Bull. Environ. Contam. Toxicol. (2000) 64:780-785
© 2000 Springer-Verlag New York Inc.
DOI: 10.1007/s001280000071

Bulletin of Environmental Contamination and Toxicology

Photodegradation of the Herbicides Butachlor and Ronstar Using Natural Sunlight and Diethylamine

Y. J. Lin, C. Lin, K. J. Yeh, A. Lee

Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung, Taiwan, 91207, Republic of China

Received: 22 November 1999/Accepted: 6 April 2000

Deterioration of water quality by pesticide residues in rivers has raised environmental safety concerns. Butachlor and ronstar are the two most widely used herbicides in Taiwan. Due to their relatively high stability and retardation factors, butachlor and ronstar were persistent environmental pollutants in waters (Widmer and Spalding, 1995, 1996). Photodegradation with natural sunlight may be one of the most natural and economical degradation routes for environmental pollutants such as pesticides. The photodegradation pathways of pesticides include direct and indirect reactions. Direct photodegradation involves the process of the excitation of organics after exposure to natural sunlight and then release of the energy of radiation through molecular restructuring (i.e. isomerization, substitution, oxidation or reduction) usually broken down to smaller compounds. Photodegradation of xenobiotics could be inhibited if inorganic anions (i.e. SO_4^{2-}, PO_4^{3-} and NO;) exist and compete for the oxidation sites or react with free radicals such as ·OH (Kochany and Lipczynska, 1992). Under indirect photodegradation, the photoreaction could be enhanced by excited states of photosensitizers, free radicals, and short-lived reactive transients (Zepp, 1988). The light energy can be absorbed by photosensitizers and transferred to the organic contaminants indirectly. Various amine groups such as diethyamine, triethylamine, and diethyl phenylene diamine have been used as photosensitizers to enhance the photodegradation of xenobiotic pollutants (Freeman et al. 1986; Lin et al. 1995; 1996). This study was conducted to determine the effects of natural sunlight and diethylamine on the degradation of butachlor and ronstar in river water.

MATERIALS AND METHODS

River water samples were collected from Dongaang stream (Pingtung, Taiwan) and kept in amber bottles on ice or 4 °C during transportation and storage, respectively. Hexane was used to extract butachlor and ronstar in water samples using an orbital shaker at 280 rpm for six hr. The extraction was repeated once. A gas chromatograph equipped with an electron capture detector (GC-ECD) (HP 5890 PLUS) and a DB 5, 30 m (id: 0.32 mm) column were used for analyses. The

---

Correspondence to: Y. J. Lin

limit of detection was 0.01 µg/mL. Nitrogen was used as carrier gas. The oven temperature was set at 230 °C isothermally. The temperatures of injector and detector were set at 240 and 280 °C, respectively.

A herbicide mixture containing butachlor (N-butoxymethyl-2-chloro-2’,6’-diethylacetanilide) (12% a.i.) and ronstar [2-tert-butyl-4 (2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazolin-5-one] (8% a.i.) was purchased from Sinon Co. (Taichung, Taiwan). The concentrations of butachlor (10 and 20 µg/mL) and ronstar (6.7 and 13.3 µg/mL) with three replicates each were prepared in filtered and non-filtered river waters. Water samples were filtered using 0.45 µrn filters. Diethylamine (0 and 200 µg/mL) was used as a photosensitizer in photoreactors for the comparison of butachlor and ronstar photodegradation with and without the photosensitizer. Samples were exposed to natural sunlight at Kenting National Park (Pingtung, Taiwan). The selected exposure times were 0, 8, 16, 32, and 64 hr (equivalent to 0, 1, 2, 4, and 8 d, respectively) from 8 a.m. to 4 p.m. on sunny days. The luminous flux and the radiant energy of natural sunlight were measured by a LX-105 light meter (Lutron, Taiwan) and a LI-250 light meter equipped with a LI-200SA pyranometer sensor (LI-COR Inc., Lincoln, NE), respectively. Samples were kept at 4 °C when not exposed to sunlight (i.e. unsuitable weather conditions).

RESULTS AND DISCUSSION

Butachlor and ronstar residues in the river water sample were below detection limits. The physical and chemical characteristics of the river water are listed in Table 1.

Table 1. Characteristics of water sample from Dongaang stream.

Characteristics	Temp (°C)	pH	DO*	PO_4^{3-}*	NO_3^-*	SS*	COD*	BOD*
Data	29.5	7.0	4.0	0.26	3.3	52.0	4.76	2.7

*concentrations in µg/mL

Figure 1 shows that the distribution patterns between the luminous flux (foot-candle, ft-cd) and radiation energy (Watt/m^2, W/m^2) of sunlight are similar. The amount of radiant energy emitted onto the water samples range from 440 to 1,260 W/m^2 between 8 a.m. and 4 p.m.. The average daily solar energy, in kilo-joule per day (kJ/d), emitted to each sample is calculated as 42 ± 2.1 kJ/d. The accumulated energy for the samples of 0, 1, 2, 4, and 8 d sunlight exposure are 0, 42, 84, 168, and 336 kJ, respectively. Hoigne et al. (1989) reported that the solar energy was around 1,000 W/m^2 at noon in summer.

The photodegradation [1n(Ct/Co)] of butachlor and ronstar in non-filtered river

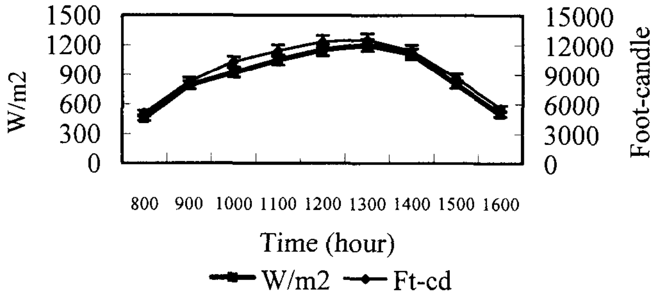

Figure 1. The luminous flux (foot-candle) and the radiation energy (Watt/m') of natural sunlight.

water is given in figures 2 and 3, respectively. The results show the concentrations of both butachlor and ronstar decrease with the increase of sunlight exposure. Lin et al., (1999) reported that the toxicity of atrazine and metolachlor in surface waters was reduced with the increase of sunlight exposure.

The initial photodegradation rates of butachlor range from 3.6 x 10^{-7} to 8.1 x 10^{-7} mol $L^{-1}hr^{-1}$ and from 4.5 x 10^{-7} to 9.9 x 10^{-7} mol $L^{-1}hr^{-1}$ for ronstar samples. The half lives and rate constants are 58.2 ± 4.5 hr and 0.012 ± 0.001 hr^{-1} for butachlor and 28.5 ± 0.7 hr and 0.0245 ± 0.001 hr^{-1} for ronstar, respectively. The data show that butachlor (with longer half-life) is more resistant to natural sunlight than ronstar. Both butachlor and ronstar have half-lives independent of their initial concentrations. Pseudo first order reaction is suggested for the photodegradation of both herbicides in this river water. Chen et al., (1982) reported that the half lives of butachlor in aqueous solution were 0.8 and 5.4 hr after exposure to 254 nm UV light and sunlight, respectively. Kochany and Maquire (1993) reported that the half-lives of metolachlor ranged from 8.2 to 54 days.

The photodegradation rates [1n(Ct/Co)] of butachlor and ronstar in filtered river water samples are given in figures 4 to 7. The results show that the concentrations of both herbicides decrease in river water with the increase of sunlight exposure with or without diethylamine.

The initial photodegradation rates of butachlor range from 2.2 x 10^{-7} to 5.8 x 10^{-7} mol $L^{-1}hr^{-1}$ (without diethylamine) and from 5.5 x 10^{-7} to 6.9 x 10^{-7} mol L-1 hr^{-1} (with diethylamine). For ronstar, the initial photodegradation rates range from 2.7 x 10^{-7} to 9.8 x 10^{-7} mol $L^{-1}hr^{-1}$ (without diethylamine) and from 8.9 x 10^{-7} to 1.7 x 10^{-6} mol $L^{-1}hr^{-1}$ (with diethylamine). Figures 5 and 7 show that diethylamine can significantly increase the photodegradation rates of butachlor and ronstar upto 3.1 and 3.2 folds, respectively. The half-lives of butachlor in filtered river water range from 76.2 to 100.4 hr (without diethylamine) and from 31.8 to 80.6 hr (with diethylamine). Comparing with ronstar, the initial degradation rate of butachlor is

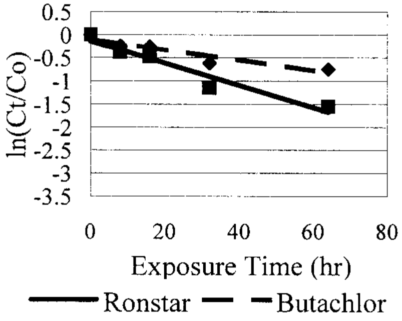

Figure 2. Photodegradation of butachlor (Co: 10 µg/mL) and ronstar (Co: 6.7 µg/mL) in non-filtered river water.

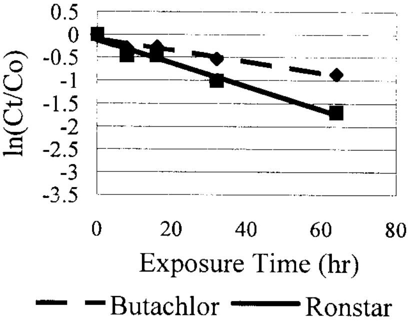

Figure 3. Photodegradation of butachlor (Co: 20 µg/mL) and ronstar (Co: 13.3 µg/mL) in non-filtered river water.

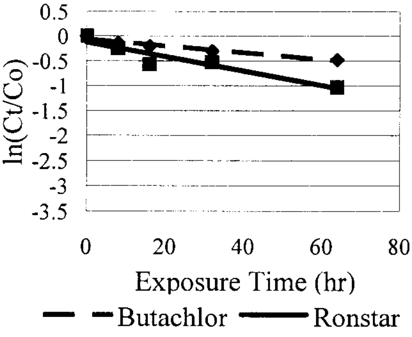

Figure 4. Photodegradation of butachlor (Co: 10 µg/mL) and ronstar (Co: 6.7 µg/mL) in filtered river water without diethylamine.

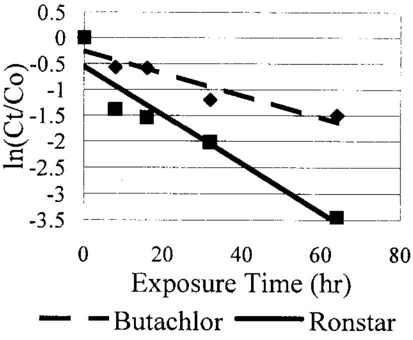

Figure 5. Photodegradation of butachlor (Co: 10 µg/mL) and ronstar (Co: 6.7 µg/mL) in filtered river water with diethylamine.

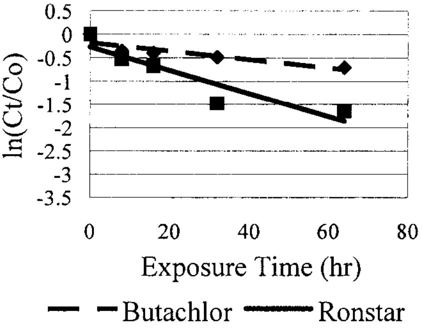

Figure 6. Photodegradation of butachlor (Co: 20 µg/mL) and ronstar (Co: 13.3 µg/mL) in filtered river water without diethylamine.

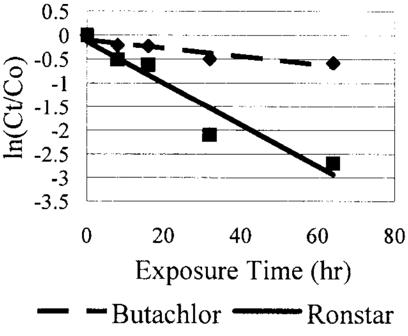

Figure 7. Photodegradation of butachlor (Co: 20 µg/mL) and ronstar (Co: 13.3 µg/mL) in filtered river water with diethylamine.

two times slower than that of ronstar. The results show that the half-lives of both herbicides in non-filtered river water are shorter than filtered water samples. This difference may be caused by the enhancement of photodegradation contributed by organic matters possibly acting as photosensitizers in non-filtered samples. Likewise, Lin et al., (1999) reported that surface waters with high concentrations of organic and suspended solid reduced the toxicity of pesticides possibly through photodegradation.

Acknowledgments. This research was supported by the National Science Council (NSC) of Taiwan, ROC under Grant NSC88-2212-E020-006.

REFERENCES

Chen YL, Lo CC, Wang YS (1982) Photodecomposition of the herbicide butachlor in aqueous solution. J Pest Sci 7:41-45

Freeman PK, Srinivasa R, Campbel JA, Denzer ML (1986) The photochemistry of polyhaloarenes. 5. Fragmentation pathways in polychlorobenzene radical anions. J American Chem Soc 108:5531-5536

Hoigne J, Faust BC, Haag W, Scully F, Zepp R (1989) Aquatic humic substances as sources and sinks of photochemically produced transient reactants. in Aquatic Humic Substances, Suffet IH, McCarthy P, Eds., American Chemical Society, Washington DC, pp. 363-381

Kochany J, Lipczynska E (1992) Application of the EPR spin-trapping technique for the investigation of the reactions of carbonate, bicarbonate, and phosphate anions with hydroxy1 radicals generated by the photolysis H_2O_2. Chemosphere 25: 1769-1782

Kochany J, Maquire J (1993) Sunlight photodegradation of metolachlor in water. “Preprint Extended Abstract” American Chemical Society, Chicago, Illinois, August 22-27, pp 36-39

Lin YJ, Karuppiah M, Shaw A, Gupta G (1999) Effect of simulated sunlight on atrazine and metolachlor toxicity of surface waters. Ecotoxicol Environ Safe 43:35-37

Lin YJ, Gupta G, Baker J (1995) Photodegradation of polychlorinated biphenyl congeners using simulated sunlight and diethylamine. Chemosphere 3:3323-3344

Lin Y, Gupta G, Baker J (1996) Photodegradation of Aroclor 1254 using simulated sunlight and various sensitizers. Bull Environ Contam Toxicol 56: 566-570

Widmer SK, Spalding RF (1995) A natural gradient transport study of selected herbicides. J Environ Qual 24:445-453

Widmer SK, Spalding RF (1996) Assessment of herbicide transport and persistence in ground water: a review. American Chemical Society, ACS Symposium Series: Herbicide Metabolites in Surface Water and Ground Water. Washington, DC 630:271-287

Zepp RG (1988) Factors affecting the photochemical treatment of hazardous waste. Environ Sci Technol 22:256-257