

## Degradation Kinetics of Some Organophosphorus Insecticides in Aksu River, Antalya

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The degradations of four organophosphorus insecticides were determined in water samples collected from the Aksu river in Antalya region in Turkey in April 2002. Water samples were spiked with an initial concentration of 50 µg/L of pesticides chlorpyrifos, azinphos-ethyl, phorate and ethion. The effects of temperature, adsorption, biodegradation, photo degradation and volatilization to the degradation of pesticides in real Aksu river water were investigated over 8 week period. The degradation kinetics was monitored in closed bottles stored in dark at three different temperatures (T = 10, 25 and 40°C) and in a system exposed to natural sunlight (at variable temperature). Aksu river water samples had been conditioned to each parameter before addition of the known amount of insecticides. For the identification of the insecticides, liquid-liquid extraction with dichloromethane followed by GC-NPD was used. Half-lives of the insecticides were determined for each parameter. It was observed that half-lives of insecticides are varying depending on the environmental conditions. It was determined that the most effective way for degradation of azinphos-ethyl and ethion is photodegradation. Biodegradation and adsorption were significantly effective on degradation of chlorpyrifos. Phorate was found to be the fastest degrading insecticide under all circumstances.

**Key Words:** Aksu river, Azinphos-ethyl, Chlorpyrifos, Degradation kinetics, Ethion, Organophosphorus insecticides, Phorate.

### INTRODUCTION

In order to meet the nutritional needs of the increasing world population, it is necessary to use pesticides. It is declared that use of the synthetic pesticides is the most effective method of controlling vegetable diseases and insects although they could cause food and environmental pollution<sup>1</sup>. Pesticides may reach surface waters, fresh or seawater through the discharge of drainage water from treated lands aerial drift and accidental spills<sup>2</sup>.

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It is important to know the persistence of these substances in aquatic environments. These pesticides are not only toxic to the target insects but also can be toxic at different degrees to untargeted animals and people by food chain. Organophosphorus insecticides, which are extremely toxic and specific molecules, affect acetyl cholinesterase activity<sup>3,4</sup>.

The toxic action of pesticide residues in water systems depends on the concentration and the length of persistence prior to degradation in the environment<sup>5</sup>. Some of the factors affecting the degradation of pesticides in aquatic medium are temperature, pH, salinity, sunlight, sediment type and presence of microorganisms<sup>6,7</sup>. When the degradation results of the same pesticides in different environmental waters and countries were compared, it can be seen that the persistence of pesticides change with the climate of countries, environmental conditions and type of the waters<sup>8-10</sup>. Therefore, the studies on this matter should be carried out. All these experiments would give insight into better understanding of real degradation pathways. To our best of knowledge, no degradation studies of pesticides in real environmental waters and conditions have been undertaken.

The aim of this study was to monitor the degradation kinetics of a mixture of four organophosphorus pesticides used in the region of Antalya around the Aksu river and to determine the effect of the factors, such as temperature, adsorption, biodegradation, photodegradation and volatilization on persistence of the organophosphorus insecticides. The structure of the selected four organophosphorus insecticides are given in Fig. 1.

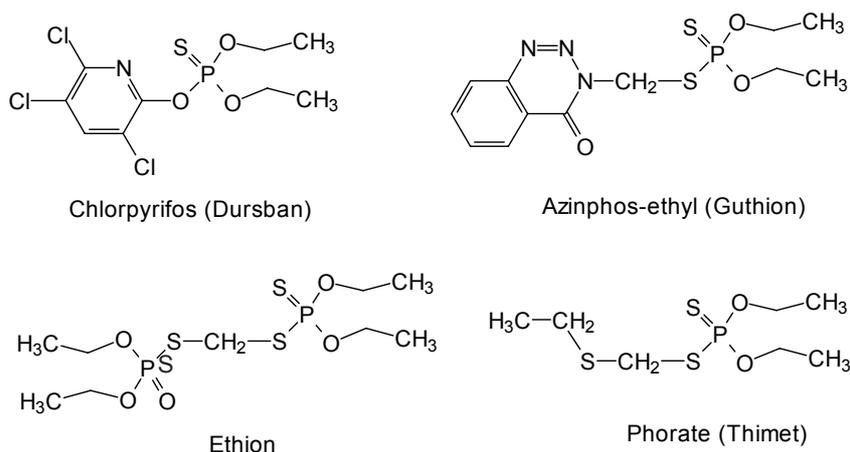


Fig. 1. Chemical structures of organophosphorus insecticides

These insecticides are widely used according to the state of agricultural office located in Antalya. An extensive flood canal network drains agricultural areas, which are located around the river. These canals, which run into the river, provide a direct pathway for pesticide introduction.

### EXPERIMENTAL

Pure analytical pesticide standards, chlorpyrifos (99.6 %), azinphos-ethyl (99.3 %), phorate (95.5 %) and ethion (99.7 %), were obtained from Riedel-de H en. HPLC grade of acetone, toluene and dichloromethane were obtained from Merck. Na<sub>2</sub>SO<sub>4</sub> (non-aqueous) was obtained from Fluka.

**Sampling location:** Water samples were collected at different distances from the riverbank and depths of the Aksu river into 2 L amber glass bottles in the beginning of April (2002) in which the use of the pesticides around the river increases. The water samples were blended and brought immediately into the laboratory to analyze and for conditioning to parameters before the degradation studies. The conductivity, pH and dissolved oxygen (DO) at 28 °C of collected water were 0.32 mS cm<sup>-1</sup>, 7.95 and 7 mg L<sup>-1</sup>, respectively. The NO<sub>3</sub><sup>-</sup>-N was 1.75 mg L<sup>-1</sup>. Pesticides residue analyses were performed in water samples before conditioning. Any pesticide residues were not determined in the river water samples. pH of water samples remained relatively constant during the 8 week period.

**Degradation conditions:** The influence of temperature was evaluated for three temperatures (T = 10, 25 and 40 °C), which covers the range of air temperatures in Antalya for a year. The bottles were put into the incubator during the degradation studies for providing a constant temperature.

The evaluation of the effect of photodegradation on the persistence of pesticides in river water samples was carried out by comparing the results of the experiments performed in darkness and in natural sunlight. To prevent the amber glass bottles more effectively from the sunlight, they were also covered with aluminum folio for darkness experiments.

The effect of biological activity was examined by comparing the rates of the degradations in sterilized (121 °C, 2 atm for 20 min) and non-sterilized water at the same conditions.

To investigate the influence of adsorption on degradation, the river water samples were filtered with 0.1 µm membrane filters and the results were compared with non-filtered water at the same conditions.

The effect of volatilization was investigated by comparing the results of the persistence of the pesticides in two different systems, one of which is open and the other one is closed to the air, providing all the other conditions being the same.

All conditioned water samples were maintained at environmental conditions similar to Aksu river water (non-filtered, exposed to sunlight, in

contact with the atmosphere). Except the constant temperature ( $T = 10, 25$  and  $40\text{ }^{\circ}\text{C}$ ) experiments, the environmental temperature varied between  $24$  and  $38\text{ }^{\circ}\text{C}$ . All conditions were studied as duplicate.

**Spiking procedures:** Measured water samples were taken into  $2\text{ L}$  of the glass bottles lined with a teflon cap.  $1\%$  (w/v) stock solutions of each pesticide standards were freshly prepared in acetone of HPLC grade and mixed. The mixture of the stock solution was diluted by acetone and pipetted into the conditioned water samples giving an initial concentration of  $50\text{ }\mu\text{g}$  of each pesticide per liter of water. Final volume of each spiked water samples was  $2\text{ L}$ .

**Extraction procedure:** Pesticides spiked river water samples were extracted at selected times in a time period of 8 weeks as will be described below. The concentrations of the pesticides in duplicate samples were monitored over time in each duplication, beginning day (as time zero), 1 and than the following days of 3, 7, 14, 21, 28, 42 and 56.

A  $25\text{ mL}$  aliquot was taken from spiked water samples and extracted with  $2 \times 4\text{ mL}$  of dichloromethane. Extracted samples were collected to the vials and the collection time was recorded. Extracts were kept in the incubator at  $-25\text{ }^{\circ}\text{C}$  until GC/NPD analysis. The extracts were dried on non-aqueous sodium sulfate and evaporated to dryness under a gentle nitrogen stream at  $35\text{ }^{\circ}\text{C}$ . Vials rinsed with toluene for several times, rinsed solutions were collected on another vial (sample vial) to remove sodium sulfate and then the sample vials were aliquot to  $500\text{ }\mu\text{L}$  with toluene. Bromophos-ethyl was used as an internal standard and  $250\text{ }\mu\text{L}$  of  $1\text{ ppm}$  internal standard solution was added to the vials just before the GC-NPD analysis.

The chromatographic analysis were performed in an Agilent 6890 Series GC-system gas chromatograph, equipped with a nitrogen-phosphorus detector and HP-5  $5\%$  phenyl-methyl siloxane,  $30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$  capillary column were used. Air and hydrogen were used as the detector gases at a flow rate of  $60$  and  $3\text{ mL min}^{-1}$ , respectively and helium was used as the carrier gas at a flow rate of  $4\text{ mL min}^{-1}$ .

Oven set at  $70\text{ }^{\circ}\text{C}$  (maintained for  $1\text{ min}$ ) to  $150$  at  $25\text{ }^{\circ}\text{C min}^{-1}$ ,  $150$  to  $200\text{ }^{\circ}\text{C}$  at  $3\text{ }^{\circ}\text{C min}^{-1}$ ,  $200$  to  $280\text{ }^{\circ}\text{C}$  at  $8\text{ }^{\circ}\text{C min}^{-1}$ , maintained for  $10\text{ min}$  at  $280\text{ }^{\circ}\text{C}$ . Temperatures of injector and detector were maintained constant at  $250$  and  $330\text{ }^{\circ}\text{C}$ , respectively. Injection volumes of  $2\text{ }\mu\text{L}$  were used in each analysis.

The recovery percent (R%) of the method was determined using the standard addition method (SAM)<sup>11</sup>. Samples of river water were spiked at levels of  $1, 10$  and  $50\text{ }\mu\text{g L}^{-1}$  in standard acetone solution of the pesticides and subjected to the same analytical procedure described previously.

Studies for recovery were done four times for each insecticide and concentration ( $n = 4$ ). The study of the insecticide recovery showed efficiency level ranged from 80 % (for chlorpyrifos) to 99 % (for phorate) as given below in Table-1.

TABLE-1  
STUDY OF THE INSECTICIDE RECOVERY  
SHOWED EFFICIENCY LEVEL RANGED FROM 80 %  
(FOR CHLORPYRIFOS) TO 99 % (FOR PHORATE)

Compound	R (%)
Chlorpyrifos	80.45 ± 0.29
Azinphos-ethyl	94.40 ± 5.67
Phorate	99.01 ± 0.80
Ethion	84.35 ± 2.12

## RESULTS AND DISCUSSION

As reported by Lartiges and Garrigues<sup>3</sup> and Medina *et al.*<sup>5</sup>, the chemical degradation of organophosphorus pesticides can be described using a first order degradation curve:

$$C_t = C_0 e^{-kt}$$

where  $C_t$  is the concentration of the insecticide at time  $t$ ,  $C_0$  is the initial concentration of the insecticide and  $k$  is the rate constant<sup>7</sup>.

By plotting the logarithm ( $\ln$ ) for the concentration of each insecticide vs. time, a straight line was observed for each time with a regression coefficients varied from 0.8448 (for chlorpyrifos at 40 °C) to 0.9993 (for azinphos-ethyl in filtered river water). The rate constant can then be used to derive the half-life  $t_{1/2}$ :

$$t_{1/2} = (\ln 2)/k$$

Persistence of all the 4 organophosphorus insecticides called chlorpyrifos, azinphos-ethyl, phorate and ethion were investigated at different conditions to determine the effects of temperature, biodegradation, photodegradation, adsorption and volatilization. The persistence of the same organophosphorus insecticides in water have been studied by various researchers<sup>3,5,8,10,12</sup>. To date, only some of these effects, which are the objectives of present study, have been investigated. Selected insecticides in this study are rather toxic and are commonly used in the region of Antalya, Turkey. Wide investigation of these was carried out in this study at the same time.

These organophosphorus insecticides underwent some degree of chemical change during 8 weeks in all conditions. The half-lives of studied insecticides for three temperatures are given in Table-2.

TABLE-2  
 HALF-LIVES  $t_{1/2}$  (DAY) FOR STUDIED INSECTICIDES IN SAMPLES  
 OF AKSU RIVER WATER AT THREE TEMPERATURES AND UNDER  
 FIVE EXPERIMENTAL CONDITIONS

Pesticide	$t_{1/2}$			
	10 °C	25 °C	40 °C	ATC
Chlorpyrifos	40.65 ± 0.36	28.17 ± 0.00	3.31 ± 0.02	15.40 ± 0.03
Azinphos-ethyl	29.31 ± 0.43	18.29 ± 0.29	12.76 ± 0.83	4.34 ± 0.31
Phorate	24.50 ± 1.17	7.30 ± 0.04	2.13 ± 0.00	3.90 ± 0.21
Ethion	119.17 ± 9.17	30.00 ± 0.00	20.34 ± 0.25	18.61 ± 0.23
	ADC	FATC	SATC	ATO
Chlorpyrifos	14.68 ± 0.82	1.72 ± 0.00	22.99 ± 0.04	4.66 ± 0.05
Azinphos-ethyl	100.52 ± 2.91	4.25 ± 0.05	3.97 ± 0.05	8.41 ± 0.27
Phorate	5.04 ± 0.01	5.69 ± 1.53	4.34 ± 0.09	3.75 ± 0.23
Ethion	50.77 ± 0.19	19.77 ± 0.14	22.46 ± 0.18	6.87 ± 0.09

ATC = Aksu transparent closed; ADC = Aksu dark closed; FATC = Filtered aksu transparent closed; SATC = Sterile aksu transparent closed; ATO = Aksu transparent open.

In Aksu river water, at the temperature of 25 °C, the fastest degrading insecticide was found to be phorate ( $t_{1/2} = 7.30$  d) and the slowest was found to be ethion ( $t_{1/2} = 30$  d). Phorate and ethion are phosphorodithioate class insecticides. However, the structure of phorate is asymmetric while ethion is symmetric (Fig. 1.). The stability of ethion may be explained by steric hindrance due to the symmetry of the molecule<sup>12</sup>. The half-lives,  $t_{1/2}$ , of chlorpyrifos were found to be 40.65, 28.17 and 3.31 days at 10, 25 and 40 °C, respectively, (Table-2). The initial pH of these water samples was 7.95 and not buffered. Freed *et al.*<sup>8</sup> reported half-lives of 53 and 13 d for chlorpyrifos at 20 and 37.5 °C, respectively, under buffered pH 7.4. These differences in the half-lives of chlorpyrifos may arise from differences of pH, temperature and nature of the water samples. A water having pH higher than 7 which creates alkaline conditions that can cause organophosphorous pesticides to undergo degradation or chemical breakdown, a process known as hydrolysis. In this study, Aksu river water samples was slightly alkaline (pH = 7.95), resulting higher degradation rates than that of the results reported by Freed *et al.*<sup>8</sup>. Azinphos-ethyl was found to be the most stable compound against the temperature changes. In general, the temperature increase led to faster degradation kinetics for each insecticide.

Reaction rate constants for each temperature are used to derive activation energy using the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

where  $k$  is the reaction rate,  $E_a$  is the activation energy,  $R$  is the ideal gas constant,  $T$  is the temperature as Kelvin and  $A$  is a constant characteristic of the reaction<sup>13</sup>.

The calculated Arrhenius parameters are shown in Table-3.  $E_a$  values show the influence of temperature on the degradation of insecticides. The activation energy  $E_a$  indicates the sensitivity of the reaction to temperature changes. As the activation energy ( $E_a$ ) increases, the sensitivity of the pesticide to temperature also increases.

TABLE-3  
ACTIVATION ENERGIES  $E_a$  (kcal mol<sup>-1</sup>) AND FREQUENCY FACTORS  
A (DAY<sup>-1</sup>) OF STUDIED INSECTICIDES

Compound	$E_a$ (kcal mol <sup>-1</sup> )	A (day <sup>-1</sup> )
Chlorpyrifos	14.70	$2.59 \times 10^9$
Azinphos-ethyl	4.88	139.8
Phorate	14.25	$2.77 \times 10^9$
Ethion	10.30	$6.12 \times 10^5$

As a result, chlorpyrifos was found to be the most sensitive to temperature whereas azinphos-ethyl was found to be the less sensitive to temperature. It is difficult to compare the results of different studies. The half-lives of same pesticides vary at different conditions. There is also a need for standardization of the degradation experiments of the pesticides<sup>3</sup>.

Influence of photodegradation on chlorpyrifos, azinphos-ethyl, phorate and ethion were given in Table-2 at columns of ATC (Aksu transparent closed) and ADC (Aksu dark closed). It is clear that there are no significant differences for degradation rate of chlorpyrifos and phorate by photo degradation. The sunlight is more effective for degradation of azinphos-ethyl and ethion than that of chlorpyrifos and phorate. Significant differences were not observed for the photo degradation effect in concentrations of phorate. Medina *et al.*<sup>5</sup> reported  $t_{1/2}$  degradation of 12.63 and 11.87 d for the phorate, in a study of Limon river in Venezuela under experimental conditions of filtered samples, exposed to sunlight and darkness, respectively. In this study, the  $t_{1/2}$  for the phorate were found to be 3.90 and 5.04 d under the conditions of non-filtered water samples exposed to sunlight and darkness, respectively. It can be said that sunlight slightly affects degradation of phorate.

Some pesticides are strongly adsorbed onto particulates and are not likely to move out into water system. The effect of adsorption for each insecticide was analyzed comparing the persistence of pesticides in filtered and non-filtered river water results at the same conditions. These

results are shown in Table-1 at columns of ATC (Aksu transparent closed) and FATC (Filtered Aksu transparent closed). According to these results, there is no significant effect of adsorption on degradation of azinphos-ethyl, phorate and ethion except for chlorpyrifos in aqueous medium. Adsorption may lead to a longer persistence of chlorpyrifos in the water system which is consistent with the results of Faust and Gomaa<sup>14</sup>. On the other hand, Malacady and Wolfe<sup>15</sup> studied on chlorpyrifos in sediment water systems and demonstrated that sorption inhibits hydrolytic degradation of chlorpyrifos.

The effect of biodegradation on persistence of the insecticides can be seen by comparing the data of half-lives of sterile (column SATC) and non-sterile (column ATC) river water samples in Table-2. Biodegradation is the breakdown of pesticides by fungi, bacteria and other microorganism. Biodegradation slightly affects phorate concentration, but it is more effective on chlorpyrifos and ethion. We observed that biodegradation was not effective on the degradation rate of azinphos-ethyl in present experimental conditions. As a result, biodegradation increases the total reaction rate.

In evaluating the effect of volatilization on persistence, in general, faster degradation rates were observed for pesticides in open system as opposed to closed system, except azinphos-ethyl [columns of ATO (Aksu transparent open) and ATC in Table-2]. The half-life of Azinphos-ethyl is found faster in closed system than open system. Medina *et al.*<sup>5</sup> found similar results for azinphos-ethyl where the half-lives of azinphos-ethyl are 6.10 and 4.86 d in non-filtered open and closed system, respectively. Vapour pressure is an important factor in determining whether a pesticide will volatilize or not. Pesticides with high vapour pressure are more likely to volatilize and escape into atmosphere. Azinphos-ethyl has a very low vapour pressure, ( $2.2 \times 10^{-7}$  mmHg at 20 °C) and is a non-volatile insecticide. Therefore, volatilization is not significantly effective on degradation of azinphos-ethyl.

As summarized in Table-1, the most effective way for degradation of azinphos-ethyl and ethion is photo degradation. It was determined that biodegradation and adsorption are effective on chlorpyrifos. Phorate was found to be the fastest degrading insecticide in all conditions.

The data obtained are important to reveal the behaviour of these insecticides in aqueous medium and will be useful for the modeling studies that will be carried out by other researchers.

Some pesticide transformation products can be as toxic as original compound or more than that of the original compound<sup>16</sup>. Further studies should include identification of degradation products and if they are found to be toxic, then their persistence should also be determined.

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