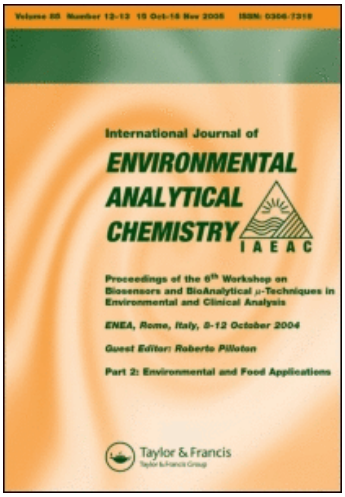

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Dissipation rates of procymidone and azoxystrobin in greenhouse grown lettuce and under cold storage conditions

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Dissipation rates of procymidone and azoxystrobin in greenhouse grown lettuce and under cold storage conditions

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The dissipation of two fungicides (procymidone and azoxystrobin) was evaluated in greenhouse grown lettuce and under cold storage conditions. Lettuce samples were collected from an experimental greenhouse during a five week period, in which two consecutive applications of these pesticides were performed. Gas chromatography (GC) with electron-capture detection (ECD) was used to study the disappearance of these compounds in lettuce. Confirmation analysis of pesticides was carried out by capillary gas chromatography coupled with mass spectrometry in the selected ion monitoring (SIM) mode. The disappearance rates of these compounds on lettuces in field after two applications were described as pseudo-first-order kinetics with strong correlation between residue concentration and time (r was in all cases higher than 0.983). The half-lives for first and second applications were of 5.31 and 4.65 days for procymidone and 6.23 and 4.87 days for azoxystrobin, respectively. When procymidone and azoxystrobin were applied two times during cultivation, at maximum recommended dose, the residues of both pesticides were below maximum residue limits (MRLs) after the established preharvest intervals. After 21 days under cold and darkness storage conditions, dissipation of procymidone and azoxystrobin was not observed.

Keywords: procymidone; azoxystrobin; lettuces; residues; fungicides; disappearance; refrigeration

1. Introduction

Pesticides are chemical substances that are widely used in agriculture to control pest and diseases that damage fruit and vegetables. Thus, the use of pesticides during cultivation plays an important role in harvest quality and food protection [1]. However, the presence of pesticide residues in food constitutes a possible risk to the consumer, because of their toxic effects to human health [2,3].

The dissipation of these agrochemicals after their application depends on several factors, such as the applied dose and formulation, application parameters, the number of applications, climatic conditions, the species cultivated, physical phenomena and chemical degradation [4–7]. Therefore, dissipation studies for a given crop in the specific conditions

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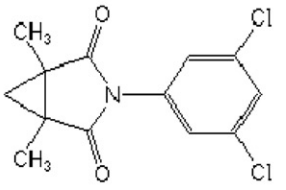
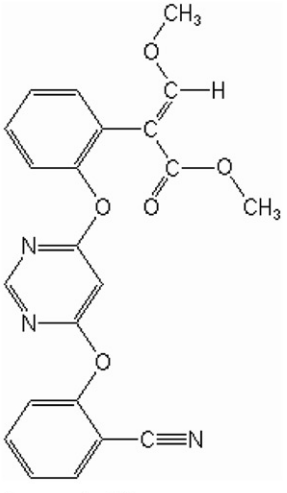


Procymidone



Azoxystrobin

Figure 1. Molecular structures of procymidone and azoxystrobin.

of each growing area are necessary to test if the established preharvest time (PT) ensures that residue levels are below the maximum residue limit (MRL).

Procymidone (*N*-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide) (Figure 1) is a dicarboximide fungicide with moderate systemic activity and commonly used for the protection of fruits and vegetables. It is used against botrytis and sclerotinia on field crops [8]. Azoxystrobin, (methyl (*E*)-2-{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate; Figure 1) is a recently developed strobilurin fungicide, used for the control of powdery mildew, downy mildew and sclerotinia in different fruits and vegetables [8]. In Spain, both fungicides are known to be registered in lettuce cultivation [9]. Lettuce (*Lactuca sativa* L.) is an important horticultural crop in the region of Murcia (southeast Spain), with almost 10,000 ha dedicated to its cultivation [10]. Studies on the dissipation behaviour of these fungicides on grapes, green beans, strawberries, apricots and tomatoes are reported in the literature [11–19], while to our knowledge no study has been carried out on lettuces. It is for that reason that our objective in this study has been to increase our knowledge in the dissipation of these fungicides in the field and in a cold chamber. The field experiment was carried out in a greenhouse, under the particular climatic conditions of Murcia (Spain).

2. Experimental

2.1 *Plant material*

Lettuce (*Lactuca sativa L.*, var. Lorciva) was planted in December 2006 in a greenhouse of an area of 300 m^2 situated in Torre Pacheco (Murcia, southeast, Spain). The plant spacing was of 75 cm × 25 cm. Plants were irrigated by drip irrigation with a total water volume of 135 $L\,m^{-2}$. Synthetic fertilizers were applied with each irrigation. Total amount of nutrients added throughout the growing season were 70 kg $N\,ha^{-1}$, 92 kg $P_2O_5\,ha^{-1}$, 220 kg K_2O ha^{-1}, 22 kg Ca $ha^{-1}$and 7 kg Mg ha^{-1}. The relative humidity during first and second applications were 23% and 24% with a temperature of 22°C and 20°C, respectively.

2.2 *Field trial*

For the field experiment, a random block scheme was used with five replications for each test; each block contained 25 plants in a single row. Treatments were carried out with a sprayer (Matabi) with an adjustable nozzle size of 1 mm. The commercial formulation: Asbelto WP (50% procymidone) and Ortiva SC (25% azoxystrobin) were used. Two applications were carried out on 13 February 2007 and 28 February 2007, respectively, at the maximum doses recommended by the manufacturers (100 g hL^{-1} for procymidone and 100 mL hL^{-1} for azoxystrobin) and the application rates of 408 g of active ingredient (ai) in 816 g ha^{-1} (procymidone), and 204 g of active ingredient (ai) in 816 mL ha^{-1} (azoxystrobin). The recommended intervals between applications according to Spanish Ministry of Agriculture, Fisheries and Food [9] are 15–20 days for procymidone and 10–12 days for azoxystrobin. Before the first application, samples of lettuces with similar ripening stage, size, and shape were located and tagged. Samples (15 kg) were taken 2 h after first application and then after 1,3,7 and 14 days. Afterwards, samples were collected 2 h after second application and then after 1,3,7 14 and 21 days. During the experiment, a control sample was taken in each sampling time. Immediately after collecting the lettuces, the samples were homogenised in a food processor (Thermomix, Vorwerk). The homogenate of each sample was then placed into polyethylene containers and frozen at −30°C.

2.3 *Refrigeration assay*

For the refrigeration experiment, lettuces (40 kg) were collected 2 h and seven days after first application and seven days after second application. The samples gathered 2 h after the first application represents collection without following good agricultural practices (GAP) since PT was not expired. On the contrary, samples gathered seven days after the first and the second treatments represents fruit recollection according to GAP. Samples were placed in the cold chamber at 4°C and in darkness. Samples for analysis were taken 3,7,14 and 21 days after they were placed in the chamber. According to other authors [20], total storage time was established as 21 days since 2–3 weeks is the normal period for lettuce storage.

2.4 *Chemicals*

Pesticide standards were obtained from Dr Ehrenstorfer (Augsburg, Germany) with purity higher than 98%. The solvents acetone, ethyl acetate and cyclohexane, were of residue analysis grade and purchased from Scharlau (Barcelona, Spain).

2.5 *Gas chromatographic analysis*

GC-ECD analysis was performed with an Agilent (Waldbronn, Germany) model HP 6890 gas chromatograph equipped with an electron-capture detector and automatic split-splitless injector model Agilent 7683 (autosampler). An HP-5MSI fused silica capillary column (30 m × 0.25 mm i.d.) and 0.25 μm film thickness, supplied by Agilent Technologies, was employed, with nitrogen as makeup gas at 25 mL min^{-1}. Helium was used as the carrier gas (constant pressure eluting, bromophos 20.08 min). A 1 μL sample was injected into the GC using splitless mode. The injector and detector were operated at 250°C and 325°C, respectively. The column temperature was maintained at 70°C for 2 min and then programmed at 25°C min^{-1} to 150°C, increased to 200°C at a rate of 3°C min^{-1} followed by a final ramp to 280°C at a rate of 8°C min^{-1}, and held for 10 min. The total analysis time was 41.87 min and the equilibrium time 2 min.

An Agilent model HP 6890 gas chromatograph equipped with a model 5973N mass spectrometric detector was operated in electron impact ionisation mode with an ionising energy of 70 eV, scanning from m/z 50 to 500 at 3.21 s per scan. The ion source temperature was 230°C and the quadrupole temperature 150°C. The electron multiplier voltage (EM voltage) was maintained at 1300 V, and a solvent delay of 4.5 min was employed. Gas chromatography was performed under the same conditions used in GC/ECD.

Analysis was performed with selected ion monitoring (SIM) mode using primary and secondary ions. Table 1 lists the pesticides along with their retention times, molecular mass, the target and qualifier ions, and their qualifier to target abundance ratios. The target and qualifier abundances were determined by injection of individual pesticide standards under the same chromatographic conditions using full scan with the mass/charge ratio ranging from m/z 45 to 500. Pesticides were confirmed by their retention times, the identification of target and qualifier ions, and the determination of qualifier-to-target ratios. The qualifier-to-target ion percentage was then determined by dividing the abundance of the selected qualifier ion (Q) by the target ion (T) and multiplying by 100. Retention times had to be within ±0.1 min of the expected time, and qualifier-to-target ratios had to be within a 10% range for positive confirmation.

Table 1. Retention time (RT, min), molecular weight (MW), target ions (T), qualifier ions (Q_1, Q_2 and Q_3) (m/z) and abundance ratios (%) of qualifier ion/target ion (Q_1/T and Q_2/T)* of the studied pesticides.

Pesticide	RT	MW	T	Q_1	Q_2	Q_3	Q_1/T	Q_2/T
Procimidone	21.96	284.1	96	283	285	67	70	47
Azoxystrobin	36.72	403.4	344	388	345	372	30	29

Notes: *Q/T (%) ratios are the results of abundance values of the qualifier ion (Q_1, Q_2) divided by the abundance of the target ion (T) × 100.

2.6 *Extraction procedure*

Pesticide was extracted according to the procedure previously described by Fenoll and colleagues [21]. A 10 g representative portion of the sample was transferred into a 100 mL beaker and homogenised with 20 mL of acetone by means of a Polytron mixer for 2 min. After homogenisation, 20 mL of ethyl acetate/cyclohexane (1/1, v/v) were added and then centrifuged for 10 min at 4000 g. Extract was filtered quantitatively through a glass funnel containing a filter paper DP302,150 mm diameter (Albet, Barcelona, Spain). The organic phase was concentrated to dryness by evaporator and the residue was re-dissolved in an appropriate volume with ethyl acetate/cyclohexane (1/1, v/v).

2.7 *Recovery assays*

Untreated lettuce samples were crushed and homogenised before being spiked with fungicides. Recovery assays were performed in the 0.05–0.30 mg kg^{-1} range. The quantification of recovery was carried out with standards dissolved into pure solvent (there is not a matrix effect with the detector used, ECD). The samples were processed according to the above procedure. At each fortification level, five replicates were analysed.

2.8 *Statistical analysis*

Statistical analyses were done using the Statistical Package for Social Sciences (SPSS 10.0) program.

3. Results and discussion

3.1 *Analytical determination*

The ECD response was linear in the concentration assayed (0.05–2 μg mL^{-1}) with correlation coefficients >0.999 for procymidone and azoxystrobin.

Blank lettuce samples were used to establish the detection (LOD) and quantification (LOQ) limits for each fungicide by GC/ECD. The LODs and LOQs of the proposed method were determined at a signal-to-noise signal ratio 3 and 10, respectively, for the individual pesticides in lettuce. The limits of detection and quantitation were 0.8 and 2.7 μg kg^{-1} for procymidone and 0.4 and 1.3 μg kg^{-1} for azoxystrobin, respectively.

The repeatability of the chromatographic method was determined by analysing the vegetable spiked at 0.2 μg g^{-1}. The sample was injected 10 times with an automatic injector. The relative standard deviation (RSD) values obtained by GC-ECD for peak areas were 2.9 and 4.5% for procymidone and azoxystrobin, respectively, whereas for the retention time they were 0.01 and 0.02%.

Recovery results of the two pesticides are shown in Table 2. The recoveries obtained from lettuce ranged from 77.6 to 99.3%. The relative standard deviation (RSD) was $<4.5\%$ in the most unfavourable case. These results demonstrate the good performance of the method.

3.2 *Dissipation field study*

Figure 2 shows the residual values of procymidone and azoxystrobin in the field samples of lettuces after the two applications. We note that after two consecutive applications

Table 2. Mean recoveries (%)[a] and RSD of the fungicides from lettuce at various fortification levels.

Fungicide	Fortification level (mg kg^{-1})	Recovery ± RSD[b] (%)
Procymidone	0.05	77.6 ± 2.8
	0.15	83.4 ± 4.5
	0.30	82.6 ± 3.1
Azoxystrobin	0.05	96.3 ± 2.6
	0.15	97.5 ± 3.0
	0.30	99.3 ± 3.8

Notes: [a]$n = 5$; [b]RSD = relative standard deviation.

with 15 days interval between them, accumulative effects of these fungicides were observed in lettuce 0 and 1 days after application. In the literature, we have found no studies concerning their dissipation in lettuces. On the basis of the linear fit carried out, the residue dissipation rate in lettuces was derived by fitting the experimental data to a pseudo first-order kinetic function [22]:

$$\frac{-\mathrm{d}[R]}{\mathrm{d}t} = k[R]$$
$$\ln[R] = \ln[R_0] + kt (\text{general formula } y = a + kt)$$

where (R) is the mean residue levels in lettuces at t days after treatment, (R_0) is the initial concentration of residue and (k) is the degradation rate constant. To test the correlation coefficient (r) obtained, a test quantity (D) was calculated to ascertain whether there was a correlation between residue and time; that is, whether the correlation coefficient differed significantly from zero:

$$D = r - t[t^2 + (n-2)]^{-0.5}$$

where r is the absolute value of the correlation coefficient and t is the value of t, for $n-2$ d.f., in the table of Student-t distribution at the contrasted level of probability.

Table 3 shows the values of the theoretical initial residue (R_0), half-life ($t_{1/2}$), the theoretical residual level corresponding to the preharvest times (R_{PT}) and the time necessary to reach the MRLs (t_{MRL}).

After the first application of procymidone, the residue level of this fungicide on lettuces was 7.52 mg kg^{-1} (Figure 2(a)), with a half-life of 5.31 days (Table 3). Immediately before the second application, the residue level was 1.53 mg kg^{-1}. After the second application, the residual level reached a value of 8.50 mg kg^{-1}and showed similar dissipation rate to that observed during the first application, with a half-life of 4.65 days. The residual level at 21 days after second application was 0.40 mg kg^{-1}.

Although a similar dissipation rate was observed in both cases (one or two consecutive application), some differences between them were detected. Thus, in the first application, significant decrease of procymidone residue was observed from 1 day after application. However, for the second application, this decrease was significant from 3 days after application. This different behaviour can be attributed to differences in the environmental

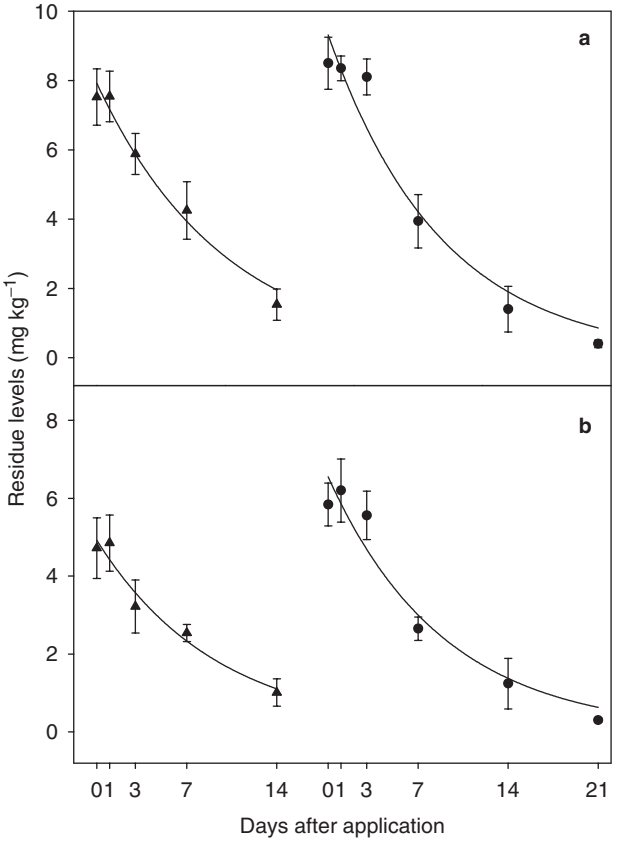


Figure 2. Dissipation of procymidone (a) and azoxystrobin (b) residues in greenhouse grown lettuce after the first application (▲) and after the second application (●).
Note: values are mean ± SD ($n = 5$).

Table 3. Theoretical values (R_0) corresponding to the initial residue levels (mg kg^{-1}), residual concentration in the preharvest time (R_{PT}) (mg kg^{-1}), half-life time ($t_{1/2}$) (days) and time necessary to reach the MRLs (t_{MRL}) (days) for the two fungicides studied.

	First treatment				Second treatment			
Fungicide	R_0	R_{PT}[a]	$t_{1/2}$	t_{MRL}[b]	R_0	R_{PT}	$t_{1/2}$	t_{MRL}[b]
Procymidone	8.54	4.45	5.31	4.10	10.34	4.90	4.65	4.87
Azoxystrobin	4.98	2.28	6.23	4.55	7.21	2.66	4.87	6.16

Notes: [a]PT, preharvest time (5 days for procymidone and 7 days for azoxystrobin); [b]MRL (5.0 mg kg^{-1} for procymidone and 3.0 mg kg^{-1} for azoxystrobin) for lettuce.

conditions during the time period in which the first and the second applications were performed.

In Spain, the established preharvest times (PT) and maximum residue limit (MRL) for procymidone are 5 days and 5.0 mg kg^{-1}, respectively, for lettuce. In our experiment,

Table 4. Linear fit of the data for the dissipation of procymidone and azoxystrobin in lettuce.

	Parameter					
Fungicide	r	r^2	TEE[a]	$a \pm$ CI[b] (95%)	$k \pm$ CI[b] (95%)	D[c]
First treatment						
Procymidone	−0.983	0.967	0.159	2.145 ± 0.317	-0.130 ± 0.044	0.1050
Azoxystrobin	−0.990	0.980	0.106	1.605 ± 0.211	-0.111 ± 0.030	0.1114
Second treatment						
Procymidone	−0.993	0.986	0.166	2.336 ± 0.268	-0.149 ± 0.025	0.1815
Azoxystrobin	−0.989	0.978	0.199	1.975 ± 0.321	-0.142 ± 0.030	0.1775

Notes: [a]Typical error of estimate; [b]Confidence intervals; [c]Test quantity for correlation.

five days after application, the residue level was below MRL in both one and two consecutive applications. These results show that, for the studied cultivar and under our experimental conditions, the PT for procymidone in lettuce is adequate to prevent residues from exceeding the established MRL.

As far as azoxystrobin is concerned, this fungicide presented similar dissipation rate to procymidone. The initial residue concentration of 4.72 mg kg^{-1} was decreased following a pseudo-first-order kinetics ($r = 0.990$) and a half-life of 6.23 days (Figure 2(b) and Table 3). According to Spanish legislation, PT and MRL for azoxystrobin in lettuce are seven days and 3.0 mg kg^{-1}, respectively. Our results showed that seven days after the first application, which correspond with the PT, azoxystrobin residue less than the MRL (2.54 mg kg^{-1}). After the second application, the residue level in lettuces was 5.84 mg kg^{-1}. The half-life calculated with pseudo-first-order kinetics ($r = 0.989$) was 4.87 days and the residue was below the MRL seven days after application. The residual level 21 days after application was 0.30 mg kg^{-1}. Similarly with procymidone, a decrease in azoxystrobin concentration in lettuce was observed from one day after the first application while the decrease occurred from three days after the second application.

Different $t_{1/2}$ to our results were found in a study of dissipation rates of procymidone and azoxystrobin in other fruits and vegetables [12–15]. Different species, weather conditions and different doses can be responsible for the different dissipation rates previously reported by these authors. In addition, a greater persistence in other fruits and vegetables in comparison to lettuce was probably due to the 'dilution effect' brought about by the rapid growth of this vegetable since the residue is expressed as a proportion of weight (mg kg^{-1}). As the weight of vegetable material increases, then the proportion of residue decreases. This is known as 'apparent elimination' and is important in rapidly growing crops.

The statistical parameters calculated for the dissipation of both fungicides in the field conditions are shown in Table 4. As can be observed, the quantity (D) was in all cases greater than 0, which confirms that there was a correlation between residual level and time. The values found for the rate constants (k) show that for the two compounds dissipation rates were similar in the first and second applications in field (Table 4). This study confirms that consecutive applications with procymidone or azoxystrobin do no affect dissipation rates of both fungicides.

Table 5. Dissipation of procymidone and azoxystrobin residues (mg kg^{-1} ± SD[a]) in lettuces under cold storage conditions.

	Days	First treatment[b]	First treatment GAP[c]	Second treatment GAP[d]
Procymidone	0	7.52 ± 0.81	4.25 ± 0.83	3.94 ± 0.77
	3	7.71 ± 0.96	4.53 ± 0.67	4.06 ± 0.86
	7	8.06 ± 0.88	4.16 ± 0.55	4.34 ± 0.32
	14	7.93 ± 0.66	4.11 ± 0.53	3.87 ± 0.61
	21	7.20 ± 0.89	4.38 ± 0.39	4.16 ± 0.54
Azoxystrobin	0	4.72 ± 0.78	2.54 ± 0.22	2.65 ± 0.30
	3	5.18 ± 0.74	2.56 ± 0.34	2.57 ± 0.46
	7	5.04 ± 0.53	2.42 ± 0.47	2.54 ± 0.36
	14	5.22 ± 0.57	2.44 ± 0.24	2.42 ± 0.46
	21	4.96 ± 0.46	2.42 ± 0.40	2.49 ± 0.37

Notes: [a]$n = 5$; [b]Samples were gathered 2 h after the first phytosanitary treatment and stored in cold chamber; [c]GAP (good agricultural practice) Samples were gathered seven days after the first phytosanitary treatment and stored in a cold chamber according to GAP; [d] Samples were treated twice and gathered seven days after the second phytosanitary treatment and stored in cold chamber according to GAP.

3.3 *Dissipation study under cold conditions*

For the first fungicides application, samples collected either without following GAP (gathered 2 h after application) or according to GAP (gathered 7 days after application) were considered. For the second application, only samples gathered according to GAP were studied. For either first or second application, the results for both kinds of samples (with or without GAP) showed that there was no decrease of procymidone nor azoxystrobin concentration under cold and darkness conditions during 21 days of storage (Table 5). Since pesticide residue concentration in fruit is expressed on a fresh weight basis, fruit water losses could lead to error. However, during storage under cold and darkness conditions, fruit weight losses are negligible. Therefore, we can conclude that disappearance of procymidone and azoxystrobin residues did not take place. Similar results have been previously found when studying procymidone degradation in kiwi fruit during storage [23]. On the contrary, for other pesticides such as cyprodinil and fludioxonil, residues dissipation has been observed under similar storage condition [24]. Since processes of evaporation or photodegradation are unlikely under these conditions, pesticide degradation was attributed to enzymatic processes.

4. Conclusions

Under our experimental conditions, residue levels at preharvest time, after two consecutive applications with procymidone or azoxystrobin, were below the MRLs established by Spanish law. In addition, lettuce storage or transport under refrigerated and darkness conditions would not contribute to dissipation of these fungicides residues. These data concerning the behaviour of both fungicides in refrigerated conditions and darkness suggest that the presence of procymidone or azoxystrobin residues can be problematic only when good agricultural practices are not followed.

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