

## Residue Analysis of Imazapyr and Chlozolinatate in Water Using Sunlight

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Pesticides are widely used in agricultural production all over the world. In different countries they have been found to contaminate ground water reservoirs (Mansour *et al.*, 1993). Various processes influence the environmental fate of pesticides. Depending on the physical and chemical properties, environmental conditions and application method of the compound, it may be adsorbed on soil by organic matter and/or degraded to various metabolites by soil micro-organisms or chemical reactions. Compounds may be translocated or transported from the field in runoff water or adsorbed on soil particles moving across the field as a result of a heavy rainfall (Mansour, 1997). The compound, or its metabolites, can enter in plants following root uptake (Shone *et al.*, 1974) or foliar adsorption (Sampaolo, 1969). Because pesticides are usually extracted from complex matrices such as vegetables, soil or water, selective detectors for chromatographic (GC and HPLC) applications have been used as analysis tools for the quantification of transformation products during the photodegradation processes (Mansour *et al.*, 1989; Mansour, 1993). Two pesticides have been selected because they have not been sufficiently investigated literature, but are very commonly used in mediterranean agriculture. Imazapyr is an imidazolinone herbicide, which has been developed in order to be used in vegetation and forestry management (Beardmore *et al.*, 1991). It is a broad-spectrum herbicide that controls grass and leaf weeds in non-cropped areas (Winfiel *et al.*, 1988). High mobility and translocation of imazapyr in soil from the site of application to roots and rhizomes could be advantageous for control of perennial weeds (Shaner, 1988; Mallipudi *et al.*, 1986). Chlozolinatate is an oxazolidine. It is a systemic fungicide with protective and curative action which can be used as a foliar spray (against *Botrytis* spp., *Sclerotinia* spp., and *Monilia* spp. in ornamentals, vegetables, vines, pome fruit, stone fruit, and strawberries), or as a soil drench (Cabras *et al.*, 1985; Flori *et al.*, 1982). The objective of this study was to develop analytical methods for imazapyr and chlozolinatate residues in water after using simulated sunlight  $\lambda \geq 290$  nm and to investigate their degradation mechanisms in presence and in absence of various sensitizer compounds.

## MATERIALS AND METHODS

Imazapyr and chlozolate standard compounds were obtained from Dr. Ehrenstorfen, Germany, (purity >98%). The pesticide solutions to be irradiated were prepared at a concentration of 1 mg/L in deionized water. Solvents used for photolysis and chromatographic measurements were of HPLC grade (Merck, Germany). TiO<sub>2</sub> (Degussa) was suspended in solution at 1 mg/L. Humic substances were purchased from Aldrich Co. and suspended in solution at 1:1 (w/w) in regard to physical and chemical properties of the pesticide. Acetone was added at 1% (v/w).

Photolysis experiments were performed at 20°C in an apparatus suitable for irradiation of the chemicals in liquid and suspended phases. The radiation source was a mercury lamp (Philips HPK 125 W) placed in the axial centre of the reaction chamber. Between the lamp and the reaction chamber, a Pyrex jacket whose task was to eliminate wavelengths shorter than 290 nm was allocated. A solution of water flowed through the Pyrex jacket in order to keep the temperature of the irradiated solution constant. A magnetic stirrer was used during the photodegradation measurements. Control solutions were kept in dark to verify degradation effects of the solvent on the pesticides.

The analysis of the compounds, and their transformation products were carried out with a HP1090 liquid chromatograph equipped with UV-Vis diode array detector at 230 nm, 20 µL sample injection loop, RP-7104-00 Baker Bond™ Octadecyl 5 µm column, flow rate 1 mL/min. Mobile phase was acetonitrile/water (4/1) for chlozolate and acidified water (pH 3)/acetonitrile (3/1) for imazapyr. Calibration solution of pesticide standards were prepared at concentrations from 0.01 to 2 mg/L. Calibration curves were linear in to the concentration range.

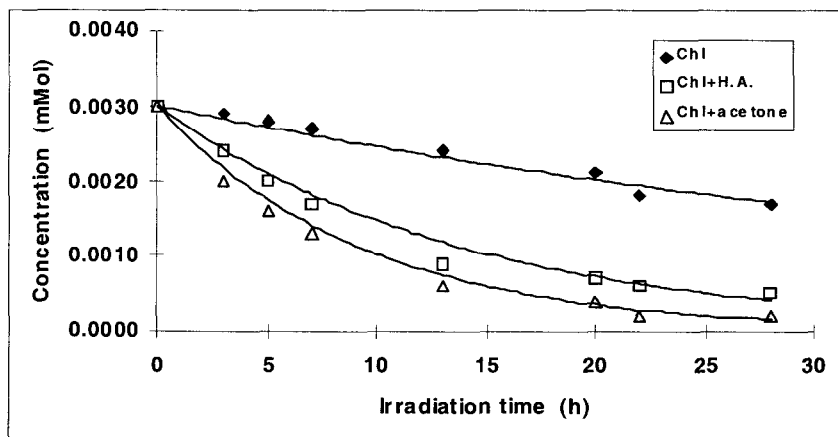
GC-MS and HPLC-MS were used to determine the structure of photoproducts. Each sample was extracted with n-hexane and dried with sodium sulphate anhydrous. After concentration of n-hexane phase the residue was injected into the chromatographic apparatus. The decomposition and disappearance of the parent compounds were followed by FID-GC (HRGC Carlo Erba, OV-1701 methylcyanopropyl-phenylsilicone column, 30 m, 0.53 mm, 1µm), GC-MS (Capillary column DB5 ms, 60 m, 0.25 i.d., injector 280 °C, program 90°C 1 min, 90°C-270°C at 10°C/min), and LC/MS (Perkin Elmer, triple quadrupole ion spray 4800V, flow rate 1 mL/min). The identity of the metabolites was confirmed by comparison with spectra recorded in literature. The minimum detectable for the investigated compounds was 1 ng.

## RESULTS AND DISCUSSION

Chlozolate in plants undergoes to hydrolysis and decarboxylation processes giving several metabolites (Tomlin CDS. (ed), 1997). Upon irradiation of chlozolate in water solution and with sensitizers the pesticide degraded with different half-lives. The dark experiments are not reported because no evident degradation was measured. The kinetic parameters calculated for the fungicide degradation are reported in Table 1. They are in accordance with first order kinetics.

The depletion of the chlozolate concentration during the photodegradation experiments is reported in Figure 1. Photolysis of chlozolate was more rapid in

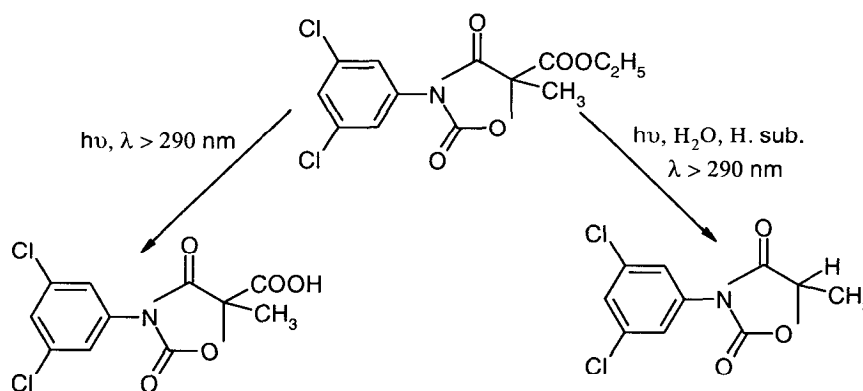
regard to pure water solution by using humic substances and acetone and we identified different photoproducts. In Figure 2 we report the pathways and the identified photoproducts.



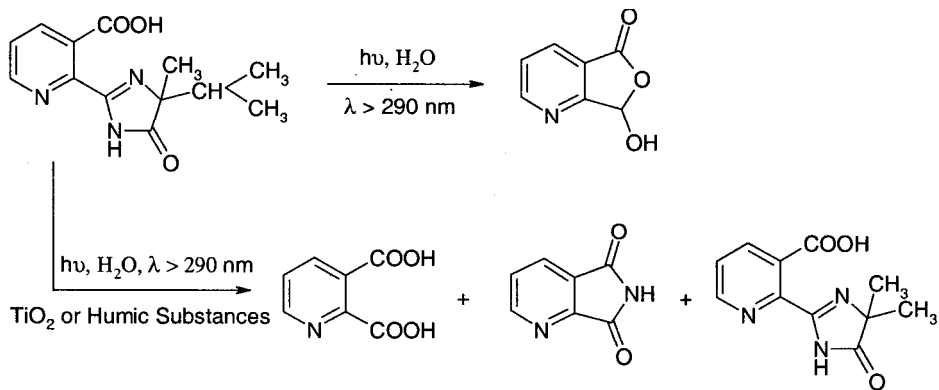
**Figure 1.** Photodegradation of chlozolinatate in aqueous solution and with humic substances or acetone.

**Table 1.** Kinetic parameters of chlozolinatate irradiated in water solutions with different sensitizers ( $t_{1/2}$  = half-life;  $k$  = kinetic constant;  $r^2$  = determination coefficient).

	Deionized water	Deionized water + acetone	Deionized water + humic substances
$t_{1/2}$ (hr)	34.66	6.44	9.71
$k$ ( $\text{hr}^{-1}$ )	0.02	0.1077	0.0714
$r^2$	0.967	0.962	0.961



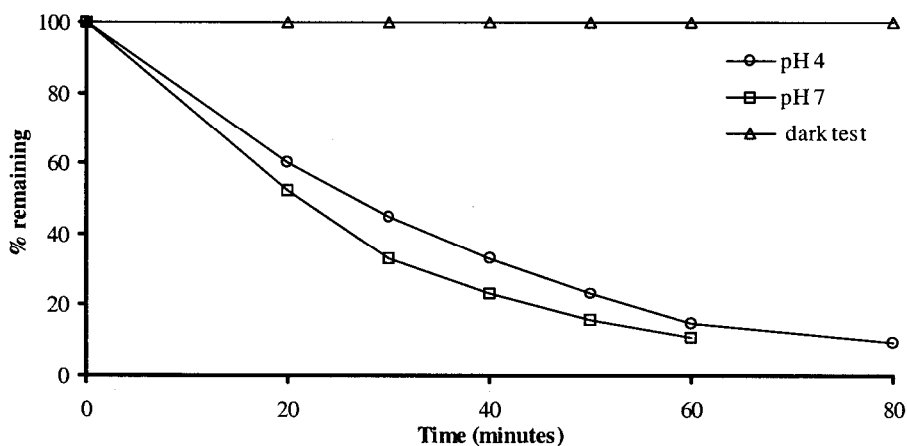
**Figure 2.** Phototransformation of chlozolinatate in water, water + acetone and water + humic substances.



**Figure 3.** Photodegradation pathway of imazapyr in water + TiO<sub>2</sub> or humic substances.

The photolysis of chlozolate in aqueous solutions at  $\lambda \geq 290$  nm resulted in 89.5% of substrate transformation within 25 hours. It appears that photoproducts of chlozolate are likely to be present as residues in aquatic ecosystems.

Also in the case of imazapyr the rate of degradation followed first order kinetics. The influence of pH on this herbicide in water under simulated light are represented in Figure 4. We found that imazapyr is rapidly photodegraded in aqueous media at pH 7 than in pH 4. Depending on pH of the environmental compartment, four imazapyr photoproducts could be obtained, in accordance with results reported earlier (Mansour, 1998).



**Figure 4.** Comparison of UV photolysis of 0.11 mM imazapyr at two pH values

HPLC may represent a rapid analysis tool for the quantification of these degradation products. Similar to other imidazolinone herbicides, imazapyr can be transformed under UV-Light ( $\lambda \geq 290$  nm) in the presence of TiO<sub>2</sub> and humic

substances in aqueous solutions (Figure 3). No degradation was observed in absence of UV irradiation.

The half-life ( $t_{1/2}$ ) determined in deionized water, at pH = 3, was 3.5 days.

The use of TiO<sub>2</sub>, humic substances and acetone remarkably increased the rate of photodegradation of imazapyr to 70% in three hours. The presence of this sensitising compound in soil could influence the persistence and the activity of the pesticide. In consideration of the variety of compounds by the photodecomposition of imazapyr and chlozolate in aqueous medium in the presence and absence of humic substances, it appears reasonable to look for the persistence of these compounds in soil, plants and their transformation products.

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