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Persistence of Organophosphorus Pesticide Residues in Limón River Waters

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The most important factors involved in the transportation of pesticide residues towards natural bodies of water are aerial dispersion by wind, volatilization, and conveyance by rain and irrigation waters (Ferrando et al 1992). The toxic action of pesticides residues in water systems depends on the concentration of these and the length of persistence prior to degradation by the environment. It is important to know the persistence of these substances in aquatic environments.

In Venezuela, organophosphorus pesticides are widely used in agriculture for crop production because of their high levels of efficiency in the control of pests, and also because of their economic convenience (Chirinos and Geraud-Pouey 1996, Geraud-Pouey et al 1997). Persistence pesticides studies have been conducted in other countries (Ferrando et al 1992, Frank et al 1994, Castillo et al 1997) however research of this type has not been carried out in our country. The purpose of this study was evaluate the persistence of the following organophosphorus pesticides in water samples from the Limón River: mevinphos, diazinon, parathion, malathion, azinphos, coumaphos, phorate, disulfoton, fenitrothion, chlorfenvinphos, methidathion, and tetrachlorvinphos. The effects of solar light, adsorption on particulates, and volatilization are also studied.

MATERIALS AND METHODS

Standard pesticides of high purity were used (Dr. Ehrenstorfer) to prepare the original solutions of each pesticide in ethyl acetate of HPLC grade (Baker). Standard solutions for calibration were prepared by dilution of the original solutions in ethyl acetate. The standard solutions employed in the spiked were prepared in HPLC grade methanol (Baker). Solid triphenyl phosphate (Riedel de Haen) at 99% purity appropriately diluted was used as an internal standard.

The analyses were performed in an Auto System Perkin-Elmer gas chromatograph, equipped with a nitrogen-phosphorus detector, a Perkin-

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Elmer automatic sampler, and a capillary column of 30m x 0.53mm x 1.2 µm film thickness, of 5% silicon methyl phenyl AT-5 (ALLTECH).

Solid-liquid extraction with discs of Cl8 was carried out. The disc was conditioned with 10 mL of ethyl acetate/acetone (80/20), followed by two 10mL portions of methanol and 10 mL of de-ionized water. Previously prepared with 5 mL of methanol and 5 grams of NaCl, 100mL of the sample were then immediately passed through the disc. The flow rate was 10 mL/min. The disc was vacuum dried for 10 minutes and then the pesticide residues were eluted with 1.5 mL of acetone and four portions of 5mL of ethyl acetate/ acetone (80/20). The extract was placed in vials containing 1 gram of anhydrous sodium sulfate. The extract was evaporated to 1 mL with a stream of nitrogen at 35 °C. It was then spiked with triphenyl phosphate (Internal Standard) and injected in duplicate samples of 1 µL in the gas chromatograph.

The efficiency of the extraction method was determined calculating the percentages of recovery. Samples of river water were spiked at levels of 1, 10 and 50 µg/L in methanol solution of the pesticides, and subjected to the extraction process previously described. Filters of cellulose acetate with a 0.45 µm porosity and 47 mm diameter (Whatman) were used to filter the water samples and borosilicate filters of 47 mm were used as pre-filters in the extraction system.

The persistence study for mevinphos, diazinon, malathion, parathion, azinphos, coumaphos, phorate, disulfoton, fenchlorphos, fenitrothion, chlorfenvinphos, methidathion and tetrachlorvinphos pesticides was done during the May-August period of 1997 in samples of Limón River water, between the Municipalities of Mara and Páez in the State of Zulia, Venezuela. The mean temperature oscillated between 26-35 °C, the hardness was 135 mg $CaCO_3$/L. The conductivity at 25 °C was 0.31 mmho/cm and the alkalinity 147 mg $CaCO_3$/L. The DQO was 11.23 mg/L.

A factorial experimental design was used for study of: photodegradation, adsorption on particulates and volatilization. Four experimental conditions with three repetitions in each condition were used in the evaluation of the effects. Table 1 describes the experimental conditions used in the study of persistence.

The organophosphorus pesticides were spiked in 2 liter samples of Limón River waters at an initial concentration of 50 µg/L. The concentration of the pesticide residues was monitored over time in each repetition, beginning day 1, and then during the following days: 2, 3, 5, 7, 9, 13, 15, 20, 25, 33, 40, 50, 60, 70, 80, 90, 100.

Table 1. Experimental Conditions in the Study of Persistence[1].

Condition	Water	Temperature	Light	Recipient
1 (FS)	Filtered	Variable[2]	Sun	Transparent[3] (closed)
2 (FD)	Filtered	Variable	Darkness	Amber[4] (closed)
3 (NFC)	Unfiltered	Variable	Sun	Transparent (closed)
4 (NFC)	Unfiltered	Variable	Sun	Transparent (open)

[1] Two liter sample, [2] Day-night temperature interval for Maracaibo, [3] Pyrex glass, [4] Amber glass covered with aluminum foil.

RESULTS AND DISCUSSION

The study of the pesticide recovery showed an efficiency level between 75% and 105% for the three levels of concentration evaluated, with a coefficient of variation of 7%. These values indicate an adequate level of accuracy and precision for the methodology of analysis utilizing C18 discs and gas chromatography.

The naparian logarithm (In) for the concentration of each pesticide was plotted over time (days) for each experimental condition. A Straight line was constructed for each case. The regression coefficients varied from 0.67 to 0.97, demonstrating good correlation of the data and the subsequent establishment of a first order degradation kinetics.

The average half-lifes were calculated, $t_{½}$ (Table 2) for the thirteen pesticide residues under the four experimental conditions.

Significant differences were observed (P<0.01) in the degradation of 11 organophosphorus pesticides as a result of the conditions of the study and the concentrations used for each day of measurement. No significant differences were observed in the degradation of phorate and diazinon.

The most rapid degradation rate was observed in non-filtered open-recipients samples exposed to sunlight, where other environmental factors such as sunlight, adsorption on particulates and volatilization were present. The average half-life for the pesticide residues increased reaching experimental conditions using filtered water in darkness where the effects of solar photodegradation, adsorption on particulates, and pesticide volatilization were not present, and where in the last case only the activity of micro-organisms present in the river water and chemical degradation intervened.

In the experiment using non-filtered water and open recipients, the water was maintained at environment conditions similar to Limón river waters

Table 2. Half-life ($t_{½}$) in days for organophosphorus pesticides in samples of Limón River water under four experimental conditions.

Pesticide	Experimental Condition			
	FD	FS	NFO	NFC
Azinphos	23.50	13.40	6.10	4.86
Chlorfenvinphos	51.20	23.78	13.18	21.69
Coumaphos	25.21	9.71	7.31	4.96
Diazinon	37.19	31.13	20.79	27.84
Disulfoton	19.95	12.57	9.22	14.84
Fenchlorphos	14.98	10.18	9.29	9.45
Fenitrothion	14.20	9.65	12.11	4.43
Malathion	10.87	10.41	9.73	10.50
Methidathion	12.42	11.79	7.77	11.76
Mevinphos	20.80	21.42	9.88	17.21
Parathion	20.72	11.32	8.77	7.49
Phorate	12.63	11.87	12.46	11.46
Tetrachlorvinphos	33.94	13.23	10.49	12.31

FD: filtered-dark, FS: filtered/sunlight, NFO: non-filtered/open, NFC: non-filtered/closed.

(non-filtered, exposed to sunlight, in contact with the atmosphere). Under these conditions, the most rapidly degrading organophosphorus pesticide was azinphos ($t_{½}$ = 6.10 days) while the most persistent pesticides was diazinon ($t_{½}$ = 20.79 days). Fortunately azinphos, one of the most toxic organophosphorus pesticides (LD_{50} = 11 mg/kg), had the fastest degradation rate under these experimental conditions, which is a significantly beneficial effect for the aquatic environmental area of Limón River.

The evaluation of the effect of photodegradation on the persistence of pesticides was carried out comparing the results of the experiments using filtered water in darkness with filtered water exposed to sunlight. In the majority of the cases the half-life times were lower in the filtered samples exposed to sunlight compared to the samples maintained in darkness (Table 2). Significant differences ($P<0.01$) were observed as to the effect of photodegradation on residues in 10 of the 13 pesticides studied. Significant differences were not found for the photodegradation effect in concentrations of methidathion, mevinphos and phorate.

Lartiges et al 1995 reported a $t_{½}$ of 52 days on the degradation of diazinon residues in Rio Eau Bourde (France) river water under experimental conditions of filtered water and darkness. However, the environmental temperature in that experiment was controlled at 22 °C. In this study, under the condition of filtered water and darkness, the $t_{½}$ was

37.19 days, which is compatible with an environmental temperature which varied between 26 and 35 °C during the persistence study.

Similar situations were presented in the cases of azinphos, coumaphos, fenitrothion and parathion. In the cases of these pesticides, Lartiges et al 1995 reported $t_{½}$ of 35, 29, 27 and 33 days respectively under the conditions of filtered water in darkness, which are higher persistence levels than those found in this study of Limón River water (23.50, 25.21, 14.20 and 20.72 days respectively).

To analyze the effect of adsorption on particulates on degradation of the pesticides studied, the results of the experiments of filtered and non-filtered water, exposed to sunlight in both cases, were compared. It was observed that in general the $t_{½}$ pesticides of the filtered samples was slightly greater than that of the non-filtered samples (Table 2). This demonstrates an effect of particulate material present in the non-filtered samples on the degradation of pesticides.

Significant differences (P<0.01) were found for the effect of particulates between filtered and non-filtered concentrations of azinphos, chlorfenvinphos, malathion and mevinphos.
The $t_{½}$ for coumaphos (4.96 days) and fenitrothion (4.43 days) for the condition of non-filtered water were similar to those reported by Lartiges et al 1995, 5 and 4 days respectively.

Frank et al 1991 reported $t_{½}$ degradation of 88, 34 and 14 days for the organophosphorus pesticides diazinon, methidathion and mevinphos respectively, in a study of Eramosa River water in Ontario (Canada) under experimental conditions of nonfiltered samples, exposed to sunlight and an environmental temperature of 21 °C. These higher values could be attributed to the lower environmental temperature and the lower solar intensity received by water in Ontario as compared to State of Zulia, Venezuela.

In evaluating the effect of volatilization on persistence, in general were observed higher $t_{½}$ values for pesticides in the non-filtered water samples in closed recipients as opposed to open recipients (both experimental conditions were exposed to sunlight), which evidences the effect of volatilization in the degradation of pesticides.

The analysis of variance showed significant differences (P<0.01) for five of the pesticides with respect to the effect of volatilization.

As to the experimental condition of non-filtered, open recipient samples exposed to sunlight, Lartiges et al 1955, reported $t_{½}$ of 8, 5, 8, and 8 days for azinphos, coumaphos, malathion and parathion respectively, values which are similar to those found for the degradation of these same pesticides in this study (6.10, 7.31, 9.73, and 8.77 days respectively).

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