

THE FATE OF PESTICIDES IN AQUATIC
ENVIRONMENT. II. HYDROLYSIS OF
DICHLORVOS IN A MODEL SYSTEM AND IN
RIVER WATER

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(Received for publication June 25, 1976)

An attempt has been made to elucidate the unusually fast decay of dichlorvos in the water of the Kupa river as compared to the behaviour of this pesticide in other river waters. The effects of pH, temperature, different ion species, organic components and concentration of dichlorvos on the decay rate were tested in a model system.

The concentration of hydrogen ions and temperature were found to be rate determining. Different ion species could have a considerable effect on the rate of hydrolysis of dichlorvos but only if present in large quantities.

Today organophosphorus pesticides are considered to be an important class of water pollutants. Their toxicological properties are thoroughly investigated, but not much is known about their distribution and fate in natural waters (1, 2). The degradation of organophosphorus pesticides in river water depends on many factors which create a multicomponent system. The information about their interrelation effects could explain sometimes unexpected behaviour of organophosphorus pesticides in natural streams, but only a few factors have been investigated systematically (3, 4).

This study was initiated when in comparison with three other rivers a much faster hydrolysis of dichlorvos was observed in the water of the Kupa river (5). To explain this phenomenon it was necessary to in-

investigate as many factors influencing the rate of dichlorvos hydrolysis as possible. The investigations were carried out with a model system, but parallels can be drawn with the natural environment.

MATERIALS AND METHODS

0,0-dimethyl-2,2-dichlorovinyl phosphate (dichlorvos, DDVP), 96%, Reference Standard Lot. No. 2996, was received from EPA, Perrine, Fla. 33157. Stock solutions of dichlorvos were prepared in absolute ethanol.

Activated carbon »Aktivkohle Typ Burrus (0.1—0.2 mm)« Bender & Hobein, Zurich, Switzerland, was a gift from Dr. Martin Reinhard, EAWAG, Dübendorf, Switzerland.

Water solutions of dichlorvos were prepared by addition of a known volume of absolute ethanolic stock solution of dichlorvos to one litre of deionized and distilled water or in a buffer solution prepared therein, giving about 80 μg of dichlorvos per litre. The solutions were kept in glass volumetric flasks with glass stoppers at room temperature (about 20 °C) or in a thermostat at 4 °C, 15 °C and 25 °C. During the experiment water solutions of dichlorvos were exposed to the sunlight and artificial light. Flasks were shaken periodically and immediately before the adsorption.

The adsorption was performed by a slow percolation of 100 ml of water solution of dichlorvos through an activated carbon microcolumn. Adsorbed dichlorvos was eluted from activated carbon at room temperature with 2 ml of distilled methanol. Eluates were dried over sodium sulphate for 24 hours (5). The procedure was carried out immediately after the solutions were prepared and at intervals of 24, 48, 72 and in some cases 144 hours.

Dichlorvos was quantitatively determined by a Varian Aerograph Moduline Series 2800 gas chromatograph equipped with alkali flame ionization detector. The column was a Pyrex glass tube 1.8 m long with 2 mm i. d., packed with Gas Chrom Q, 80—100 mesh, coated with 4% SE-30 and 6% OV-210. Carrier gas was nitrogen with a flow rate of 45 ml/min. The working temperatures were: injection block 230 °C; column 195 °C; and detector 235 °C.

RESULTS AND DISCUSSION

Chemical analyses of the Kupa and Sava river waters carried out routinely for a period of several years do not show marked differences in any parameter determined and therefore it is not very likely that chemical parameters cause different behaviour of dichlorvos in either

river (5). Investigations carried out in a model system, although under nonenvironmental conditions, offer a possibility to interpret the results in the terms of analogy and common general trend. It is probable to expect similar interrelations between parameters in the model system to exist also under environmental conditions but naturally with some variations.

Half-lives are used in this paper to indicate the experimentally determined rates of hydrolysis. The hydrolysis of dichlorvos, a phosphate ester, follows the second order kinetics, but if one reactant is in large excess or its concentration is kept constant, as is the case in our study, it can be considered to follow the first order kinetics. To prove definitely that the hydrolysis of dichlorvos follows the pseudo first order kinetics, we measured the rates of hydrolysis with concentrations of dichlorvos ranging from 75 $\mu\text{g/l}$ to 1500 $\mu\text{g/l}$ in a phosphate buffer pH 8.0 at room temperature. The determined half-lives were nearly identical pointing out the correctness of our presumption (Table 1). Each rate of

Table 1

Dependence of hydrolysis rate of dichlorvos on the concentration of dichlorvos used in a phosphate buffer pH 8.9 at room temperature

Concentration of dichlorvos ($\mu\text{g/l}$)	Half-life/hours
75.23	23
150.05	24
752.30	20
1500.50	19

hydrolysis was recalculated assuming 100% dichlorvos at zero time. The mean rate constant is the mean value of the constants obtained in single determinations. The half-lives were calculated from the mean rate constants.

Changes in alkalinity strongly influenced the rate of dichlorvos hydrolysis. The experiment was carried out in a phosphate buffer at room temperature (about 20°C). The values of pH were chosen to cover the usual range of hydrogen ion concentrations in natural streams. With an increase in alkalinity the rate of dichlorvos hydrolysis rose too. Half lives were 79, 46, 32 and 27 hours (Fig. 1).

The rate of dichlorvos hydrolysis can be increased two to five times for every ten kelvin rise in temperature (Fig. 2). It also depends on the buffer solution used. This indicates further the influence of different ion species on the rate of hydrolysis. If the temperature and pH value are constant, the rate of dichlorvos hydrolysis rises in the sequence:

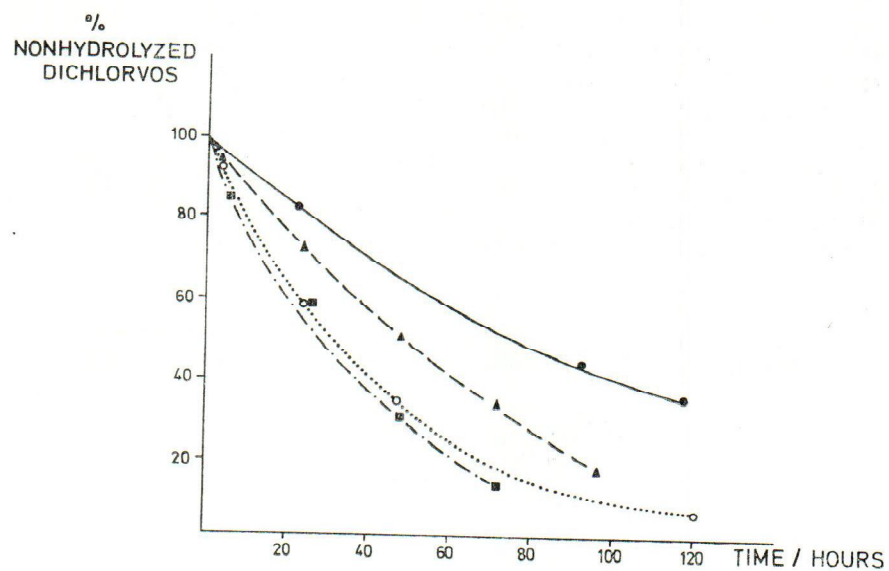
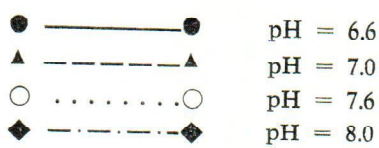


Fig. 1. Influence of pH value on the rate of dichlorvos hydrolysis in a phosphate buffer at room temperature



Each point represents the mean value of two determinations recalculated assuming 100% dichlorvos at zero time

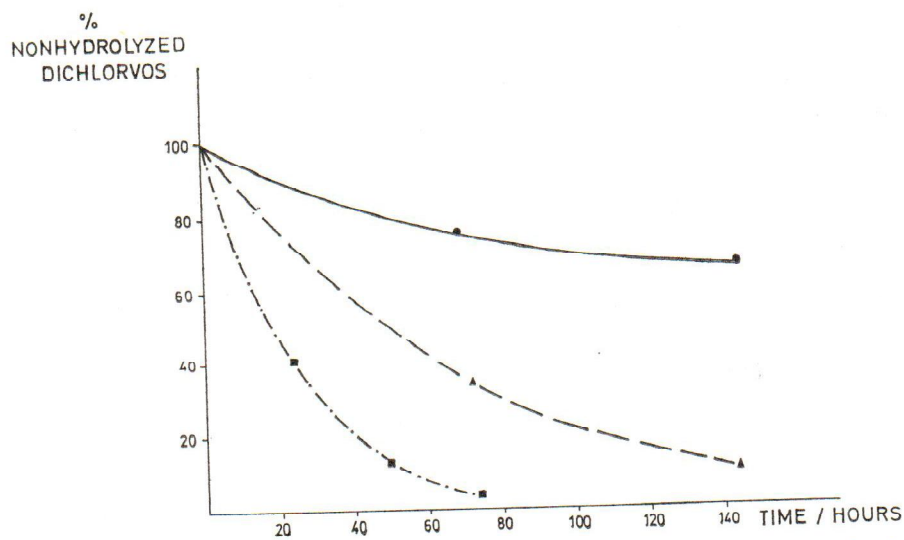


Fig. 2. Influence of temperature on the rate of dichlorvos hydrolysis in a phosphate buffer pH 8.0



Each point represents the mean value of two determinations recalculated assuming 100% dichlorvos at zero time.

Table 2.

Influence of the temperature and the ion species present on the rate of dichlorvos hydrolysis under constant hydrogen ion concentration (pH 8.0)

Solution of dichlorvos (80 $\mu\text{g}/\text{l}$)	Half-life/hours		
	4 °C	15 °C	25°C
in borate buffer	1422	205	61
in bicarbonate solution	130	98	49
in phosphate buffer	165	50	17

borate buffer, bicarbonate solution, phosphate buffer (Table 2 and Fig. 3). However, this effect requires a careful interpretation because the work carried out so far has not been sufficient to draw a firm conclusion.

Besides, the concentrations of ions were relatively high and did not resemble those occurring naturally.

As high concentrations of dihydrogen phosphate ion considerably increased the rate of dichlorvos hydrolysis, it was important to find out whether the small concentrations show the same effect. To verify it 63

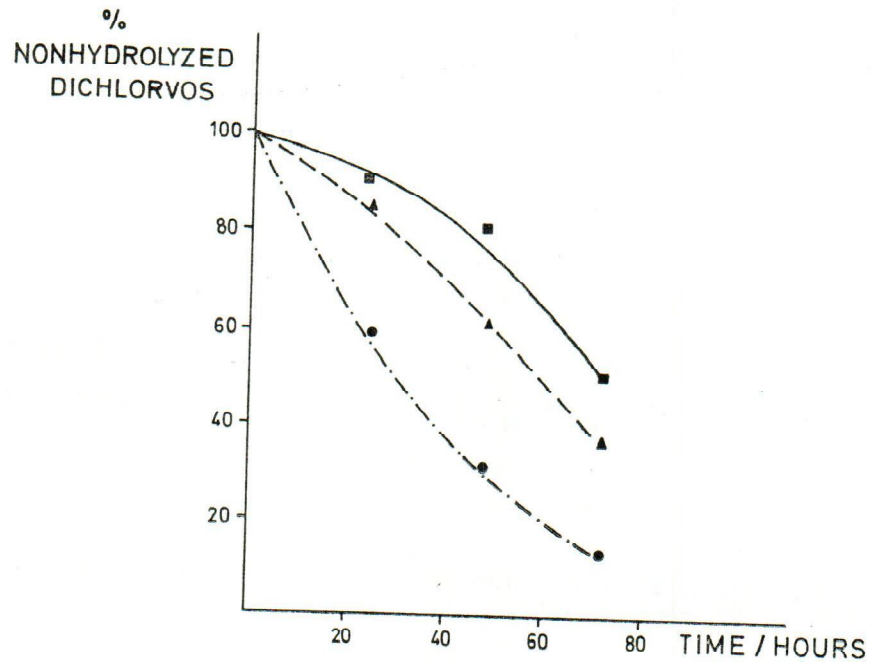
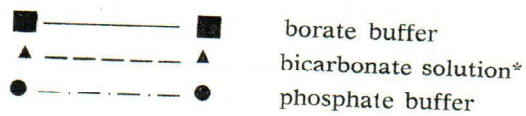


Fig. 3. Persistence of dichlorvos in different ion surroundings at pH 8.0 and room temperature



Each point represents the mean value of two determinations recalculated assuming 100% dichlorvos at zero time

* pH value of the bicarbonate solution changed during the experiment from 8.0 to 8.5

$\mu\text{g P/l}$ in the form of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ was added to borate buffer solution of dichlorvos pH 8.0 at room temperature. A solution of dichlorvos in a borate buffer under the same conditions was used as a blank.

Practically negligible deviations were observed if the half-lives were compared indicating that ion species could influence the rate of dichlorvos hydrolysis only if present in large quantities (Fig. 4).

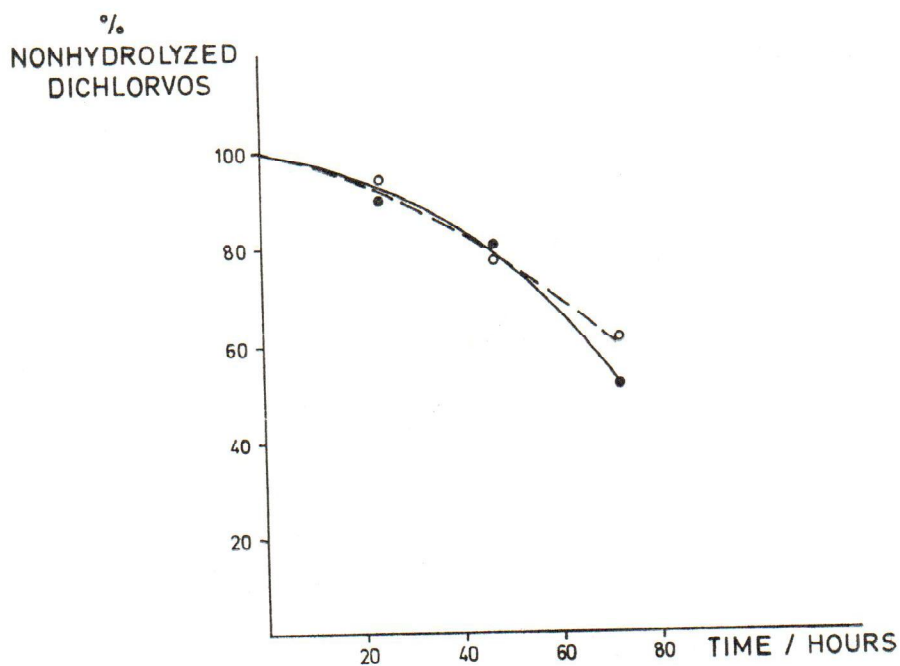


Fig. 4. Persistence of dichlorvos in a borate buffer pH 8.0 at room temperature under the influence of a small concentration of dihydrogen phosphate ion (63.0 g P11)

- ——— ○ dichlorvos in borate buffer + dihydrogen phosphate ion
 ● ——— ● dichlorvos in borate buffer (blank)

Each point represents the mean value of two determinations recalculated assuming 100% dichlorvos at zero time

We studied the effect of organic components on the rate of hydrolysis of dichlorvos in the water of the Kupa river by comparing the rate of dichlorvos hydrolysis in untreated water of the Kupa river and in the water of the Kupa river in which organic components were largely eliminated by percolation through activated carbon microcolumn before dichlorvos was added. The rate of hydrolysis was nearly the same in both cases (Fig. 5).

The influence of alkalinity and temperature on dichlorvos hydrolysis was found to be rate determining. Differences in the two parameters could cause different persistence of dichlorvos in natural streams. In the

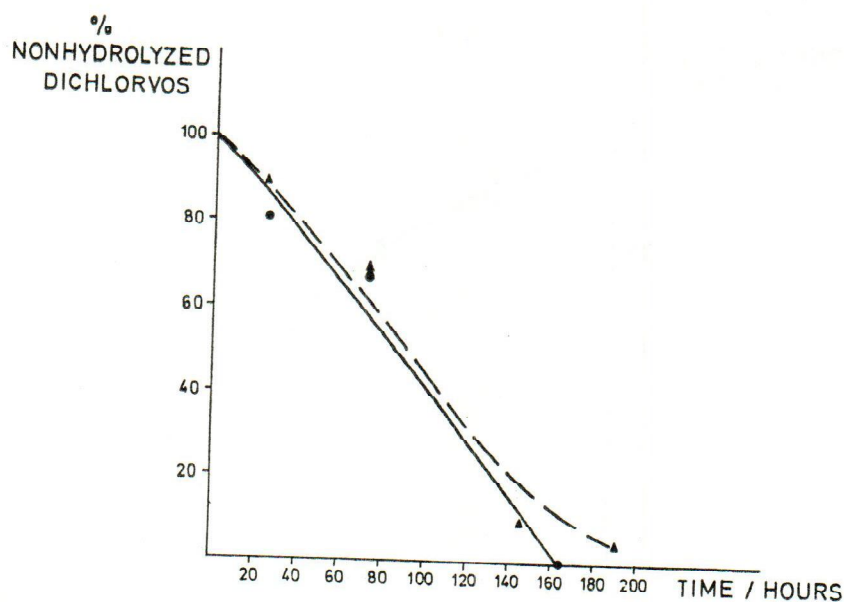


Fig. 5. Influence of organic components on the rate of hydrolysis of dichlorvos added to the water of the Kupa river

- ——— ● dichlorvos added to untreated water of the Kupa river
- ▲ - - - - ▲ dichlorvos added to the water of the Kupa river previously percolated through activated carbon microcolumn

Each point represents the mean value of two determinations recalculated assuming 100% dichlorvos at zero time

case of the Kupa river where a higher rate of hydrolysis was observed than in the other rivers, it would be difficult to attribute the responsibility for such a behaviour to the mentioned parameters because they were practically the same during the experiment. However, differences in biological and bacteriological properties of the Sava and Kupa rivers (6) lead to the presumption that different selfpurification powers of the two rivers could cause different persistence of dichlorvos in their waters.

This fact emphasizes the need for as complete a chemical analysis as possible when a multicomponent system such as river water is dealt with and for a correlation of the obtained data with biological and bacteriological analysis.

ACKNOWLEDGEMENT

The authors wish to thank Professor Zlata Štefanac for helpful suggestions and interest in this work.

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Sažetak

PONAŠANJE PESTICIDA U VODENOJ SREDINI. II. HIDROLIZA DIKLORVOSA U MODELNOM SISTEMU I U RIJEČNOJ VODI

Zapažena je vrlo brza razgradnja diklorvosa u vodi rijeke Kupe za razliku od ponašanja tog pesticida u vodi rijeke Save. U modelnom sustavu ispitani su utjecaji temperature, pH, različitih ionskih vrsta, organskih komponenti, te koncentracije diklorvosa na brzinu razgradnje diklorvosa.

Temperatura i pH su faktori koji znatno utječu na brzinu razgradnje dok različite ionske vrste mogu imati značajan utjecaj samo ako su im koncentracije vrlo visoke.

Usporedbom rezultata provedenih kemijskih analiza vode rijeka Save i Kupe nije nađeno nikakvo značajno odstupanje te je stoga teško izdvojiti ijedan ispitani kemijski pokazatelj kao osnovni uzrok brze razgradnje diklorvosa u vodi rijeke Kupe. Nasuprot tome biološki i bakteriološki profili ovih rijeka znatno se razlikuju te bi se brza razgradnja diklorvosa u vodi rijeke Kupe mogla objasniti njezinom većom moći samoočišćenja.

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Primljeno 25. VI 1976.