2. Deposition fractions and initial mass distribution

Fractions deposited on lettuce leaves f_{lettuce} after azoxystrobin sprayed on 3.2 plants per m^2 (experiments B) and 7.6 plants per m^2 (experiment C) as measured in the tracer test are presented in Table 3 to evaluate the influence of crop density on deposition fractions. At application time, we measured $f_{\text{lettuce}} = 0.23$ for experiment B and $f_{\text{lettuce}} = 0.50$ for experiment C, i.e. respectively 23% and 50% of the total quantity of pesticide applied deposited on lettuce. Multiplying f_{lettuce} with the pesticide amount applied (mg ha^{-1}) and normalizing for the lettuce fresh weight (kg ha^{-1}) yields initial quantities deposited on lettuce of 3.82 mg kg^{-1} and 3.65 mg kg^{-1} for experiments B and C, respectively. 1 hour after application, analytical samples showed for experiment B 3.64, 4.04 and 3.99 mg kg^{-1} with a mean of 3.89 ± 0.18 mg kg^{-1}, and for experiment C 4.11, 3.65 and 3.67 mg kg^{-1} with a mean of 3.81 ± 0.21 mg kg^{-1}. Variations are in both cases less than 5%, i.e. 1.83% for experiment B and 4.38% for experiment C. However, remaining uncertainties in the tracer test have been identified to be mainly related to varying spray droplet size.

Some differences are found for experimental f_{lettuce} between experiments B and C at different days showing the influence of crop density on plant deposition fractions. Until 25 days after planting similar experimental f_{lettuce} are found for both experiments with a deviation of around 8%. After 25 days onwards, differences increase and reach a maximum deviation at harvest day, where $f_{\text{lettuce}} = 0.45$ was obtained from experiment B and $f_{\text{lettuce}} = 0.95$ from experiment C with a total deviation of 41%.

Results from the tracer test for low density crops show that more than half of quantity sprayed would reach the soil even for developed growth stages mainly due to the type of sprayer which is not adaptable to space between plants. For higher densities as shown in experiment C, the quantity applied would mostly reach the plant for the same type of sprayer proving that deposition on lettuce depends on growth stage, plant density and also on type of sprayer.

Table 3

Fractions of azoxystrobin deposited on lettuce leaves for experiments B and C measured from the tracer test and calculated according to (1) as a function of LAI and according to (2) as a function of VC.

	f_{lettuce} (experiment B)			f_{lettuce} (experiment C)		
days after planting	measured	f(LAI)	f(VC)	measured	f(LAI)	f(VC)
10	-	-	-	0.08	0.04	0.09
14	0.15	0.08	0.14	-	-	-
23	-	-	-	0.25	0.32	0.33
24[a]	0.23	0.36	0.36	-	-	-
30[b]	-	-	-	0.50	0.64	0.62
32	0.35	0.71	0.57	-	-	-
45	0.45	0.88	0.78	>0.95	0.88	0.78

[a]application day of experiment B; [b]application day of experiment C

Table 3 also summarizes f_{lettuce} for experiments B and C at different points in time calculated according to (1) with LAI(t) estimated with (4) as well as calculated according to (2) with VC(t) estimated with (5). Calculated values of f_{lettuce} for experiment B show an overall deviation from measured results of 58.4% for LAI based calculations and 31.1% for VC based calculations. Higher differences between modeled and experimental results are found for experiment B with a density of 3.2 plants per m^2, which was only used for evaluating the influence of crop density on lettuce LAI and VC development, since it does not comply with common agricultural practice (MARM, 2006). Hence, crop density in experiment B was not considered in (4) and (5) for estimating LAI(t) and VC(t), respectively. Correspondingly, the reduced deviation between experiment C and modeled results is attributable to the higher crop density of 7.6 plants per m^2. However, although decreasing crop density per m^2 also decreases crop yield (Moniruzzaman, 2006), the implications of reduced pesticide deposition fractions reaching the lettuce surface should be considered for future agricultural practice in respect of human health. The relation between pesticide application amount and crop design was studied by Escolà (2010) proposing to calculate optimal application amounts as a function of LAI and crop density.

Generally, predictions overestimate deposition fractions reaching lettuce compared to experimental results starting around 20 days after plantation, thereby indicating that applying a generic drift fraction might lead to underestimating losses to air. However, results are considerably lower, if calculated as a function of VC compared to results calculated as a function of LAI. This trend is particularly relevant for 45 days after plantation onwards in experiment C, where calculated results as a function of VC start to be below measured values.

Using the LAI approach leads to high predictions of pesticides deposited on lettuce at final growth stages (12%), since LAI reflects an increased vegetative growth compared to using the area covered by the crop only. In earlier crop stages, however, doses reaching lettuce are higher, if the VC approach is applied. The foliar architecture of lettuce can explain these differences; in early stages, few leaves have more open arrangement leading to a higher value for VC compared to LAI, whereas at final stages, this relationship reversed by the head development structure of the plant (see Fig. 1).

3.3. Development of residues in harvest

Pesticide residues in lettuce leaves at different points in time (1 hour and 1, 4, 7 and 14 days after application) are presented in Fig. 3 for experiments A, B and C. Since measured residues follow a general first order decrease with time, first order kinetics are assumed in all experiments for estimating overall degradation half-lives in lettuce. We calculated half-lives

HL (d) from the bulk degradation rate constant k (d^{-1}) in $C(t) = C(0) \times \mathrm{e}^{-k \times t}$ with C [mg kg^{-1}] as pesticide concentration in lettuce according to $\mathrm{HL} = \ln(2)/k$.

For imidacloprid (experiment A), residues range from 5.97 mg kg^{-1} at 1 hour after application to 0.69 mg kg^{-1} at 14 days after application, from which a half-life in lettuce of 4.36 days was obtained ($\mathrm{R}^2 = 0.99$). For azoxystrobin applied to lettuce grown in line with common agricultural practice (experiment C), residues decreased from 3.81 mg kg^{-1} at 1 hour after application to 1.35 mg kg^{-1} at day 14 after application, yielding a half-life in lettuce of 11.2 days ($\mathrm{R}^2 = 0.86$). For azoxystrobin applied to lettuce with smaller crop density per m^2 (experiment B), residues range from 3.89 mg kg^{-1} at 1 hour after application to 1.48 mg kg^{-1} at 14 days after application, from which we derived a half-life in lettuce of 10.2 days ($\mathrm{R}^2 = 0.95$). The higher accuracy of predicting half-life of azoxystrobin in lettuce from residues in experiment B than in experiment C might be a result of the high temperature in the greenhouse of 30°C at day 1 after application in experiment C leading to increased degradation processes at that time. Acceleration of pesticide degradation by temperature is discussed e.g. in Beulke et al. (2005). However, standard deviations for measured residues are highest for day 1 after application in both experiments B and C (see Fig. 3), indicating that sampling uncertainties might also play a role for the accuracy in estimating half-lives. In contrast, no differences were found between hydroponic and soil design in azoxystrobin experiments.

< Fig. 3 >

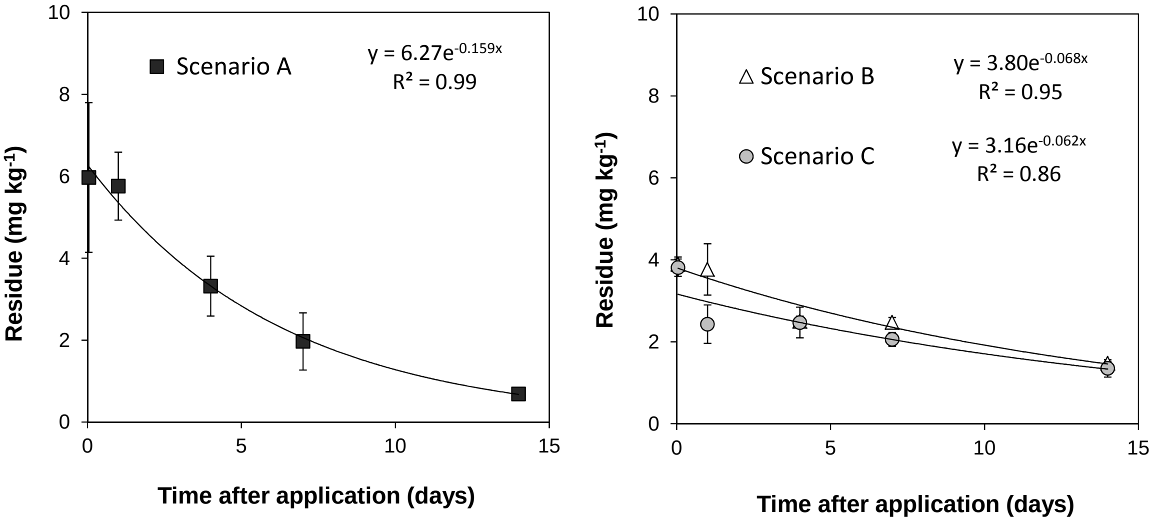

Fig. 3. Evolution of residues in lettuce (mg kg^{-1}) for experiments A, B and C.

Official European maximum residue levels in lettuce are MRL = 3 mg kg^{-1} for azoxystrobin and MRL = 2 mg kg^{-1} for imidacloprid (EC, 2005), and recommended minimum pre-harvest intervals according to Spanish legislation are PHI = 7 days for both pesticides (MARM, 2011). In all experiments, mean residues ($n = 3$ for each experiment and day) in lettuce at recommended PHI are below official MRLs. However, for spray application onto lettuce, a PHI of 3 days was found for imidacloprid in Spain (FAO, 2002) and 14 days for azoxystrobin in France, Germany and The Netherlands (FAO, 2009). Applying these PHI values in the present experiments would yield in imidacloprid residues exceeding the official MRL, whereas azoxystrobin residues would broadly comply with official MRLs. These results suggest that for residues in lettuce, the time between application and harvest is at least as important as application amounts. Consequently, similar application amounts will lead to residues exceeding official MRLs in cases where pre-harvest intervals are too short. To comply also with the MRL for imidacloprid in lettuce, we derive a PHI of almost 7 days from experiment A.

3.4. Food processing factors and human intake fractions

Food processing factors due to washing lettuce after harvest of $fp = 0.44$ (56% removed), $fp = 0.47$ (53% removed) and $fp = 0.57$ (43% removed) are obtained for experiment A with imidacloprid and experiments B and C with azoxystrobin, respectively. Our results are in accordance with other studies, in which washing reduces pesticide residues in lettuce e.g. by 30% for malathion (Leyva et al., 1998) or by 64% for permethrin (Holland et al., 1994), thereby indicating that food processing factors vary between substances applied to same crop.

Experimental processing factors of $fp = 0.25$ (75% removed) for washing azoxystrobin and imidacloprid residues from grapes (Lentza-Rizos et al., 2006; Spiegel, 2001) and $fp = 0.78$ (22% removed) for washing imidacloprid from tomatoes (Juraske et al., 2009) were reported. Since these factors are significantly higher than our processing factors for lettuce, it can be concluded that experimental processing factors show large variation when applied to different crop surface structures.

For finally calculating human intake fractions iF (kg_{intake} $kg_{applied}^{-1}$) from consumption of washed lettuce, we consider the amount of 219 g ha^{-1} applied imidacloprid (experiment A) as well as 261 g ha^{-1} and 127 g ha^{-1} applied azoxystrobin (experiments B and C, respectively), a time between pesticide application and crop harvest of 14 days in all our experiments and food processing factors of 0.44 for imidacloprid and 0.50 for azoxystrobin. Human intake fractions range from 0.045 kg_{intake} $kg_{applied}^{-1}$ via 0.17 kg_{intake} $kg_{applied}^{-1}$ to 0.14 kg_{intake} $kg_{applied}^{-1}$ for experiments A, B and C, respectively. Fenoll et al. (2008) reported experimental residue up to 7 days after application of 204 g ha^{-1} azoxystrobin on lettuce of 1.05 mg kg^{-1}. To compare results from Fenoll et al. (2008) with our experiments, we extrapolated their residues to arrive at 14 days after application and considered our processing factor for azoxystrobin due to washing, with what we would obtain an intake fraction of 0.13 kg_{intake} $kg_{applied}^{-1}$, which is in line with our experimental results.

3.5. Comparison with model results

To compare measured residues with model results, we introduced experimental application amounts, days of plantation, pesticide application and harvest, measured lettuce characteristics and degradation half-lives in lettuce in the modeling approach. Furthermore, we implemented the calculation of initial mass conditions on the one hand as a function of LAI development according to (1) and (4) as well as on the other hand as a function of VC development according to (2) and (5) to contrast both approaches with respect to their accuracy in predicting pesticide residues in lettuce.

Fig. 4 shows both measured and modeled residues at different points in time for experiments A, B and C. Experimental and modeled residues deviated between a factor 1.2 when using LAI for modeling residues in experiment A and a factor 1.4 when using LAI for modeling residues in experiment C. Standard errors of the log of residuals are 0.031, 0.071 and 0.074 when using LAI for modeling residues in experiments A, B and C, respectively, and 0.059, 0.067 and 0.073 when using VC for modeling residues in experiments A, B and C, respectively. Highest deviations between measured and modeled results are found between 1 hour and 1 day after application of azoxystrobin in experiment C. A relatively high temperature at day 1 after application in experiment C is leading to increased degradation compared to modeled degradation. This demonstrates the influence of varying environmental and weather conditions on model accuracy, where boundary conditions are usually kept constant.

< Fig. 4 >

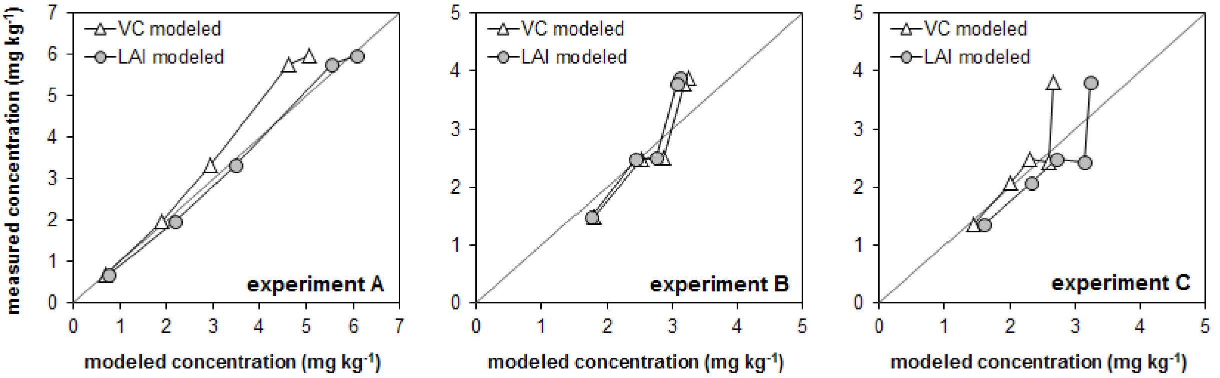

Fig. 4. Comparison of measured residues in lettuce at different days after application for experiments A, B and C with model results using LAI and VC for estimating initial mass distribution.

Results indicate that neither LAI nor VC can generally be seen as the more accurate measure to estimate leaf area for lettuce, since for imidacloprid modeled residues are less deviating from measurements, if LAI is used in the model to estimate leaf area (Fig. 4, experiment A), whereas for azoxystrobin modeled residues show higher correlation with measurements, if VC is used in the model to estimate leaf area (Fig. 4, experiments B, C). However, using LAI yields different fractions deposited onto lettuce leaves compared to using VC in the model, thereby emphasizing its influence on the final residues over time. In the model, different rate constants are competing for residual pesticide mass in lettuce. Since it will depend on the substance properties to choose the correct approach to estimate leaf area growth and finally the fraction deposited on lettuce and soil. More specifically, whenever a pesticide degrades quicker than it is taken up via the root system, the fraction deposited on soil becomes important, which is the case for both studied substances. However, for pesticides with very short degradation half-lives in lettuce, the fraction deposited on soil becomes insignificant; for such substances, both measures LAI and VC lead to very similar residues in lettuce, since the transfer from soil to roots dominates the system dynamics, which is in line with the findings from Fantke et al. (2012).

4. Conclusions

From this study it can be concluded that both LAI and VC can be used in the prediction of pesticide deposition fractions and subsequent estimation of residues on lettuce foliage. Both measures lead to very similar residues indicating that neither LAI nor VC can generally be seen as the more accurate measure. Through field experiments increasing plant density was shown to directly influence the deposition fraction. Based on experimental data dynamic LAI and VC equations were derived using logistic growth functions. Pesticide residues dynamics were shown to follow first order decay from which half-lives of azoxystrobin and imidacloprid were derived. In all experiments, at recommended PHI, mean residues in lettuce were below official MRL. Experimental and modeled residues corresponded well and deviated up to a factor of 1.4.

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