

Pesticide Reactivity toward Hydroxyl and Its Relationship to Field Persistence

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To estimate the reactivity of organic pesticides toward hydroxyl, a standard competitor, *p*-nitroso-*N,N*-dimethylaniline (PNDA), competes with a particular compound for the radicals produced by the photolysis of hydrogen peroxide. The rate at which the pesticide competes with PNDA for hydroxyl determines its reactivity. Of 10 pesticides tested, carbaryl was the most reactive, carbofuran and MCPA were of intermediate reactivity, and hexazinone was one of the least reactive. Experiments in irradiated field water, both in the laboratory and in sunlit rice paddies, showed that pesticide dissipation rates followed the order of reactivity with hydroxyl radical.

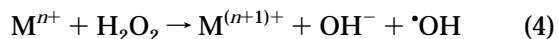
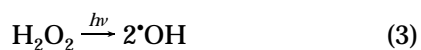
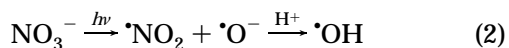
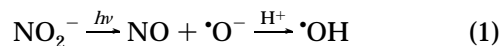
Keywords: *Hydroxyl radical; indirect photolysis; pesticides; aquatic fate*

INTRODUCTION

Agrochemicals and other organic pollutants find their way into natural waters either through direct application as in pesticides applied intentionally to rice fields or from unintentional drift, atmospheric deposition, and runoff from agricultural fields and other human activity. The pollutants are dissipated from the water column by volatilization and sorption to sediments and degraded by hydrolysis, direct photolysis, and indirect photolysis.

Indirect photolysis, or sensitized photolysis, has been shown to be an important degradative mechanism for some organic chemicals that do not undergo rapid direct photolysis and are resistant to hydrolysis. The reactions are thought to be due to various transient reagents such as singlet oxygen (Haag and Hoigne, 1986), alkylperoxy radicals (Mill et al., 1980), triplet states (Zepp et al., 1985), and hydroxyl radical ($\cdot\text{OH}$) (Draper and Crosby, 1984) as intermediaries in this degradation. Of these, $\cdot\text{OH}$ is known to be the most reactive toward a wide variety of organic compounds (Buxton et al., 1988).

Sources of $\cdot\text{OH}$ in natural waters include photolysis of dissolved organic matter (DOM) (Takahashi et al., 1988), nitrate, nitrite (Alif and Boule, 1991), and hydrogen peroxide (H_2O_2) (Buxton et al., 1988) and Fenton-type reactions between reduced metals (Fe, Cu, and Mn) and H_2O_2 (Barnes and Sugden, 1986; Zepp et al., 1992) (eqs 1–4). The concentration of $\cdot\text{OH}$ results from a balance between the rates of production, P_{OH} , and consumption by natural scavengers, C_{OH} . Typically, DOM, bicarbonate, and carbonate account for nearly all the scavenging of $\cdot\text{OH}$ in most waters (Haag and Hoigne, 1985).



Natural waters vary in the predominant mechanisms

by which $\cdot\text{OH}$ is produced and consumed. Steady-state hydroxyl concentrations ($[\cdot\text{OH}]_{\text{ss}}$) have been reported in the range of (5×10^{-16}) – (1.5×10^{-18}) M in natural freshwaters (Mill et al., 1980; Russi et al., 1982) and 1.1 – 12×10^{-18} M in coastal and open ocean surface water (Mopper and Zhou, 1990). Additionally, $\cdot\text{OH}$ is found in cloud and fog waters from vapor-phase diffusion (Chameides and Davis, 1982), and Faust and Allen (1993) have shown that photoproduction in cloud waters is equally important.

Chemical reactivity toward $\cdot\text{OH}$ has generally been measured using pulse radiolysis as a source of $\cdot\text{OH}$ and competition kinetics to determine relative rates of reactivity, although some direct measurements have been made (Buxton et al., 1988). Relative rates yield absolute rates if the rate of reaction of $\cdot\text{OH}$ with the competitor is known. Recent investigators have generated $\cdot\text{OH}$ by Fenton's reaction (Sedlak and Andren, 1991), photolysis of H_2O_2 (Kochany and Bolton, 1992), and the photo-Fenton reaction (Haag and Yao, 1992). Most organic compounds react with $\cdot\text{OH}$ with second-order rate constants of 10^9 – 10^{10} ; compilations of hydroxyl rate data are available (e.g., Buxton et al., 1988) but, until recently, contained no references to pesticides (Haag and Yao, 1992). However, the importance of hydroxyl reactions in the degradation of many aquatic pollutants seems evident.

Agricultural rice fields represent a situation in which all the major generators of hydroxyl are known to occur, along with a relatively large input of pesticides. Our previous research has suggested that the principal products from pesticide degradation in natural waters often are those expected from reactions with hydroxyl. Our present goal was to determine whether a relationship exists between a chemical's reactivity toward $\cdot\text{OH}$ and its field persistence in the sunlit aquatic environment. To this end, we measured the laboratory reaction rates of a series of pesticides that have wide use in agriculture (Figure 1) and compared the results for four of them with their measured persistence under laboratory and field conditions; the dissipation rates indeed mirrored reactivity toward hydroxyl.

MATERIALS AND METHODS

Chemicals. *N,N*-Dimethyl-4-nitrosoaniline (*p*-nitroso-*N,N*-dimethylaniline, PNDA; Aldrich Chemical Co.) was recrystallized from aqueous ethanol and was pure by gas chromatog-

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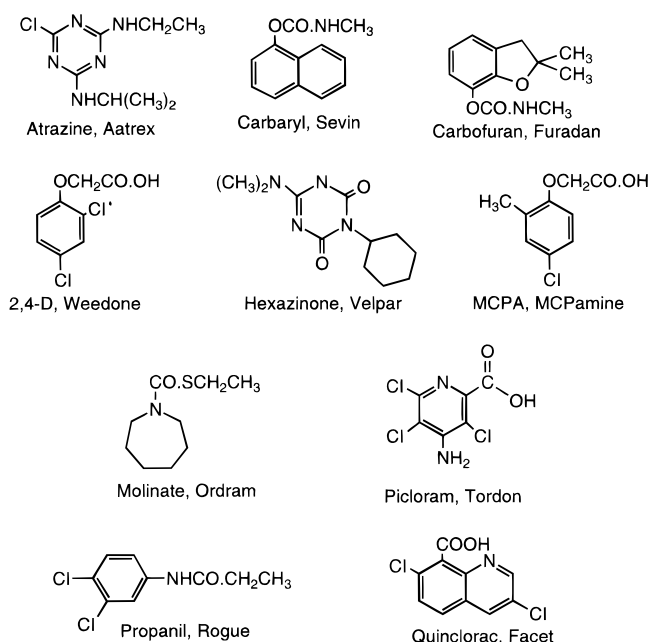


Figure 1. Structures and chemical and trade names of pesticides.

Table 1. HPLC Conditions for Pesticide Analysis^a

pesticide	detection wavelength (nm)	mobile phase (H ₂ O:CH ₃ CN)	retention time (min)
atrazine	263	35:65	5.3
carbaryl	280	35:65	5.3
carbofuran	278	35:65	5.0
2,4-D	284	50:50 ^b	6.4
hexazinone	254	35:65	4.7
MCPA	280	50:50 ^b	6.2
picloram	250	75:25 ^b	4.3
propanil	250	35:65	5.5
quinlorac	240	50:50 ^b	4.5

^a C-18 reverse-phase column. ^b Water adjusted to pH 2.5 with trifluoroacetic acid.

raphy (GC) with flame ionization detection (Varian Model 3300). Sodium tetraborate decahydrate (Aldrich) and 30% hydrogen peroxide (Fisher Scientific) were used as received. Carbaryl, 2,4-D, MCPA, propanil, quinlorac, molinate, and atrazine (Figure 1) were available from previous investigations in this laboratory, were recrystallized from solvents such as aqueous methanol, as required, and were pure by HPLC with UV detection at appropriate wavelengths (Table 1). Hexazinone (98%), carbofuran (99%), and metribuzin (99%) were purchased from Chem Service (West Chester, PA), and the purity was checked by HPLC with UV detection. Picloram was a gift from Tracy Sterling and was used as received. Sevin 5 WP, Furadan 4F, MCPamine, and Velpar 90WP for field applications of carbaryl, carbofuran, MCPA, and hexazinone, respectively, were obtained from The UC-Davis Weed Science Program. All solvents were HPLC grade (Fisher Scientific), and water was deionized and charcoal filtered (Milli-Q, Millipore Corp.).

Analysis. PNDA was determined spectrophotometrically at 440 nm with a Hewlett Packard 8452 UV/vis diode-array spectrophotometer. Monitoring of pesticides during laboratory experiments was by RP-HPLC with a 25 cm C-18 column (Alltech) and an ISCO gradient programmer, pump, and detector (V⁴ UV/visible). The solvent system was either methanol (MeOH) or aqueous acetonitrile (CH₃CN) (isocratic), and detection wavelength was appropriate for each pesticide (Table 1). For MCPA, 2,4-D, and quinlorac, the pH of the aqueous phase was modified to pH 3 with trifluoroacetic acid (Aldrich). HPLC conditions are illustrated in Table 1.

During laboratory irradiations and field investigations of dissipation, pesticides were extracted from water onto C-18 solid-phase extraction cartridges (Analytichem) conditioned

with two column sequential volumes of CH₃CN, MeOH, and H₂O, eluted with CH₃CN, and determined by HPLC.

Competition Kinetics. A typical test solution consisted of 1.20×10^{-5} M PNDA, an appropriate concentration of probe pesticide (0–8 times that of PNDA), and 2.65×10^{-3} M H₂O₂ in 0.01 M sodium tetraborate buffer at pH 8.9. The mixture was irradiated with a 40 W fluorescent UV lamp (Light Sources FS-40; UV max at 310 nm) at a constant 25 °C in a steady stream of air (for mixing and oxygen saturation) in a photoreactor first described by Crosby and Tang (1969). Generally, samples were taken every 30 min for spectrometric analysis. Control experiments consisted of the same mixture and irradiation conditions without the H₂O₂. Pseudo-first-order kinetic analysis resulted in a rate constant (*S*) for each [pesticide]/[PNDA] ratio. These data were transformed into plots of pesticide/PNDA vs *S*₀/*S*, resulting in a slope of *k*_p/*k*. Each measurement was replicated at least twice.

Laboratory Persistence. Carbaryl, carbofuran, MCPA, and hexazinone were chosen as representative of a wide range of reactivity. Filter-sterilized field water (0.45 μm) containing each of the four pesticides (ca. 1×10^{-5} M) was placed outdoors, at constant temperature (range 22–28 °C) under water, under full September sunlight (1800 μW/cm²). Solutions were held in borosilicate roller bottles, and aliquots were retrieved at appropriate time intervals. Laboratory irradiations were carried out with similar solutions in the photoreactor that closely simulated the UV portion of natural sunlight (Crosby and Tang, 1969).

Field Dissipation. The commercial formulations were applied via backpack sprayer to 20 m² plots enclosed by aluminum rings embedded in a flooded rice field at the UC-Davis Rice Research Facility. Application rates were designed to yield approximately 5×10^{-6} M of each pesticide in field water. Applications were conducted in July at a time of maximum sunlight intensity (2000 μW/cm², at noon). The pH of the water varied between 7 and 8.3, temperature between 18 and 35 °C, and dissolved oxygen between 3.5 and 6 ppm, and conductivity was approximately 300 μS. At appropriate intervals, triplicate grab samples of water were collected, combined, and immediately returned to the laboratory for analysis as previously described.

To assess the contribution of volatility to the dissipation of these four pesticides, Henry's law constants were measured in a bubble chamber slightly modified from that described by Mackay et al. (1979), and analysis of pesticide loss from distilled water, under a constant stream of nitrogen, was monitored by HPLC.

RESULTS AND DISCUSSION

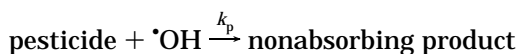
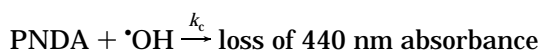
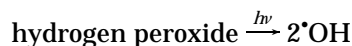
Competition Kinetics. Sedlak and Andren (1991) utilized competition kinetics, with Fenton's reaction for the production of •OH, to measure the relative reaction rates of 28 constituents of a PCB mixture (Aroclor 1242) with hydroxyl. Kochany and Bolton (1992) also used competition kinetics, with photolysis of H₂O₂ as a source of •OH, and detected •OH with the spin trap 5,5-dimethylpyrrolone *N*-oxide following the increase in the DMPO adduct signal by electron paramagnetic spectroscopy (EPR) to obtain absolute rates of reaction for some halobenzene derivatives. Haag and Yao (1992) used competition kinetics, generating •OH with the photo-Fenton system, although other methods were used for specific substrates; they measured second-order rate constants for reactions of 25 compounds. A general drawback to these systems is the sophisticated equipment required, such as the EPR spectrometer, or the necessity of analytically monitoring both the competitor and probe chemicals.

We adapted the competition kinetics system, producing •OH by photolysis of H₂O₂ and employing a standard competitor, PNDA (Kraljic and Trumbore, 1965), the loss of which was monitored by spectrophotometry. This method utilizes relatively simple analytical methodology

(UV/vis spectrophotometry) and is rapid and reproducible. There is no requirement for monitoring all species present except in the control used to determine the stability of the pesticide. Concentrations of pesticide, competitor, and $\cdot\text{OH}$ are all designed to yield a simple competition between the pesticide and PNDA for the radical. Approximately 60% of the PNDA was degraded when no pesticide was present, yielding simple pseudo-first-order kinetics.

This method would not be suitable for determining the reactivity of pesticides significantly lost to hydrolysis, direct photolysis, or volatilization from the solution during the time course (150 min) of the experiment. Additionally, moderate solubility (>10 mg/L), in water, is required for the competition experiment to yield results for [pesticide]/[PNDA] ratios of 8, although lower solubilities can provide smaller ratios.

The reactivity of a particular pesticide was deduced from the degree to which it competed with PNDA for hydroxyl:



If the competition were simply between the pesticide and standard competitor, it follows that

$$\frac{S_0}{S} = 1 + \frac{k_p[\text{pesticide}]}{k_c[\text{PNDA}]} \quad (5)$$

where S_0 represents the rate of loss of PNDA with no probe and S when the pesticide is present in the system and k_c and k_p are the rates of hydroxyl reaction with PNDA and pesticide, respectively. A plot of S_0/S versus [pesticide]/[PNDA] produced a straight line with a slope of k_p/k_c ; as the second-order rate constant for PNDA oxidation k_p is reported to be $1.25 \times 10^{10} \text{ M s}^{-1}$ (Buxton et al., 1988), an absolute value can be calculated for k_c .

A requirement of the competition kinetics system was that competition for $\cdot\text{OH}$ be simply that between PNDA and the probe pesticide. Significant contributions from degradation products of PNDA or pesticide would alter the competition. Control experiments indicated that PNDA was stable to the UV irradiation used and to H_2O_2 in the dark over the time course of the experiments.

Figure 2 shows a typical plot of first-order loss of PNDA, at varying [carbofuran]/[PNDA] ratios, during the 150 min irradiation time. Similar plots were obtained for the other pesticides with the exception of metribuzin. As the ratio of metribuzin to PNDA increased, degradation of PNDA also was observed to increase, in contrast to the expected decrease due to competition for $\cdot\text{OH}$. Pape and Zabik (1972) have previously reported the production of a radical intermediate upon irradiation of aqueous solutions of metribuzin; we hypothesize that this radical was reacting with PNDA.

All other pesticides showed first-order degradation. These data were transformed according to eq 5, and a typical plot (Figure 3) provides the combined results obtained from all probe pesticides; the steeper the slope (k_p/k_c), the more reactive the chemical toward hydroxyl. Second-order rate constants are shown in Table 2. The three pesticides which are carboxylic acids would have

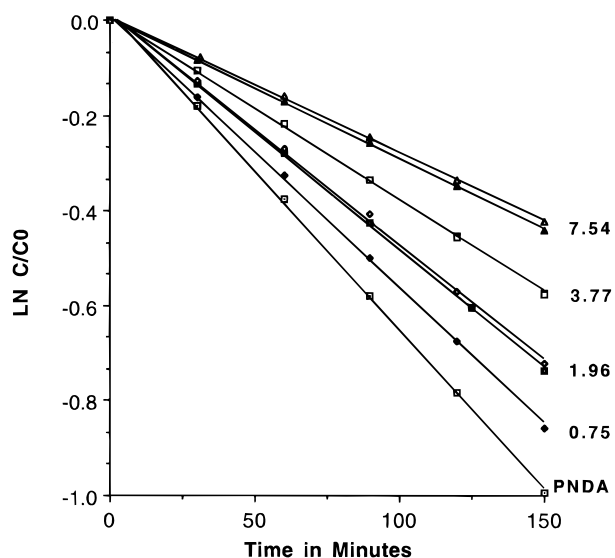


Figure 2. Competition of carbofuran with PNDA at various concentration ratios of carbofuran to PNDA. Numerical values represent [carbofuran]/[PNDA].

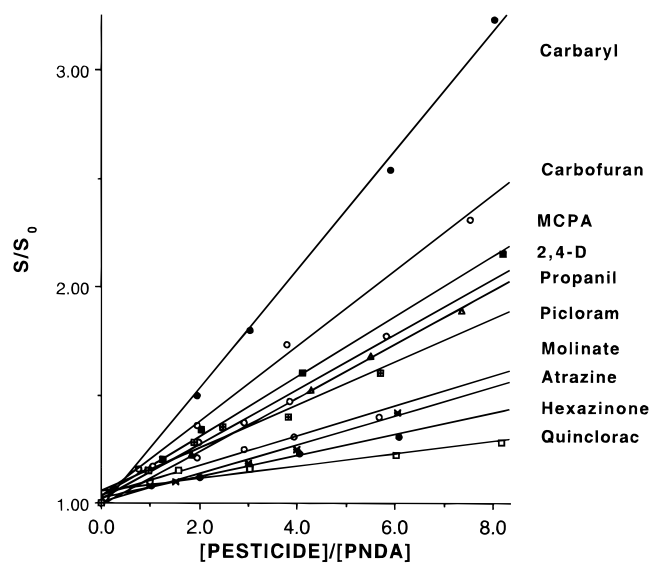


Figure 3. Relative rates of reaction for pesticides with hydroxyl.

Table 2. Rate Constants for Reactivity with Hydroxyl

pesticide	rate constant ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)		Henry's Law ($\text{atm m}^3/\text{mol}$)
	measd	lit.	
carbaryl	3.4		$<10^{-7}$
carbofuran	2.2		$<10^{-7}$
MCPA	1.7		$<10^{-7}$
2,4-D	1.6	5.0 ^a	$5.4 \times 10^{-6} \text{ }^c$
propanil	1.6		$3.5 \times 10^{-8} \text{ }^c$
picloram	1.3	3.4 ^a	$3.3 \times 10^{-10} \text{ }^c$
molinate	0.85		$3.1 \times 10^{-6} \text{ }^c$
atrazine	0.82	2.6 ^a	$2.8 \times 10^{-9} \text{ }^c$
hexazinone	0.62		$<10^{-7}$
quinclorac	0.36		
benzoic acid	3.2	5.9 ^b	

^a Haag and Yao, 1992. ^b Buxton et al., 1988. ^c Suntio et al., 1988.

been in the ionized state at the pH 8.9 used during the experiments.

Carbaryl, a carbamate insecticide, was the most reactive toward hydroxyl followed by another carbamate, carbofuran. The electron-rich aromatic rings present in both would be the most likely primary site of addition reactions with hydroxyl; hydrogen abstraction could also

contribute to the reactivity, particularly for carbofuran, although hydrogen abstractions generally are slower than additions.

The phenoxy herbicides MCPA and 2,4-D along with the pyridinecarboxylic acid herbicide picloram and the anilide herbicide propanil were of intermediate reactivity. Again, addition of $\cdot\text{OH}$ to the aromatic ring was the likely reaction mechanism for MCPA, 2,4-D, and propanil, with the reduction in reactivity relative to the carbamates probably due to ring deactivation by the chlorines. Additionally, $\cdot\text{OH}$ could have also reacted by hydrogen abstraction from the methyl of MCPA or the aliphatic side chain on propanil. Ring addition to picloram could have occurred along with hydrogen abstraction from the amine. Products were not identified.

A triazine herbicide (atrazine), a quinolinecarboxylic acid (quinclorac), a thiocarbamate (molinate), and a triazinone (hexazinone) were relatively unreactive toward hydroxyl. The lower reactivity of molinate and hexazinone could be due to the reduced presence of olefinic character relative to the more reactive pesticides, with hydrogen abstraction being the primary mode of attack by $\cdot\text{OH}$. The electron-withdrawing effect of two chlorines and a carboxylic acid contribute to the low reactivity observed for quinclorac. Additionally, the quinoline ring may also reduce reactivity, as observed for the lower second-order rate constant for reaction with pyridine compared to benzene, 3.1 vs $7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988).

During the course of this project, Haag and Yeo (1992) reported rate constants for the reaction of $\cdot\text{OH}$ with atrazine, picloram, and 2,4-D. Our values are significantly lower: atrazine, 8.2×10^8 versus $2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($3.1\times$); 2,4-D, 1.6×10^9 versus $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($3.1\times$); and picloram, 1.3×10^9 versus $3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($2.6\times$). However, our rate constant for benzoic acid (as benzoate ion), $3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, was 54% of that reported in the literature (Buxton et al., 1988). Literature values for multiple determinations with a particular chemical vary typically within 10% (e.g., benzoate ion) (Buxton et al., 1988).

Laboratory Persistence. The irradiation of carbaryl, carbofuran, MCPA, and hexazinone in field water under natural sunlight and in the laboratory under simulated solar radiation produced degradation rates that closely followed the measured relative reactivity of these pesticides toward $\cdot\text{OH}$ (Figure 4). Dark controls showed only minor loss. Hexazinone, coincident with its low reactivity, was extremely stable under these irradiation conditions, with no distinguishable loss observed. In contrast, carbaryl was very labile, with a half-life of less than 5 h under sunlight and less than 3 h under laboratory irradiation.

Field Dissipation. Dissipation rates from a shallow (10 cm) field water again mirrored those observed under more controlled laboratory conditions (Figure 5) and was not due to volatilization or soil adsorption. Henry's law constants, measured in the bubble chamber, indicated that carbaryl, carbofuran, MCPA, and hexazinone were essentially nonvolatile from water ($H = <10^{-7} \text{ atm m}^3/\text{mol}$), and literature values for sorption to sediment likewise indicated that these four pesticides would not be strongly bound to sediment or organic material in the water column ($K_{oc} = 230$ for carbaryl and <30 for the other pesticide as calculated from K_{ow}) (Worthing and Hance, 1991).

Seiber et al. (1978) investigated the fate and persistence of carbofuran under rice paddy conditions. They observed aqueous dissipation half-lives of 67 h for paddy

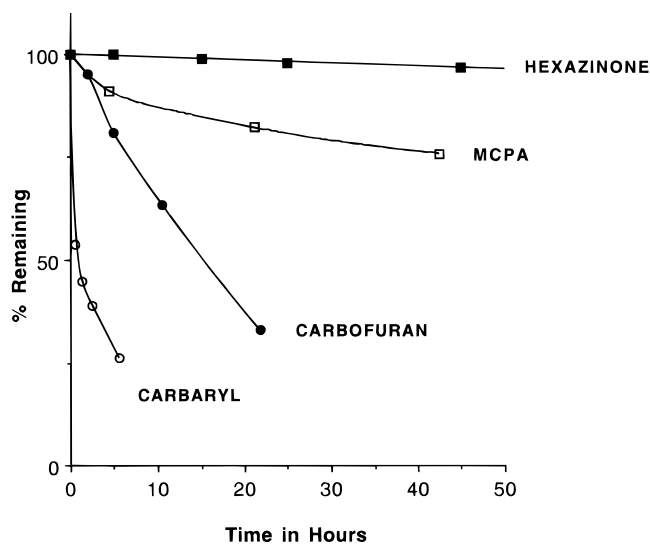


Figure 4. Simulated-sunlight laboratory persistence of pesticides in filtered field water.

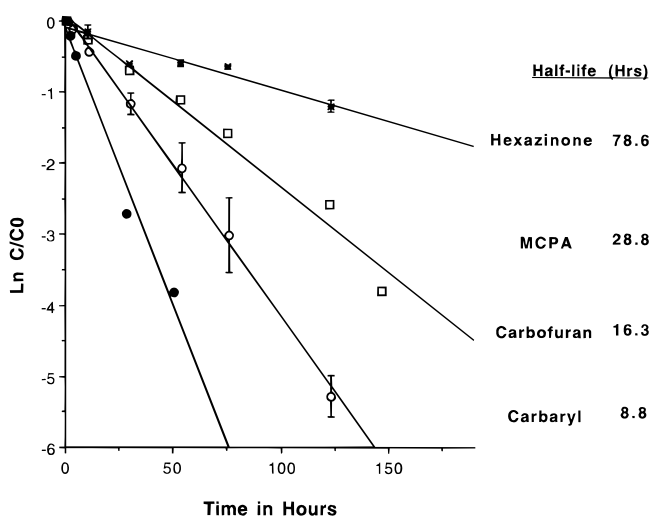


Figure 5. Field dissipation rates (half-life, h) of pesticides in water, linearized to pseudo-first-order kinetics.

fields and 48 and 55 h for two farm ponds. Under laboratory conditions, without irradiation, hydrolysis was a major degradation pathway, with half-lives at pH 7 of 864 and 240 h in deionized and field water, respectively. MCPA dissipated with a half-life of 17 days in dilute aqueous solution under laboratory irradiation (Soderquist and Crosby, 1975) and approximately 5 days under field conditions; these authors suggested that microbial degradation contributed to the dissipation of MCPA under field conditions. Hexazinone was photodegraded very slowly under natural sunlight; 70% remained after 5 weeks in a standard reference water (pH 8.1), while, in river water, 49% remained after 5 weeks (Rhodes, 1980). However, there was no determination of what contribution, if any, microbial degradation made to hexazinone degradation under these conditions. Carbaryl has been shown to be degraded rapidly under direct photolysis conditions; Zepp and Cline (1977) reported a sunlight photolysis half-life for carbaryl, in pure water, of approximately 63 h. These data are in accord with our results and, in general, with the competition kinetics data when volatilization is taken into consideration.

It is difficult, in the final analysis, to subtract the contribution of direct photolysis and hydrolysis to the dissipation of these model pesticides under field conditions, although it may be large for carbaryl and carbo-

furan in particular. Thus, although an empirical relationship exists between pesticide reactivity toward hydroxyl and persistence, a valid correlation cannot be drawn. However, it is clear that hydroxyl contributes to the degradation of pesticides, particularly in shallow sunlit rice field waters, thus limiting the overall persistence of these water pollutants.

CONCLUSIONS

The method described for the measurement of pesticide reactivity toward hydroxyl radical is simple, is rapid, and results in rate constants that are similar to those reported by others. Currently, the method is limited to those pesticides with aqueous solubilities in the low-mg/L (ppm) range, due to the use of UV/vis spectrophotometry for monitoring the competing PNDA. It should be relatively simple to extend this method to more hydrophobic chemicals by using gas chromatographic analysis or liquid chromatography with UV/vis detection.

It is clear that direct photolysis and hydrolysis contributed to the dissipation of carbaryl and carbofuran under laboratory and field conditions. The contribution of direct photolysis to the dissipation of MCPA and hexazinone would have been small under the time course of these experiments. The contributions of these other degradation mechanisms have not been subtracted from the dissipation curves shown in Figures 4 and 5. Yet, it is apparent that the loss of these four pesticides in natural waters is influenced by reaction with $\cdot\text{OH}$. The relative rates of loss mirror those of relative reactivity and cannot be wholly explained by the other dissipation mechanisms of volatilization, sorption to organic material, microbial degradation, or direct photolysis.

This method would be of particular use in assessing the persistence of recalcitrant aquatic pollutants that are not degraded by the pathways of direct photolysis and microbial action or dissipated through volatilization. Additionally, this laboratory kinetic system represents a simple method for determining the contribution of indirect photolysis to the overall persistence of new agrochemicals.

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LITERATURE CITED

- Alif, A.; Boule, P. Photochemistry and environment, Part XIV. Phototransformation of nitrophenols induced by excitation of nitrite and nitrate ions. *J. Photochem. Photobiol.* **1991**, *59*, 357.
- Barnes, A. R.; Sugden, J. K. The hydroxyl radical in aqueous media. *Pharm. Acta Helv.* **1986**, *61*, 218–227.
- Buxton, B. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\text{O}^-$) in aqueous solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886.
- Chameides, W. L.; Davis, D. D. The free radical chemistry of cloud droplets and its impact upon the composition of rain. *J. Geophys. Res.* **1982**, *23*, 4863–4877.

- Crosby, D. G.; Tang, C. S. Photodecomposition of 3-(p-chlorophenyl)-1,1-dimethylurea (Monuron). *J. Agric. Food Chem.* **1969**, *17*, 1041–1044.
- Draper, W. M.; Crosby, D. G. Solar photooxidation of pesticides in dilute hydrogen peroxide. *J. Agric. Food Chem.* **1984**, *32*, 231–237.
- Faust, B. C.; Allen, J. M. Aqueous-phase photochemical formation of hydroxyl radical in authentic cloudwaters and fogwaters. *Environ. Sci. Technol.* **1993**, *27*, 1221–1224.
- Haag, W. R.; Hoigné, J. Photo-sensitized oxidation in natural water via $\cdot\text{OH}$ radicals. *Chemosphere* **1985**, *14*, 1659–1671.
- Haag, W. R.; Hoigné, J. Singlet oxygen in surface waters. 3. Photochemical formation and steady-state concentrations in various types of waters. *Environ. Sci. Technol.* **1986**, *20*, 341–348.
- Haag, W. R.; Yao, C. C. D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environ. Sci. Technol.* **1992**, *26*, 1005–1013.
- Kochany, J.; Bolton, J. R. Mechanism of photodegradation of aqueous organic pollutants. 2. Measurement of the primary rate constants for reaction of $\cdot\text{OH}$ radicals with benzene and some halobenzenes using an EPR spin-trapping method following the photolysis of H_2O_2 . *Environ. Sci. Technol.* **1992**, *26*, 262–265.
- Kralgic, I.; Trumbore, C. N. p-Nitrosodimethylaniline as an OH radical scavenger in radiation chemistry. *J. Am. Chem. Soc.* **1965**, *26*, 2547–2550.
- Mackay, D.; Shiu, W. Y.; Sutherland, R. P. Determination of air-water Henry's law constants for hydrophobic pollutants. *Environ. Sci. Technol.* **1979**, *13*, 333–337.
- Mill, T.; Hendry, D. G.; Richardson, H. Free-radical oxidants in natural waters. *Science* **1980**, *207*, 886–887.
- Mopper, K.; Zhou, X. Hydroxyl radical photoproduction in the sea and its potential impact on marine processes. *Science* **1990**, *250*, 661–664.
- Pape, B. E.; Zabik, M. J. Photochemistry of bioactive compounds. Solution-phase photochemistry of asymmetric triazin-5(4H)-ones. *J. Agric. Food Chem.* **1972**, *20*, 72–75.
- Rhodes, R. C. Studies with ^{14}C -labeled hexazinone in water and bluegill sunfish. *J. Agric. Food Chem.* **1980**, *28*, 306–310.
- Russi, H.; Kotzias, D.; Korte, F. Photoinduzierte Hydroxylierungsreaktionen organischer Chemikalien in natürlichen Gewässern. *Chemosphere* **1982**, *11*, 1041–1048.
- Sedlak, D. L.; Andren, A. W. Aqueous-phase oxidation of polychlorinated biphenyls by hydroxyl radicals. *Environ. Sci. Technol.* **1991**, *25*, 1419–1427.
- Seiber, J. N.; Catahan, M. P.; Barril, C. R. 1978. Loss of carbofuran from rice paddy water: chemical and physical factors. *J. Environ. Sci. Health* **1978**, *B13*, 131–148.
- Soderquist, C. J.; Crosby, D. G. Dissipation of 4-chloro-2-methylphenoxyacetic acid (MCPA) in a rice field. *Pestic. Sci.* **1975**, *6*, 17–33.
- Suntio, L. R.; Shiu, W. Y.; Mackay, D.; Seiber, J. N.; Glotfelty, D. Critical review of Henry's Law constants for pesticides. *Rev. Environ. Contam. Toxicol.* **1988**, *103*, 1–60.
- Takahashi, N. M. I.; Mikami, N.; Matsuda, T.; Miyamoto, J. Identification of reactive oxygen species generated by irradiation of aqueous humic acid solution. *J. Pestic. Sci.* **1988**, *13*, 429–435.

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