Photodegradation of Imidacloprid

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The photolytic decomposition of the insecticide imidacloprid (**1**) in HPLC grade water and of imidacloprid as the formulated product Confidor insecticide in tap water was studied using HPLC methodology. The structures of several degradates have been determined in aquatic medium, and the DT_{50} values of imidacloprid and Confidor have been measured. In addition, the influence of TiO_2 on the photodegradation of Confidor was studied. The photoproduct 1-(6-chloro-3-pyridinyl)-methyl-2-imidazolidinone (**5**) has been identified as the main degradate in each of the three series of experiments by several analytical techniques. The photolytic half-lives for imidacloprid under the conditions of this study were 43 min in HPLC grade water, 126 min formulated as Confidor in tap water, and 144 min formulated as Confidor in tap water in the presence of TiO_2.

Keywords: *Imidacloprid; Confidor insecticide; HPLC; quantification; TiO_2*

INTRODUCTION

Imidacloprid, 1-(6-chloro-3-pyridyl)methyl-2-nitroiminoimidazolidine (**1**) (Figure 1), represents one example of a new and modern potent insecticide that interacts—like nicotine, epibatidine, and the nereis toxin analogues—with the postsynaptic nicotinic acetylcholine receptor. It is the first highly effective insecticide for which the mode of action has been found to deviate from the almost complete and irreversible blocking of the postsynaptic nicotinergic acetylcholine receptors (Benson, 1989; Tomizawa, 1993, 1995; Yamamoto et al., 1995; Abbink, 1991). It belongs to a novel class of insecticides called "chloronicotinoids" and shows a high activity, especially against a great number of sucking pests such as aphids, leaf- and planthoppers, thrips, whiteflies, and other pest species including resistant strains (Altmann and Elbert, 1992; Elbert and Overbeck, 1990). Exposure to the active ingredient can be through contact as well as through ingestion. Nevertheless, it shows excellent systemic properties, which makes it suitable for seed, soil, and foliar treatment. On the German market, the active agent is embodied in the trade products Gaucho for seed treatment and Confidor for leaf and soil treatment, with the typical application rate ranging from 0.005 to 0.125 lb/acre (Leicht, 1993, 1996).

Under typical field application conditions only a small portion of the applied pesticide reaches its final destination, that is, the biological target. The majority is released into the ecosystem, and there it has to be degraded biologically, abiotically, and photochemically to prevent accumulation or contamination. This degradation process usually leads to the formation of less harmful breakdown products, but in some instances also more toxic products could be produced, which may be a risk for the environment (Aharonson, 1987). A further possibility is that the pesticide will be very resistant to degradation by any means and thus remain unchanged in the environment for long periods of time.

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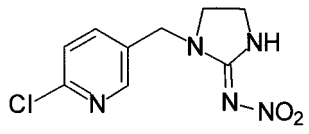

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Figure 1. Structure of imidacloprid.

In aqueous medium and soil, pesticides react chemically; they will hydrolyze, oxidize, or form isomers if water or oxygen is present. In surface water and in the upper soil cover the degradation of substances can be accelerated by photolysis. The phototransformation of xenobiotics can undergo either direct phototransformation through an excited state or indirect phototransformation by photosensitized processes, with special regard to sensitizers, for example, TiO_2 and quenchers.

We have focused our research on the fate of imidacloprid under simulated environmental conditions, which includes its stability upon treatment with hydrolyzing solvents, oxygen, and sunlight. Regarding this, at first we investigated the behavior of neat imidacloprid in HPLC grade water as a model for the action of simulated sunlight on this compound using reversed phase high-performance liquid chromatography (HPLC) and UV—vis spectroscopy as the analytical method. In the course of this work, we have developed a rapid analytical method with the aim to identify as many decomposition products as possible. In a second experiment series we used tap water instead of HPLC grade water and the formulated product Confidor to reflect more realistic use conditions and to study the influence of the formulation on the photodegradation behavior of imidacloprid. In a third experiment series we wanted to study the influence of the semiconductor TiO_2 as a well-known sensitizer on the rate of the photodegradation of Confidor.

MATERIALS AND METHODS

Materials. The solvents used were of HPLC grade. The following compounds had been prepared according to the description in the literature: **3** (Ziegler, 1969; Tilley, 1979) and **9** (Shiokawa, 1986).

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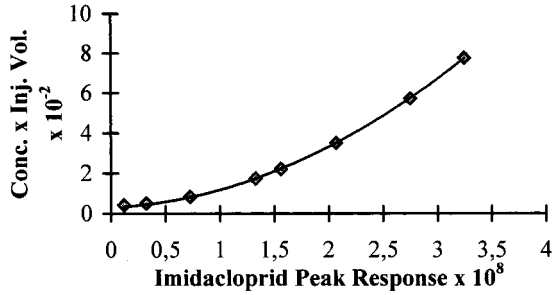

Figure 2. Calibration curve of imidacloprid.

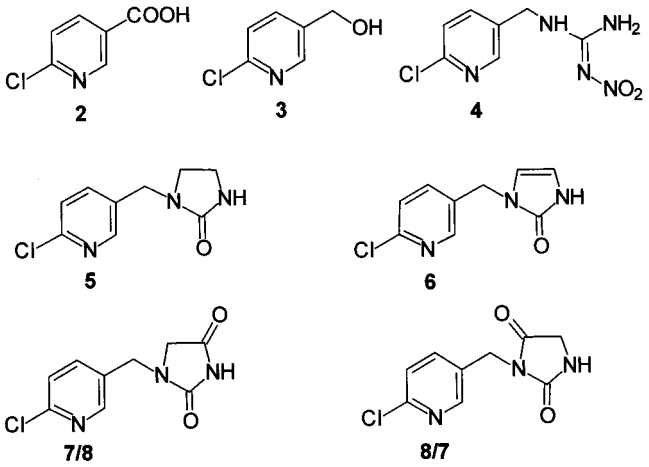

Figure 3. Photoproducts of imidacloprid (**1**).

Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker spectrometer at 250 MHz.

Preparation of 4. To a solution of 1-(2-chlorpyrid-5-ylmethyl)-2-nitroimino-5-cyclopropylperhydro-1,3,5-triazine (Maienfisch et al., 1991) (0.466 g, 1.5 mmol) in 4 mL of methanol was added 2.6 mL of aqueous hydrochloric acid (2 N) in one portion; the mixture was stirred for 4 h at 50 °C until the solid completely dissolved. Stirring the solution for another 24 h at room temperature precipitated a white solid, which was recrystallized from methanol: yield = 0.133 g (48%); mp 181−183 °C; IR ν_{max} (KBr) cm^{-1} 3373, 3285, 3171, 1603, 1305; NMR (250 MHz, DMSO-d_6) δ_H 4.42 (2H, d, J = 6.16 Hz), 7.52 (1H, d, J = 8.12 Hz), 7.71 (1H, dd, J = 8.25 and 2.46 Hz), 8.05 (2H, sb), 8.29 (1H, d, J = 1.72 Hz), 8.9 (sbb); NMR (250 MHz, DMSO-d_6) δ_C 148.00, 124.04, 138.74, 138.56, 148.82, 40.62, 159.18. Anal. Found: C, 36.75; H, 3.60; N, 29.24%. Calcd for $C_7H_8ClN_5O_2$: C, 36.6; H, 3.5; N, 30.5%.

The trade product Confidor was purchased on the market. The synthetic standard imidacloprid was received from Promochem GmbH (Wesel, Germany), and the 6-chloronicotinic acid was acquired from Aldrich Chemical Co. (Milwaukee, WI).

The pure substance imidacloprid was easily and quantitatively extracted from the formulated product Confidor using absolute methylene chloride in a Soxhlet extractor.

Photolysis Procedures. Three different series of experiments were realized, respectively, within an immersion reactor from Mangels (Bornheim-Roisdorf, Germany) equipped with a Solidex filter (λ > 280 nm). The pesticide solutions were circulated to ensure a constant irradiation by a high-pressure mercury lamp (HPK 125 from Philips).

Typically, 1.5 × 10^{-3} M imidacloprid or Confidor was irradiated in, respectively, HPLC grade and tap water. In the third series of experiments, 1 × 10^{-3} M TiO_2 was added. To dissolve imidacloprid, the solution was sonicated for 15 min before irradiation. A filtered [microfiltration element, Fa; CS-Chromatographie-Service GmbH (Langerwehe), 2 μm] 0.5 mL aliquot was taken in adequate periods of time.

HPLC Measurement. The HPLC equipment consisted of two pumps (Waters 501 and 510) for gradient elution, a variable wavelength UV−vis detector (190 nm ≤ λ ≤ 600 nm, Waters 484), and a photodiode array detector (Waters 990). The analysis was carried out using a 100-5 C_{18} Nuleosil column [250 × 4 mm, Macherey-Nagel (Düren, Germany)] equipped with a Nucleosil 120-5 C_{18} precolumn (30 × 4 mm).

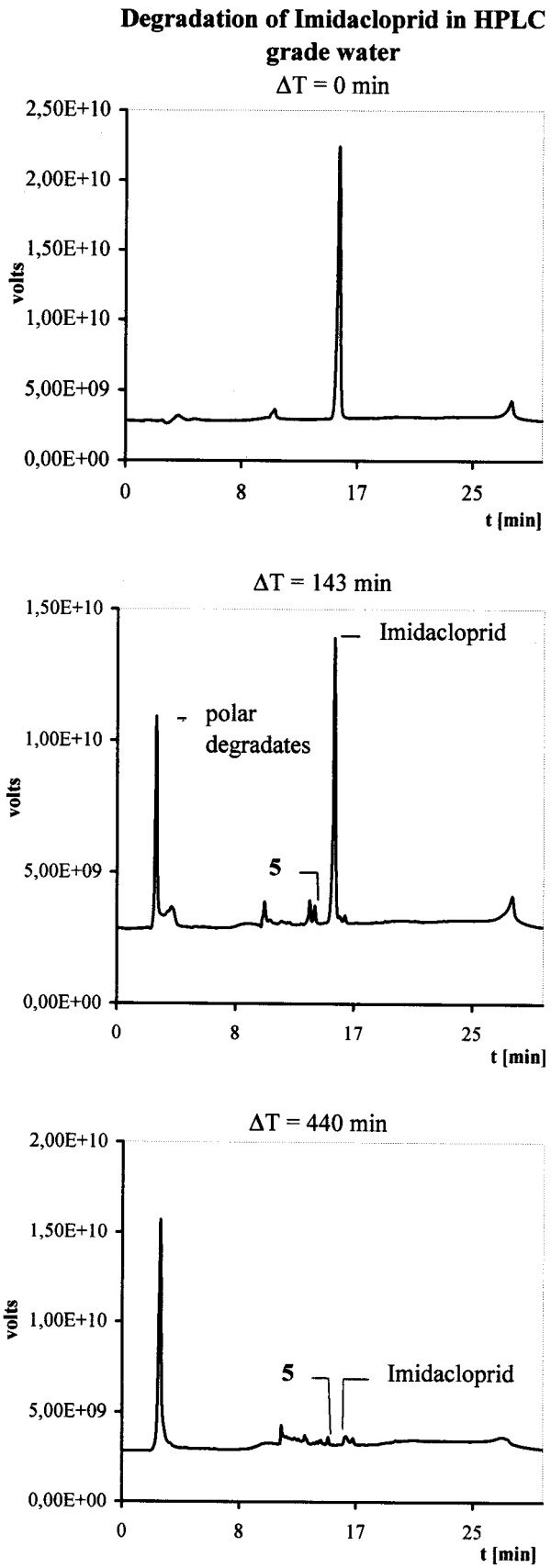

Figure 4. HPLC chromatograms of imidacloprid.

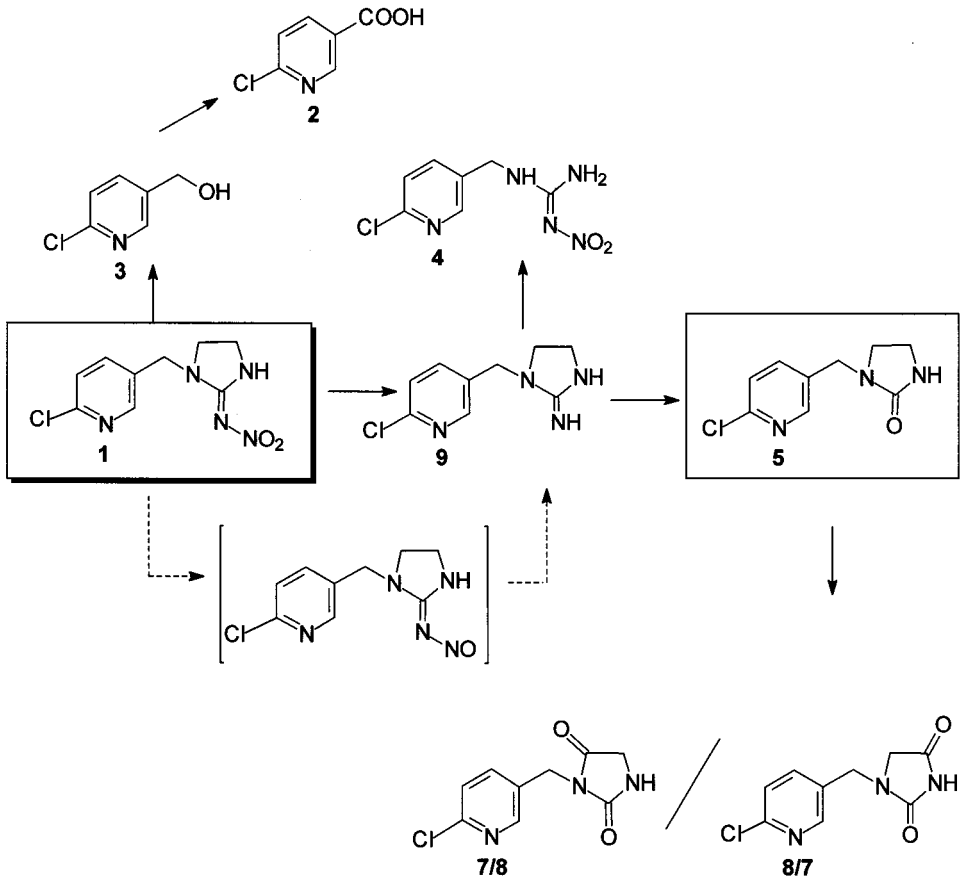

Figure 5. Hypothetical photodegradation pathway of **1** by photolysis.

Table 1. Retention Time, Electronic Absorption Spectra, and MS Spectral Data of Imidacloprid and Photoproducts

compd	retention time (min)	λ_{max} (nm)	MS spectral data [*m/z* (relative intensity)]
1	15.3	190, 215, 270	255.1 (M^+, 1), 209 (100), 195 (8), 173 (32), 126 (32), 83 (5), 69 (10)
2	10.9	190, 226, 268	157 (M^+, 100), 140 (50), 112 (23), 76 (10)
3	12.2	190, 214, 268	143 (M^+, 100), 114 (85), 108.1 (40), 78 (92.5), 51 (30)
4	13.0	190, 212, 270	183.1 [$(M - NO_2)^+$, 5], 167.1 (13), 154 (40), 141 (25), 126 (100)
5	13.8	190, 214, 268	211 (M^+, 100), 182 (10), 140 (18), 126 (60), 99.1 (35)
6	13.1	213, 269	209 (M^+, 45), 126 (100), 99 (15), 90 (22)
7/8	11.5/14.3	212, 268	225 (M^+, 100), 197 (22), 168 (20), 154 (32), 126 (35), 113 (35)

The HPLC separations were carried out for 30 min using gradient separation at a flow rate of 1.0 mL min^{-1}. Solvent A was water and solvent B acetonitrile (both from Riedel-de Haën). Linear gradient profiles were established to deliver 5, 25, 40, 80, 80, and 5% solvent B at 0, 4, 11, 14, 20, and 22 min, respectively, to achieve baseline separation of the degradates.

The progress of photolysis of imidacloprid was monitored from the integrated peak area corresponding to imidacloprid with respect to the sampling interval. The total injection volume of the sample was 50 μL.

Calibration Curves. To correlate the peak areas to the amount of the substances imidacloprid and the degradation product **5**, two calibration curves with eight different concentrations were recorded (Figure 2).

Because of the high amounts of imidacloprid, the regression curves were best described by a quadratic equation:

$$c = 3.97045 \times 10^{-3} + 1.3835 \times 10^{-10}R + 6.5613 \times 10^{-17}R^2 \quad (1)$$

The calibration curve for **5** was best described by the following equation:

$$c = 8.85185 \times 10^{-4} + 1.9194 \times 10^{-9}R + 5.1255 \times 10^{-17}R^2 \quad (2)$$

Isolation of 5. The 1-(6-chloro-3-pyridinyl)methyl-2-imidazolidinone was separated by using a semipreparative 120-5 C_{18} Nucleosil column (250 × 4.6 mm, Macherey-Nagel). Thus, 500 mg of imidacloprid was photolyzed as described before in 1000 mL of pure water. The degradation of imidacloprid was monitored by thin-layer chromatography (TLC) (silica gel F-254, E. Merck, Darnstadt, Germany) until almost all of the starting material had disappeared. The reaction solution was then extracted using solid-phase Sep-Pak C_{18} cartridges (Waters). After drying, the degradates were eluted with acetonitrile and **5** was separated by HPLC as described above. The compound was characterized as follows: ^{1}H NMR (250 MHz, DMSO-d_6) δ_H 3.20 (4H, s), 4.25 (2H, s), 6.50 (1H, sb), 7.49 (1H, d, J = 8.25 Hz), 7.73 (1H, dd, J = 8.24 and 2.47 Hz), 8.30 (1H, d, J = 2.45 Hz); HR-MS(EI) (calcd for $C_9H_{10}ClN_3O$, 211.05124; found, 211.0510) *m/z* 211 (100%, M^+), 182.0 (10%, $M^+ - C_2H_5$), 140.0 (18%), 99.1 (36%, $M^+ - C_5H_3ClN$); UV−vis spectra (acetonitrile) λ_{max} = 190, 214, 268 nm.

RESULTS AND DISCUSSION

The continued use of HPLC in pesticide residue analysis may be related to its suitability for determining thermally labile and polar pesticides and their degradates (Sherma, 1989, 1995).

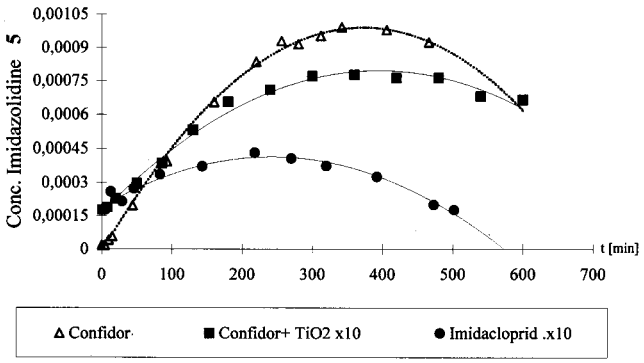

Figure 6. Formation of 1-(6-chloro-3-pyridinyl)methyl-2-imidazolidinone (**5**).

We aspired to a fast analytical HPLC method with reversed phase columns using a mobile phase gradient as the previously reported isocratic elution (Ishii et al., 1994) did not give baseline separation of all degradates.

Direct irradiation of **1** in HPLC grade water or its formulated trade product Confidor in tap water resulted in the formation of complex photoproduct mixtures containing up to 23 components, some of which are depicted in Figure 3.

Figure 4 show some of the HPLC chromatograms of the photolysis of imidacloprid in HPLC grade water at various sampling intervals. Imidacloprid and the degradation product 5 are labeled.

Similar product distributions are obtained in all three experiment series. Product **5** was identified as the major degradation product as described above. Retention times, electronic absorption spectra, and MS spectral data of the different compounds are summarized in Table 1. All compounds have been identified by HR-MS (EI) spectrometry, conducted on a Kratos MS 30 or MS 50 high-resolution mass spectrometer.

The photolytic pathway of imidacloprid is presented in Figure 5. During irradiation of **1** the photoreaction affects only the imidazolidine moiety of the molecule while the 6-chloropyridine moiety remains unchanged.

This photodegradation pathway is supported by some postulated metabolic pathways of imidacloprid in plants after spray and granular application (Nauen, 1998; Koester, 1992).

Concentration of the irradiated solution and employing HPLC measurements of the concentrate show even more degradates, some of them much more polar so that they are not retained on the reversed phase column and, hence, could not be separated and identified. Other minor components are unstable upon concentration or isolation attempts.

Upon checking the measurement series we found that 1-(6-chloro-3-pyridinyl)methyl-2-imidazolidinone (**5**) is formed in various amounts with regard to the initial concentration of imidacloprid. Thus, **5** is formed in 3.2% yield from imidacloprid in HPLC grade water, in 6.7% yield from the trade product Confidor in tap water with addition of TiO_2, and in 9.7% yield from Confidor in tap water (Figure 6).

The photodegradation rates of imidacloprid and confidor were determined using a first-order velocity law

$$[c_t] = \ln[c_0] - Kt \qquad (3)$$

and the dissipation half-life value calculated as (Walter et al., 1993; Timme et al., 1986)

Table 2. Summarized Calculated Values of the Rate Constant k and the DT_{50} Values

	imidacloprid in HPLC grade water	Confidor in tap water	Confidor in tap water, TiO_2
k (10^{-3} s^{-1})	105.8	5.5	4.8
DT_{50} (min)	43	126	144
kinetics	$y = -0.1508x - 6.3226$	$y = -0.0056x - 6.8131$	$y = -0.0048x - 6.6982$

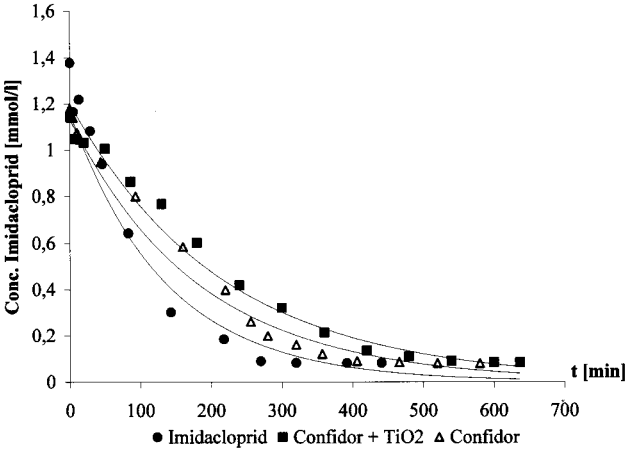

Figure 7. Degradation of imidacloprid and Confidor during irradiation.

$$DT_{50} = \ln 2/b \qquad (4)$$

The calculated results are summarized in Table 2.

The rate constant k is measured as the slope of the plot of ln[imidacloprid] versus the reaction time.

The decrease of the concentration of imidacloprid during the irradiation is represented by Figure 7.

As already mentioned, we have studied the influence of the semiconductor TiO_2 in the third series of measurement. Semiconductor photocatalysis has been applied to a variety of problems of environmental interest (Hoffmann et al., 1995; Legrini et al., 1993; Klöpfer, 1991; Mathews, 1992; Mill et al., 1980; Mills et al., 1993; Serpone and Terzian, 1993). It can act as sensitizer for light-reduced redox processes due to their electronic structure. During the irradiation active oxygen species are generated, usually leading to an enhanced degradation of pesticides. In the case of Confidor the degradation rate decreases, unexpectedly.

We think that the described deceleration is an order of the formulation, the effect of which is reinforced by the supplement of TiO_2. In addition, we could observe that the irradiated solutions differ in their colors. Irradiated imidacloprid delivered a bright yellow solution, Confidor a yellowish brown solution, and Confidor with TiO_2 a light brown solution. We now asume that the entire wavelength range is no longer available due to the increasing brown dyeing of the solution. A lightweight turbidity of the solution observed also prevents the entire range in light intensity from being used.

CONCLUSION

Reverse phase HPLC employing a UV detector and a diode array detector allows a rapid and highly sensitive determination of imidacloprid and the resulting photodegradates in water. As a result, the behavior of degradation times of imidacloprid and the main me-

tabolite, 1-(6-chloro-3-pyridinyl)methyl-2-imidazolidinone, can be ascertained. The photodegradation was rapid and first-order. This degradation rate can be influenced by the nature of the applied aquatic medium. The degradation half-life of imidacloprid was 46 min in pure water, 126 min formulated as Confidor in tap water, and 144 min as Confidor with the admixture of TiO_2.

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