Environ. Sci. Technol. **1998**, *32,* 3479−3484

Rapid Degradation of Propanil in Rice Crop Fields

TERESA CRISTINA R. SANTOS,[†]
JULIO CESAR ROCHA,[‡]
ROSA MARIA ALONSO,[§]
ELENA MARTÌNEZ,[§]
CARLES IBAÑEZ,[⊥] AND
DAMIA BARCELÓ*,[§]

Department of Chemistry, Federal University of Maranhao (UFMA), Avenida Portugueses, s/no, 65.080-040, Sao Luìs, MA, Brazil, Department of Analytical Chemistry, University Est. Paulista (IQ/UNESP), Cx. Postal 355, 14.800-400, Araraquara - SP - Brazil, Department of Environmental Chemistry, CID-CSIC, c/ Jordi Girona, 18-26, 08034, Barcelona, Spain, and Sociedad Española de Ornitologia (SEO) BIRDLIFE, c/ Mayor, 10, 43580, Deltebre Tarragona, Spain

Propanil and its major degradation product, 3,4-dichloroaniline (DCA), were monitored in surface water and soil samples from two rice fields of the Ebre Delta area (Tarragona, Spain) following agricultural application. On-line solid-phase extraction (SPE) (water) and Soxhlet extraction (soil) followed by liquid chromatography/diode array detection (LC/DAD) were used for the trace determination of both compounds. Unequivocal confirmation/identification was conducted by using liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry, LC/APCI-MS (using negative and positive ionization modes). Concentrations of the herbicide propanil in water samples varied from 1.9 to 55.9 μg/L. Propanil degraded very rapidly to DCA, and high concentrations of this product were found, varying from 16.5 to 470 μg/L in water and 119 ± 22 μg/kg in soil samples. No detectable DCA (<0.001%) was found in the applied pesticide formulation, indicating that DCA formation took place after propanil application. These field results compared favorably with laboratory experiments showing that humic interactions had a strong influence on the pesticide degradation. The half-lifes under real conditions for propanil and DCA, calculated using a first-order decay, were 1.2 and 1.6 days, respectively.

Introduction

Pesticide monitoring is the best way to follow the dissipation, transportation, environmental behavior, and degradation mechanism of these compounds. In the Ebre Delta area (350 km^2, in the northeast of Spain), rice is the dominant agricultural cultivation, and different classes of pesticides are applied over the year.

Several papers have been published concerning pesticide monitoring in surface or estuarine waters. Herbicides such as propanil, molinate, MCPA, bentazone, and 8-hydroxybentazone have been determined in irrigation canals of the Ebre river. Molinate has presented the highest concentration (about 4 μg/L) (*1*−*3*). Organophosphorus insecticides such as temephos (*4*), fenitrothion (*5, 6*), and their degradation products were also determined. Other rice pesticides such as carbendazim (*7*) and diazinon (*8*) were determined in spiked estuarine water, whereas carbofuran and thiobencarb were detected in the surface microlayers from a flooded rice field (*9*). Among rice pesticides, propanil is one of the most applied in the Ebre Delta area (Tarragona, Spain). It is also used extensively in the Delta Region of the Mississippi (U.S.A.) (*10*). In the Ebre area about 50 ton/year of the herbicide are sprayed before rice planting, over the dry fields, during the summer (*1*). Propanil, or propanide (3′,4′-dichloropropionanilide), is a contact herbicide used worldwide to control weeds through inhibition of photosynthesis. A short duration of activity has been reported for propanil, with rapid degradation to 3,4-dichloroaniline (DCA), the major product formed (11−13). The main degradation pathway is through enzymatic hydrolysis (80−85%) with a lower photodegradation rate (6%) (*14*). Propanil degradation is directly dependent on the environmental conditions and rate of application of the pesticide. In rice plants a fast degradation resulted in the total transformation of the pesticide within 5 days. The disappearance in water was correlated with absorption by rice foliage, but elevated soil salinity retarded its degradation (*15*−*16*). Half-lives of 2 days was reported (*13*) for the herbicide at pH 8, but at higher pH half-lives of 20 days were obtained. Propanil degradation is fast at pH 7−8, which also presented faster DCA degradation (*17, 18*).

The determination of propanil and DCA in water samples has generally been performed by gas-chromatography with both compounds derivatized to the corresponding iodobenzene (*19*) and using a Florisil column cleanup (*16*). Liquid chromatography has also been used (*11, 12, 18*). MS detection has not been reported up till now. Most studies have been made at high concentrations (mg/L) of spiked samples, generally under laboratory conditions. Results cannot therefore be perfectly extrapolated and compared with those found in the real conditions of the rice fields.

In view of the previous work, the purpose of this study was (i) the monitoring of propanil and DCA in two rice crop fields from the Ebre Delta, just after and immediately the herbicide application; to monitor the decay of both compounds using LC/DAD-APCI-MS with an on-line solid-phase extraction (SPE) enrichment step (following suitable method development) (*20*), (ii) to determine the half-life of propanil and DCA under field conditions, and (iii) to compare the degradation of propanil under environmental field conditions and laboratory experiments.

The analytical approach reported in this paper is new since it involves an automated SPE method followed by LC-DAD and LC-APCI-MS, without a derivatization step prior to the chromatographic analysis and with MS confirmation. For this reason the reported study represents an advantage over current protocols for the analysis and transformation of propanil and DCA under field conditions.

Materials and Methods

Chemicals. Propanil and 3,4-dichloroaniline were acquired from Dr. Ehrenstorfer (Augsburg, Germany). Acetonitrile, methanol, and HPLC-grade water were obtained from Merck (Darmstadt, Germany). Acetic acid was obtained from Panreac (Barcelona, Spain).

Sampling and Sample Handling of Water. The study was conducted at the Ebre Delta area in June, 1997. During

---

[*] To whom correspondence should be addressed. e-mail: dbcqam@cid.csic.es.

[†] Fed. University of Maranhao (UFMA).

[‡] University Est. Paulista (IQ/UNESP).

[§] CID-CSIC.

[⊥] Sociedad Española de Ornitologia (SEO) BIRDLIFE.

10.1021/es980212k CCC: $15.00

TABLE 1. LC/APCI-MS Fragment Ions of Propanil and DCA in Positive (PI) and Negative (NI) Mode of Operation

compound	M_w	m/z (rel intensity %) [characteristic ions]	
		PI	NI
3,4-dichloroaniline	161	101(10) 113(30)$[M + H - CH_2Cl]^+$ 122(10) 138(10)$[M + CH_3COOH - CHCl_2]^+$ 162(100)$[M + H]^+$	134(20) 160(100)$[M - H]^-$
propanil	217	126(100)$[M + H - COCH_2CH_3 - Cl]^+$ 162(43)$[M + H - COCH_2CH_3]^+$ 218(10)$[M + H]^+$	124(7)$[M - Cl - COCH_2CH_2]^-$ 160(100)$[M - COCH_2CH_3]^-$ 216(72)$[M - H]^-$

the sampling period high temperatures and no precipitation were observed. Riselect (Enichem), the herbicide formulation which contained 35% of the active ingredient, was manually sprayed together with a leaf fertilizer, at a rate 1:0.15. The herbicide was applied over the dry fields of the rice cultivation. Two treatments were carried out over the same area in different days, merged with a day without spraying. Two days after that the fields were flooded, and the samples were collected on the subsequent day and during a week. The total amount of the pesticide formulation sprayed was 18 L/ha, and the concentration of propanil was estimated as approximately 12 mg/L at the beginning (5 cm deep) and 3 mg/L when the fields were totally flooded (20 cm deep). A blank was collected just before the herbicide treatment and showed nondetectable levels of propanil. The samples collected were filtered through 0.45.μm membrane filters (Millipore Corp. Bedford, MA). Sample volumes of 75 mL were preconcentrated using 10 × 2 mm i.d. precolumns, packed with the copolymer PLRP-S from Polymers Laboratories (Church Stretton, UK), in a On-line Sampling Preparator (OSP-2, Merck, Germany), connected to a the L-6200A Intelligent Pump (Merck-Hitachi, Germany). Before the preconcentration the precolumns were conditioned with 5 mL of methanol and 5 mL of HPLC-grade water at 1 mL/min, followed by sample preconcentration at 2 mL/min. The recoveries obtained immediately after spiking paddy waters at 20 μg/L of propanil and DCA were 98% (CV of 4) and 93% (CV of 2), respectively, for $n = 3$.

Degradation Studies. To follow the propanil degradation under laboratory conditions, Milli-Q water was spiked at 10 μg/L of the herbicide and settled at different conditions. Humic acid at 10 mg/L was added in two samples. The humic material had been obtained from a Brazilian estuarine sediment. The extraction was carried out with air-dried and sieved sediment (120 μm mesh), shaken with sodium hydroxide 0.5 mol/L for 4 h, under nitrogen atmosphere. Humic acid was isolated from the solution by precipitation at pH 2 with chloridric acid, afterward purified by anionic and cationic exchange resins. The freeze-dried humic acid was used in the presented study (carbon 33.09%, hydrogen 4.67%, nitrogen 3.54%, and sulfur 2.41%). Photodegradation experiments were carried out with a Suntest CPS (W. C. Heraeus Co., Hanau, Germany), which has a spectrum close to natural sunlight (*21*).

Soil Samples. The presence of propanil in soil was also investigated in soil samples collected just before the herbicide application in each rice crop field and also in another sample collected one month after the propanil treatment in which, initially, fenitrothion dissipation has been investigated. The procedure used for the soil pretreatment followed basically the method cited in Durand and Barceló (*22*). Briefly, the soil samples were freeze-dried and sieved through 120 μm mesh, and 10 g was extracted with methanol in a Soxhlet system during 18 h. The extracts were concentrated, evaporated to dryness, and redissolved in 500 μL of *n*-hexane. The cleanup was made using Florisil, previously activated overnight at 300 °C and deactivated with 2% water. Glass columns were packed with 2 g of deactivated Florisil and rinsed with *n*-hexane, and, after they had been passed through the columns, the extracts were eluted with 20 mL of 50% ethyl ether in *n*-hexane. Finally the concentrated extracts were evaporated to dryness and dissolved in 1 mL of acetonitrile. The recoveries obtained after 24 h of spiking soil samples at 50 μg/Kg of propanil and DCA were 95% (CV of 10) and 76% (CV of 10), respectively, for $n = 5$.

Chromatographic Conditions. A liquid chromatograph equipped with a diode array detection (LC/DAD), Model HP 1090 (Hewlett-Packard, CA), was used for the on-line elution using a 150 × 4.6 mm i.d. analytical column packed with 5 μm octadecylsilica Ultracarb 5 ODS-30 from Phenomenex (Torrance, CA) and gradient from 5% of acetonitrile and 95% of water, both containing 0.1% of acetic acid, to 100% of acetonitrile in 45 min, at a flow rate of 1 mL/min. Quantitation of propanil and 3,4-dichloroaniline was done at 220 nm. The identification of propanil and its degradation product was made by liquid chromatography/atmospheric pressure chemical ionization-mass spectrometer from Hewlett-Packard, Model HP1100, using either positive (PI) or negative (NI) mode of ionization. At NI, the fragmentor was settled at 150 V, the drying gas flow at 4.0 L/min, and the nebulizer pressure at 60 psi. The temperatures of the quadrupole, the drying gas, and the vaporizer were 100, 350, and 320 °C, respectively. Capillary voltage was 2500 V, and the corona current was settled at 20 Å. To attain sensitivity gain and to obtain more information about the degradation product formed, PI was made at similar conditions, with the fragmentor settled at 60 V and corona current at 4.0 μA. The analytical column and LC gradient elution conditions were the same as those used for on-line analysis of the water samples.

Results and Discussion

Analytical Methods. Current analytical methods used in this work involve the routine use of on-line SPE followed by LC-DAD. Although DAD gives structural information by the UV spectra of the analytes, unequivocal structural information can only be achieved by MS. For this reason propanil degradation was followed by LC/APCI-MS, at PI and NI mode, according to previously cited conditions. The typical fragment ions are shown in the Table 1. Some fragmentation was observed when acetic acid was added to the eluent. Propanil and 3,4-dichloroaniline were identified by molecular ions and other characteristic fragment. For propanil identification NI mode presented better sensitivity with limit of detection (LOD) of 0.1 μg/L, while for DCA confirmation a PI mode was preferred with a LOD of 0.5 μg/L. Total ion current chromatograms were recorded under full scan conditions, and typical fragments ions were obtained at the m/z values of 216 $[M - H]^-$, 160 $[M - COCH_2CH_3] -$ and 124 $[M - Cl- COCH_2-CH_2]^-$ for propanil (NI mode) and 162 $[M + H]^+$, 138 $[M + CH_3COOH - CHCl_2]^+$ and 113 for DCA (PI mode).

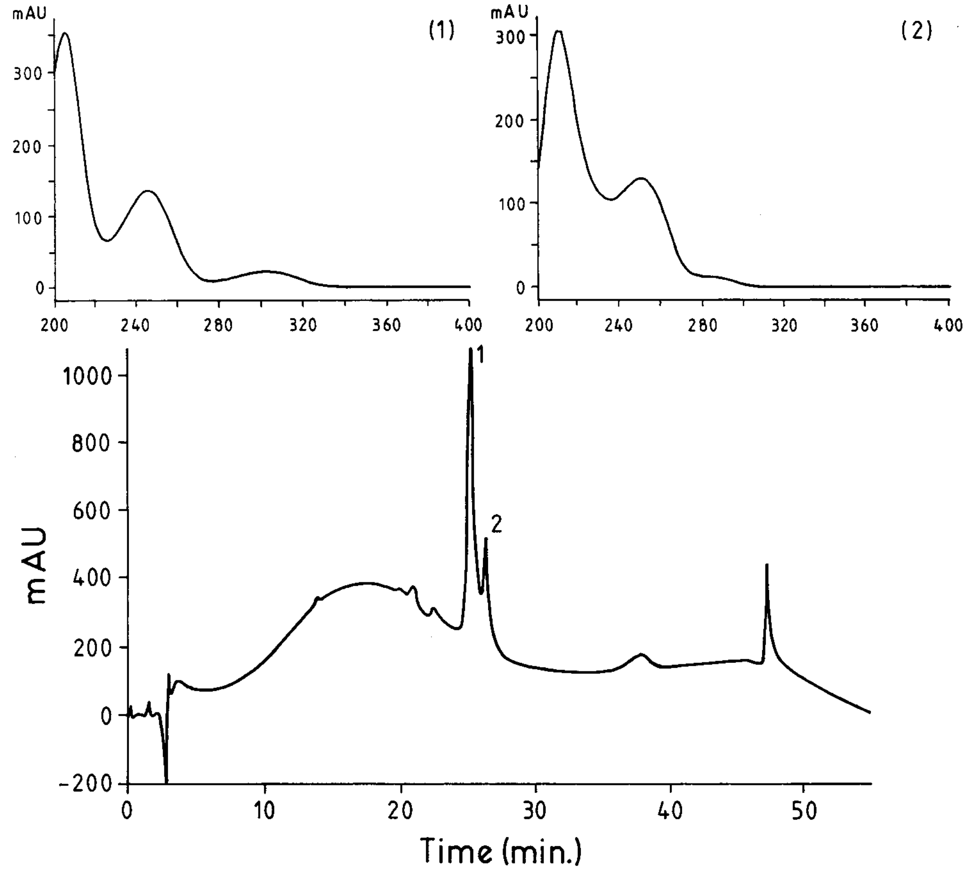

FIGURE 1. On-line SPE LC/DAD chromatogram of 75 mL of rice crop field water (field 2). Peak identification: (1) 3,4-dichloroaniline and (2) propanil. Precolumn PLRP-S, analytical column Ultracarb 5 ODS-30, gradient elution from 5% acetonitrile and 95% water, both containing 0.1% acetic acid, to 100% acetonitrile in 45 min; detection at 220 nm.

Field Studies. Two rice crop fields were analyzed, and the results obtained for propanil and DCA are shown in the Table 2. Although similar amounts of the pesticide were sprayed over the two fields, different concentrations were encountered. This was attributed to the distinct water volume in each field that became full at different periods of time. The concentrations obtained at the first day were, respectively, only 0.5% and 1.86% of the estimated concentration for propanil considering that the fields were filled in that day. The high solubility (130 mg/L) and vapor pressure (0.062 mPa) should hasten the herbicide dissipation. Meanwhile, high concentrations of DCA were observed, and it was suspected that it could arise from an incomplete synthesis process of the applied herbicide or degradation in the formulation. Nevertheless, the analysis of the commercial formulation did not present detectable amounts of DCA (less than 0.001%). The long contact time of propanil with the dry soil (72 h), under high temperatures and sunlight, probably induced the fast degradation of the propanil. In the soil samples collected before propanil treatment no detectable amounts of the parent compound and its degradation product were observed. However for soil sample collected at the subsequent month relatively high DCA concentrations were found and varied from 119 ± 22 μg/kg, whereas no detectable amounts of propanil were observed. Figures 1 and 2 show the LC/DAD and LC/APCI-MS chromatograms obtained for a rice paddy water sample extract.

Figure 3 shows the evolution of the levels of propanil in water samples. The propanil concentrations obtained for the field 2 were used to calculate the half-life, considering a first-order eq 23

$$C_t / C_o = e^{-}\ kt$$

TABLE 2. Concentration of Propanil and 3,4-Dichloroaniline in the Rice Paddy Water

day following fields flood	propanil (μg/L) field 1	propanil (μg/L) field 2	3,4-dichloroaniline (μg/L) field 1	3,4-dichloroaniline (μg/L) field 2
1	15.22	55.87	469.97	222.41
2	29.49	71.07	129.99	277.05
3	30.08	54.21	146.47	264.03
4	14.87	16.14	70.52	74.27
5	16.6	6.45	51.79	39.77
8	5.98	1.89	16.46	18.54

where C_t is the concentration at time t, C_o is the initial concentration, and k is the rate constant. When 50% of the pesticide is degraded, the half-life is $t_{1/2} = \ln 2/k$ and the degradation constant, k, is the slope obtained plotting ln C versus time. The propanil half-life was 1.24 days at field 2, but a half-life of 3.83 days was obtained for field 1. Propanil was detected in both fields up to the eighth day after herbicide application. The disappearance of propanil was somewhat slow when compared with the reported data by Deuel et al. (*16*), which did not detect the herbicide 48 h following flood application. Despite that similar amounts of propanil were applied in that work (7 kg/ha), the existence of rice foliage should have contributed to the faster disappearance. It is known that the enzyme aryl acylamidase, present in rice plants and microorganisms, plays an important role in the propanil degradation (*11, 12, 19, 24*−*26*). So, a linear decrease in the herbicide concentration should be directly associated with the foliar rice absorption. In the present work, no rice foliage in the fields was present during that propanil application, and this probably permitted somewhat longer propanil persistence in water. Some reports have also been

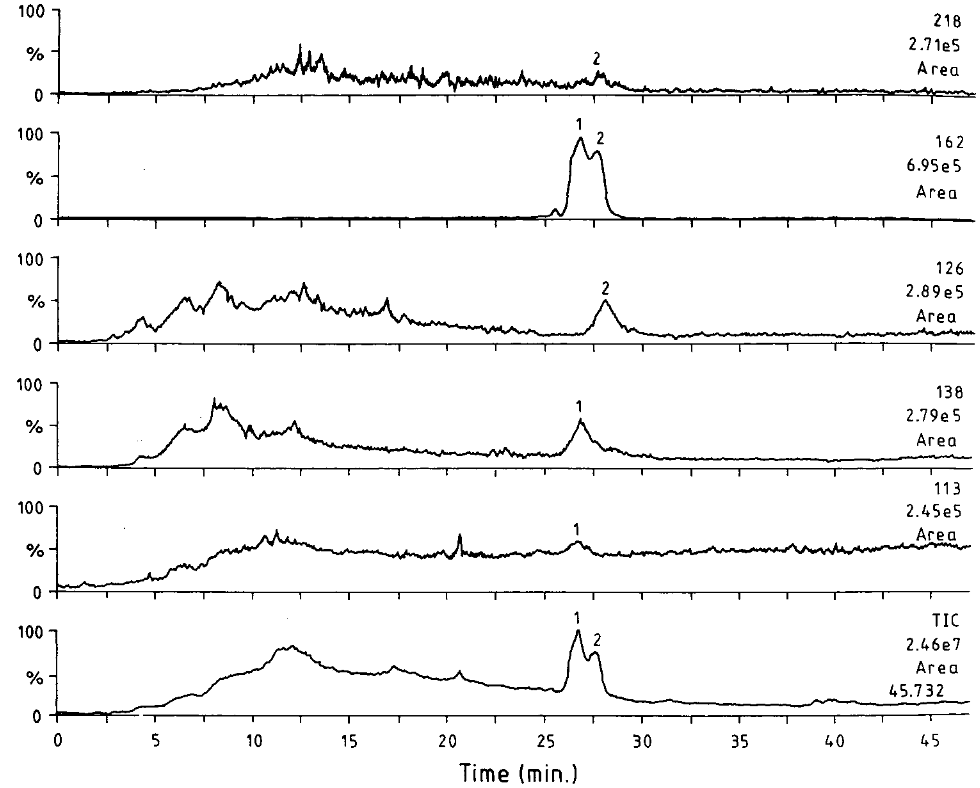

FIGURE 2. TIC and selected ion chromatograms of a rice paddy water sample obtained after on-line SPE-LC/APCI/MS with positive ionization. Peak identification: (1) 3,4-dichloroaniline and (2) propanil. Conditions as described in the text.

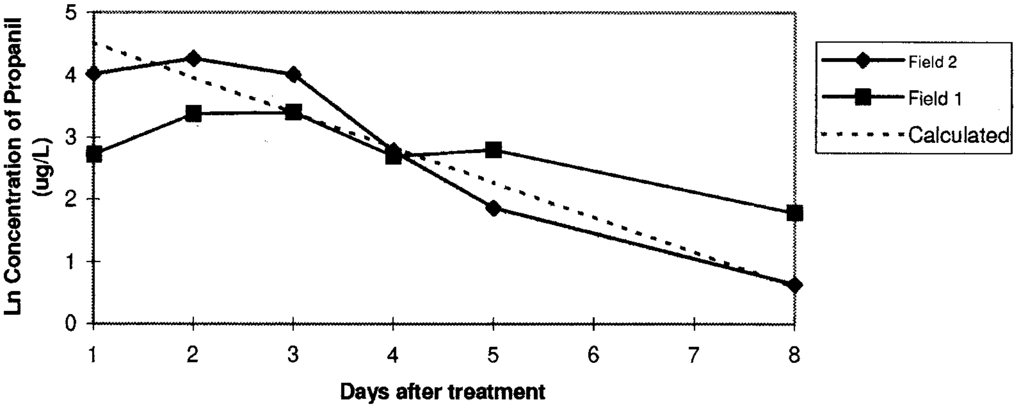

FIGURE 3. Evolution of the levels of propanil in rice paddy water. The plotted ln of concentration versus time give both measured and calculated values, according to first-order decay. Calculated values were obtained from samples of the field 2 ($R^2 = 0.92$).

shown that the DCA mineralization rate is directly dependent on the temperature (*13–16, 26–28*). The high temperatures promote a rapid DCA incorporation by the soil, forming bound residues with the organic material (humics) that are gradually mineralized. However, it has been previously cited that 20% remains intact, and it is a possible contamination source of DCA in the soil (*27*). In this work, 3.5% (field 1) and 8.3% (field 2) of the DCA concentrations were found at the last sampling (eighth day), when compared to the initial DCA amounts, obtained at the first sample collection. Field conditions favored not only the propanil degradation but also the DCA association with organic matter in the soil. The DCA bounded to the organic matter was gradually not extractable from the water matrix resulting in the decrease instead to an increase that could be expected due to propanil degradation. The half-lives obtained for DCA were 1.58 and 1.63 days for the fields 1 and 2, respectively.

The results obtained in our study showed that propanil had a somewhat higher persistence when compared with organophosphorus pesticides applied over the rice crops fields of the Ebre area. For example, fenitrothion half-lives varied from 11 to 19 h with a quick decay within the first hours after pesticide application, followed by a slow disappearance (*5, 6*).

Degradation Study under Laboratory Conditions. The magnitude of the factors affecting the propanil transformation was investigated during a week using spiked Milli-Q water at different laboratory conditions. Paddy field waters were not used in this study, since the microbial influence over the propanil degradation had been reported in several papers (*11, 12, 16, 19*). The study was carried out to evaluate the influence of other environmental parameters using a propanil concentration as close as possible to that found in the paddy fields. Figure 4 shows how propanil and DCA were recovered from spiked Milli-Q water and maintained at different laboratory conditions, i.e., temperature, humic material, and Suntest light irradiation. It was observed that high temperature and light favored the propanil transformation. For

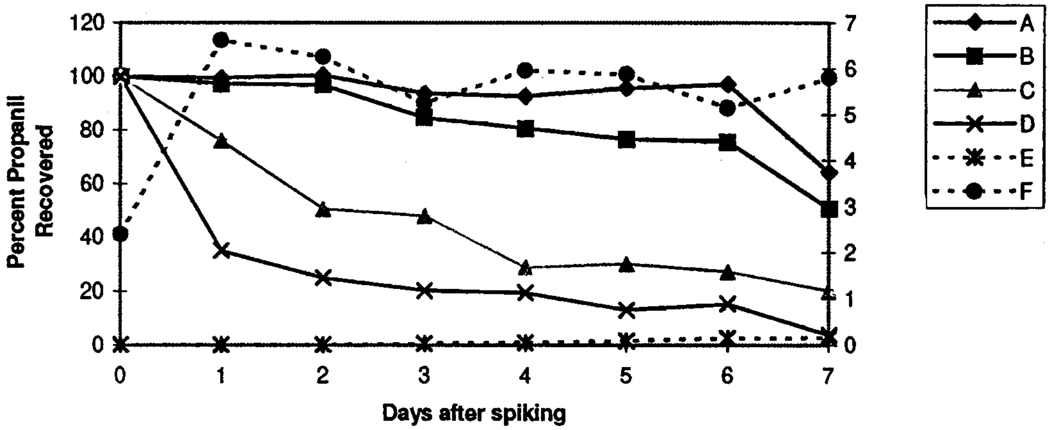

FIGURE 4. Percent propanil recovered in spiked Milli-Q water (10 μg/L, mantained at different conditions: at 4 °C (A), at 20 °C (B), at 35 °C and under Suntest light irradiation (C), at 35 °C, under Suntest light irradiation and with 10 mg/L of humic acid (D). DCA appearance in the samples maintained at 20 °C (E) and at 35 °C, under Suntest light irradiation and with 10 mg/L of humic acid (F).

TABLE 3. Comparative Data of the Half-Life for Propanil under Different Conditions

sample type and conditions (propanil concentration)	half-life (days)	ref
rice paddy water from Ebre Delta, 20−30 °C, sunlight	1.24	*a*
Milli-Q spiked water (10 μg/L), 4 °C, dark	12.27	*a*
Milli-Q spiked water (10 μg/L), 20 °C, dark	7.58	*a*
Milli-Q spiked water (10 μg/L), 35 °C, Suntest light	2.95	*a*
Milli-Q spiked water (10 μg/L), 35 °C, Suntest light, 10 mg/L humic acid	1.73	*a*
buffered distilled water (50 mg/L), 28 °C	2.50	12
alkaline solution (400 mg/L), 106.5 °C	1.88	18
soil-contacted water (5 mg/L), pH 9, without urea addition	20.0	13
soil-contacted water (5 mg/L), pH 8, 0.2 g urea	2.0	13
lake water from Northeast Georgia (0.5 mg/L), 25 °C	6.02	11
lake and water samples from Moscow Region (0.1 mg/L), 17−22 °C	1.04	19

[a] This paper.

propanil it can be noticed that when increasing the water temperature—from 4 to 20 °C (A to B)—or when increasing the humic content at the same temperature (C to D) higher degradation can be observed. For DCA the effect of humic acid is totally different, and it can be noticed that at 10 mg/L of humic acid, the degradation is much slower as compared to the same sample irradiated without humic acid (E to F). In the case of DCA it can be postulated that light has a very small effect because humic protects dichloroaniline from degradation. In addition it can be added that the binding of dichloroaniline with humic substances, that contain phenolic and carboxylic structures, is favored over the interaction with propanil that does not contain an aniline group.

The propanil half-lives obtained in such conditions (at 35 °C, under light irradiation, with and without humic acid addition) were 2.95 and 1.73 days, respectively, and are indicated in Table 3. These results suggest the strong influence of the organic matter over propanil transformation, as reported by Hsu and Bartha (*25*). It could be supposed that, at the field pH (between 7.8 and 8.8) (*4*), the organic matter (humics) should strongly favor propanil degradation as it was confirmed by the experiments performed under controlled laboratory conditions. Table 3 compares propanil half-lives obtained for different water samples, carried out in this work, and from literature data. For samples with organic matter with a fertilizer addition (urea) and pH 8 (13), quite similar to the conditions of the Ebre fields, there was a close similarity among the herbicide half-lives. However we should point out that most of the experiments were performed with much higher analyte concentrations as compared to the present work, which unfortunately makes it difficult to compare propanil half-lives.

Acknowledgments

SEO (Sociedad Española de Ornitologia) is thanked for the sampling assistance. This work was supported by OWWA (Wastewater Cluster), Contract N(ENV4-CT97-0608, CICYT AMB97-2083-CE and by LIFE96NAT/E/313. T.C.R. Santos gratefully acknowledges financial support from CAPES (Proc. BEX 1843/95-6) and Federal University of Maranhão (Brazil). We also would like to thank Imma Ferrer (CID/CSIC).

Literature Cited

(1) Barceló, D.; Chiron, S.; Fernandez-Alba, A.; Valverde, A.; Alpendurada, M. F. In *Herbicide metabolites in surface water and groundwater*; Meyer, M. T., Thurman, E. M., Eds.; ACS Symposium Series No. 630, American Chemical Society: Washington, DC, 1995; pp 238−253.
(2) Soderquist, C. J.; Bowers, J. B.; Crosby, D. G. *J. Agric. Food Chem.* **1977**, *25*, 940−945.
(3) Chiron, S.; Papilloud, S.; Haerdi, W.; Barceló, D. *Anal. Chem.* **1995**, *67*, 1637−1643.
(4) Lacorte, S.; Ehresmann, N.; Barceló, D. *Environ. Sci. Technol.* **1996**, *30*, 917−923.
(5) Lacorte, S.; Barceló, D. *Environ. Sci. Technol.* **1994**, *28*, 1159−1163.
(6) Oubiña, A.; Ferrer, I.; Gascón, J.; Barceló, D. *Environ. Sci. Technol.* **1994**, *28*, 1159−1163.
(7) Salau, J. S.; Alonso, R.; Batló, G.; Barceló, D. *Anal. Chim. Acta* **1994**, *293*, 109−117.
(8) Lacorte, S.; Lartigues, S. B.; Garrigues, P.; Barceló, D. *Environ. Sci. Technol.* **1995**, *29*, 431−438.
(9) Gever, J. R.; Mabury, S. A.; Crosby, D. G. *Environ. Toxicol. Chem.* **1996**, *15*, 1676−1682.
(10) Battaglin, W. A.; Goolsby, D. A. *Spacial Data in Geographic Information System Format on Agricultural Chemical Usage, Land Use and Cropping Practices in the United States*; U.S. Geological Survey Water Resources Investigation: 1995; 94-4176, p 87.

(11) Correa, I. E.; Steen, W. C. *Chemosphere* **1995**, *30*, 103−116.
(12) Dahchour, A.; Bitton, G.; Coste, C. M.; Bastide, J. *Bull. Environ. Contam. Toxicol.* **1986**, *36*, 556−562.
(13) Strekozov, B. P. In *Mekh. Deistviya Gerbits. Sint. Regul. Rosta Rast. Ikh Sud′ba Biosfere;* Sokolov, M. S., Ed.; Simp. Stran-Chlenov SEV 10th, 1975; Vol. 2, pp 93−96.
(14) Sokolov, M. S.; Knyr, L. L.; Nevzorov, M. I.; Kryzhko, B. A.; Chubenko, A. P.; Shandybin, V. E. *Izv. Akad. Nauk USSR* **1976**, Ser. Biol. *2*, 171−181.
(15) Agarkov, V. D. *Vestn. S-Kh. Nauk* **1978**, *6*, 71−76.
(16) Deuel, L. E., Jr; Brown, K. W.; Turner, F. C.; Westfall, D. G.; Price, J. D. *J. Environ. Qual.* **1977**, *6*, 127−132.
(17) Kolesnikova, T. Kh.; Semenova, L. F. *Gidrokhim. Mater.* **1974**, *60*, 100−102.
(18) Lekevicius, R.; Sabaliunas, D.; Knabikas, A.; Jankauskas, V. *Int. J. Environ. Anal. Chem.* **1992**, *46*, 141−147.
(19) Steen, W. C.; Vasilyeva, G. K.; Anan′eva, N. D. *Chemosphere* **1986**, *15*, 917−922.
(20) Santos, T. C.; Rocha, J. R.; Barceló, D. *Intern. J. Environ. Anal. Chem.* (in press).
(21) Bard, L. A. *Am. Lab. News De* **1992**, Feb.
(22) Durand, G.; Barceló, D. *Toxicol. Environ. Chem.* **1992**, *36*, 225−234.
(23) Peñuela, G.; Barceló, D. *J. Chromatogr. A* **1996**, *754*, 187−195.
(24) Hirase, K.; Matsunaka, S. *Pest. Biochem. Physiol.* **1991**, 302−308.
(25) Pothuluri, J. V.; Hinson, J. A.; Cerniglia, C. E. *J. Environ. Qual.* **1991**, *20*, 330−346.
(26) El-Dib, M. A.; Aly, O. A. *Water Res.* **1976**, *10*, 1055−1059.
(27) Hsu, T.-S.; Bartha, R. *J. Agric. Food Chem.* **1976**, *24*, 118−122.
(28) Völkel, W.; Choné, Th.; Andreux, F.; Mansour, M.; Korte, F. *Soil Biol. Biochem.* **1994**, *26*, 1673−1679.

Received for review March 3, 1998. Revised manuscript received July 30, 1998. Accepted August 4, 1998.

ES980212K