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THE FATE OF PESTICIDES IN AQUATIC ENVIRONMENT. I. THE PERSISTENCE OF SOME ORGANOPHOSPHORUS PESTICIDES IN RIVER WATER

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The efficacy of enrichment of organophosphorus compounds present as micropollutants in river water by extraction with organic solvents is compared with that achieved by adsorption on the activated carbon microcolumn.

The procedure including the adsorption on and elution from the activated carbon column was applied for the investigation of the persistence of organophosphorus pesticides — dichlorvos, malathion and parathion — in river waters of different pollution level.

The concentration of each added compound decreased in all river water samples studied, but at a different rate, while in bidistilled water it did not change very much. However, compared to the published half lives of 0.7—28 hours the compounds present in concentrations 60—100 μg/l were found to be relatively persistent. In all water samples the half lives were longer than 72 hours with a further decrease even much lower. The only exception was the fast degradation of dichlorvos in the water of the river Kupa.

Dichlorvos was detected neither in filtrate after the perccolation through activated carbon nor in the precipitate formed in water during the experiment.

The total carbon and total organic carbon, determined as parameters of water pollution level, were shown to be insufficient to elucidate this behaviour.

The procedure for the determination of organophosphorus pesticides has to be expanded by a systematic investigation of all parameters influencing the hydrolysis and by as complete water analysis as possible.

The systematic search for pesticides in aquatic environment has become more complex owing to the comprehension of additional parameters and to the growing need for information in a wider variety of conditions (1–3).

Organophosphorus pesticides were detected repeatedly in many river and other surface waters (4, 5), but no relevant information is available on their occurrence in Yugoslav rivers. As these pollutants can be not only of agricultural, but also of industrial origin, especially in some regions of the Sava and Kupa rivers, the investigations were undertaken with the aim to determine their persistence in differently polluted river waters.

The monitoring of the amount of organophosphorus pesticides added to river waters of different origin and pollution level as function of time is expected to yield valuable data. Namely, the length of the period of increased pollution after the outbreak of pollutants would indicate the distance of the pollution source on one side and the preferable location of the sampling sites on the other.

MATERIALS AND METHODS

O,O-dimethyl-2,2-dichlorovinyl phosphate (dichlorvos, DDVP) 93%, was obtained from WHO, Geneva, Switzerland. Parathion 99%, was obtained from Bayer AG, Leverkusen, FR Germany. Malathion 96%, Reference Standard Lot. No. 2576, was received from EPA, Perrine, Fla. 33157. Stock solutions of organophosphorus compounds were prepared in ethanol. Activated carbon, »Aktivkohle Typ Burrus 0.1–0.2 mm«, Bender & Hobein, Zürich, Schwitzerland, was a gift from Dr. Martin Reinhard, EAWAG, Dübendorf, Switzerland.

The extraction of water samples to which a known amount of DDVP was added, was performed with a mechanical stirrer. A faster separation of organic layer was achieved by the introduction of Na_2SO_4 into the separatory funnel. The separated organic phase was dessiccated with $MgSO_4$ during 24 hours and analyzed by gas chromatography.

The adsorption of DDVP, malathion and parathion, separately and in mixture, was tested by percolation of 100 ml water samples to which known amounts of the compounds were added through a 1 cm x 0.5 cm microcolumn of activated carbon. The optimal flow rate was found to be 0.5 ml/min. The elution of DDVP was performed with 2 ml of methanol, and subsequently parathion and malathion were eluted with 2 ml of solvent mixture isoamyl alcohol : n-heptane : benzene (2:98:400). The optimal flow rate of the eluent was shown to be 0.1 ml/min. The eluates were dried on dehydrated Na_2SO_4.

For percolation of large volumes of river water samples the apparatus shown in Fig. 1. was found to be useful.

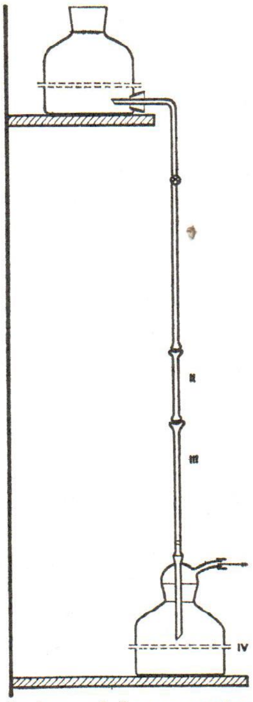

Fig. 1. *Apparatus for percolation of large water samples through activated carbon*

I water-tank
II glass wool precolumn (13 × 1 cm) withholding mechanical impurities
III glas column (23 × 1 cm) with sintered glass disc supporting activated carbon
IV receiving bottle connected to water pump enabling flow-through adjustment by evacuation

The total carbon and total organic carbon were determined as parameters of the pollution level of different river waters as described previously (6).

For qualitative and quantitative determination of organophosphorus compounds present in higher concentrations TLC on Kieselgel G (nach Stahl, Typ 60) layer with solvent systems chloroform : acetone (1:1) (7) or benzene:acetone:n-hexane (10:25:65) (1) for the development was applied. The spots were visualized by spraying with silver nitrate (7) and quantitatively evaluated with CAMAG TLC Scanner using filter 831 (460–470 nm). The relevant data will be published elsewhere.

Gas chromatographic analyses were performed on a Varian Aerograph Moduline Series 2800 instrument. The determination of DDVP was performed under the following conditions: Pyrex glass column 1.8 m x

2 mm packed with 5% OV–225 on Gas-Chrom Q 80–100 mesh; the flow rate of nitrogen as a carrier gas 75 ml/min, column temperature 170°C and alkali flame ionization detector. For the determination of malathion and parathion the following conditions were applied: Pyrex glass column 1.8 m × 2 mm packed with 1.95% DC QF-1 + 1.50% OV-17 on Gas Chrom Q 80–100 mesh, at 170°C, nitrogen carrier flow rate of 90 ml/min and Sc ^3H electron capture detector.

For the identification of individual organic components in the river water the gas chromatographic-mass spectrometric system Varian Aerograph Series 1400-Varian MAT CH 7 was used.

TLC qualitative analysis of complex eluates obtained by percolation of large volumes of river water through activated carbon microcolumn was performed on Silicagel G layer. For development solvent system petroleum ether:carbon tetrachloride (1:1) (8) or methylene chloride (9) were used.

The spots were visualized by the fluorescence in UV light and by spraying with conc. H_2SO_4 and heating.

RESULTS AND DISCUSSION

The enrichment of organophosphorus compounds, present as micropollutants in surface waters, was performed by extraction with organic solvents or by adsorption on a microcolumn of activated carbon.

To evaluate extraction procedures, the recovery with different solvent systems was compared. In Table 1. are given extraction values for DDVP which is an active component of pesticides most frequently produced and used in this country.

Table 1

Extraction of DDVP with a series of solvents and solvent systems

Solvent	Recovery %	
	single extraction	double extraction
Petroleum ether	9.9	31.5
Isooctane	5.9	13.9
Benzene	87.7	98.3
Isoamyl alcohol+n-heptane+toluene (2 ml + 98 ml + 400 ml)	80.2	96.6
Isoamyl alcohol+isooctane+benzene (2 ml + 98 ml + 400 ml)	81.6	100.2
Isoamyl alcohol+n-heptane+benzene (2 ml + 98 ml + 400 ml)	83.4	100.7

The concentration of DDVP in all experiments was 3—30 μg/ml.

The ratio of the water sample volume to the extractant was 100:10. The volume of water may be increased but that of the extractant ought to be as small as possible. The reduction of the extractant volume by evaporation should be avoided because of the volatility of DDVP (b. p. 76.6° C at 1 mm Hg pressure).

In a series of experiments it was shown that after evaporation to dryness at different temperatures not exceeding 45° C, only 80–20% of the originally added DDVP remained.

This was the reason for omitting methylene chloride in our work, a solvent often utilized for the extraction of organophosphorus compounds. The evaporation to dryness and dissolution with a small volume of some other solvent more suitable for gas chromatographic analysis is inevitable when an electron capture detector is used. Moreover, with methylene chloride as solvent the column bleeding was often observed.

Ethylacetate was not used either because of its relatively high solubility in water which causes considerable errors at the volume ratio used.

The limitations inherent in extraction procedure were avoided by adsorption effected by sucking the samples regardless of volume through a microcolumn of activated carbon. The elution was performed with a small volume of solvent. In this way the concentration by evaporation involving a loss of volatile compounds (e. g. dichlorvos) and enrichment of impurities present in solvents is avoided. A choice of solvents for elution is larger than for the extraction procedure which excludes the application of water soluble solvents. Moreover, the preseparation of certain classes of organic micropollutants can be achieved and possibly improved if elution is performed with various solvents and at different temperatures. Of the organophosphorus compounds listed above only dichlorvos was eluted with methanol and completely separated from malathion and parathion, which in turn were satisfactorily desorbed with a solvent mixture isoamyl alcohol : n-heptane : benzene (2:98:400) after the elution of dichlorvos with methanol was completed.

In Table 2. the results are shown illustrating the adsorption of the compounds listed, one by one and as a mixture, as well as their elution from the activated carbon microcolumn. The efficacy of adsorption and desorption depended on the flow rate and on the concentration of the aqueous sample as proven with three different carbon species. The results were obtained by gas chromatographic analysis under optimal working conditions determined before. Samples of higher concentration were anlysed by quantitative thin-layer chromatography. After percolation none of the investigated compounds could be detected in water samples.

The adsorption procedure and elution from the activated carbon microcolumn was applied in the studies of the persistence of organophosphorus pesticides in the aquatic environment. The results shown in Fig. 2 represent graphically the persistence during two weeks of

Table 2

Adsorption of organophosphorus compounds and elution from the activated carbon microcolumn

Compound	DDVP	Malathion	Parathion	Mixture		
				DDVP	Malathion	Parathion
Concentration mg/ml	$9.4 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$6.9 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$6.1 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$
Solvent	Methanol	Solvent* system	Solvent* system	Methanol	Solvent* system	Solvent* system
Recovery %	90.5 ± 1.2	76.7 ± 2.4	69.8 ± 1.1	85.9 ± 1.6	75.9 ± 3.1	70.8 ± 3.7

* Solvent system:

Isoamyl alcohol	2
n-heptane	98
benzene	400

dichlorvos, parathion and malathion added to samples of river water of different origin. Each point represents the mean value of 2–4 determinations. In the case of the Sava and Kupa rivers the sampling was performed twice.

By comparison with the behaviour of the investigated compounds in bidistilled water a faster decrease in concentration was evident with profile depending on water origin.

The added amount of organophosphorus compounds in the studied systems was high in relation to the pollution level of the river water (1), and no interferences in thin-layer or gas chromatographic assays were encountered.

The total carbon and total organic carbon content of investigated water samples – the Sava, Kupa, Korana and Slušnica rivers – were taken as possible parameters for a correlation of decay profiles (Fig. 3).

In addition to the determination of the degree of organic pollution the characterization of organic compounds present was also attempted. Samples of 5 l from the Sava river were percolated through an active carbon microcolumn and elution was performed with different solvents. Thin-layer chromatographic assay of the methanolic eluate showed the presence of only 2–3 components. However, the eluate with the solvent system isoamyl alcohol:n-heptane:benzene contained at least 6–7 components fluorescent in UV light. According to the solvent system used for the development of thin-layer chromatograms and according to R_f values of the spots it was assumed that some softeners, esters of phthalic, adipic, sebacic or/and phosphoric acid were present. By gas chromatographic analysis seven components were found (Fig. 4). Even with 5 l samples the concentration of organic pollutants was too low for

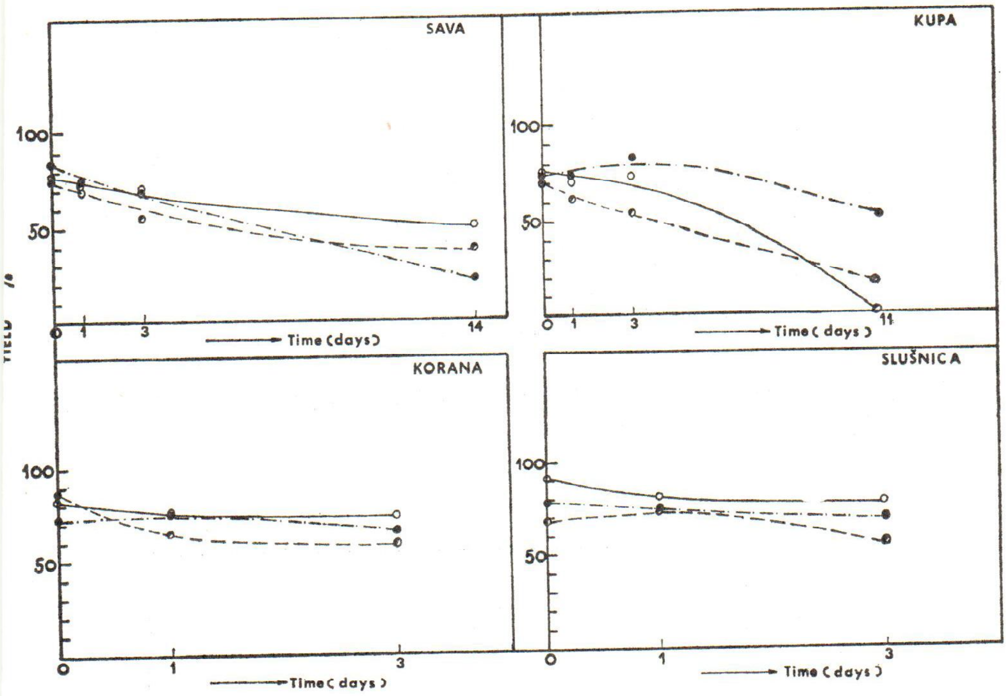

Fig. 2. *The persistence of organophosphorus pesticides added to samples of river water of different origin (Rivers: Sava, Kupa, Korana and Slušnica)*

O————O DDVP
●—·—·—● Malathion
◑ — — — — ◑ Parathion

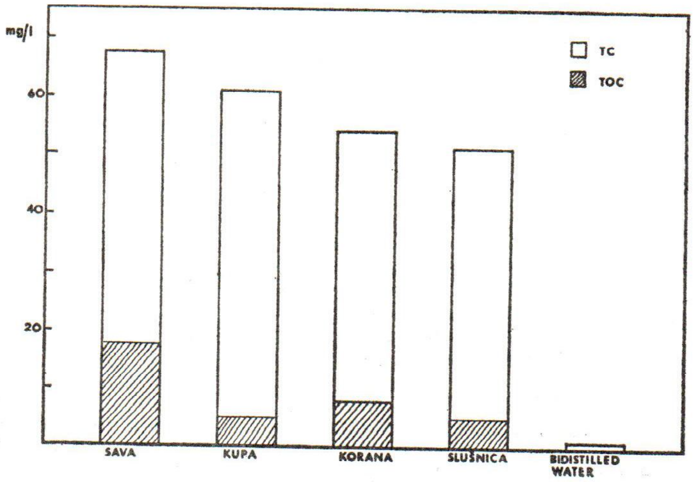

Fig. 3. *The content of total carbon (TC) and total organic carbon (TOC) in river waters investigated*

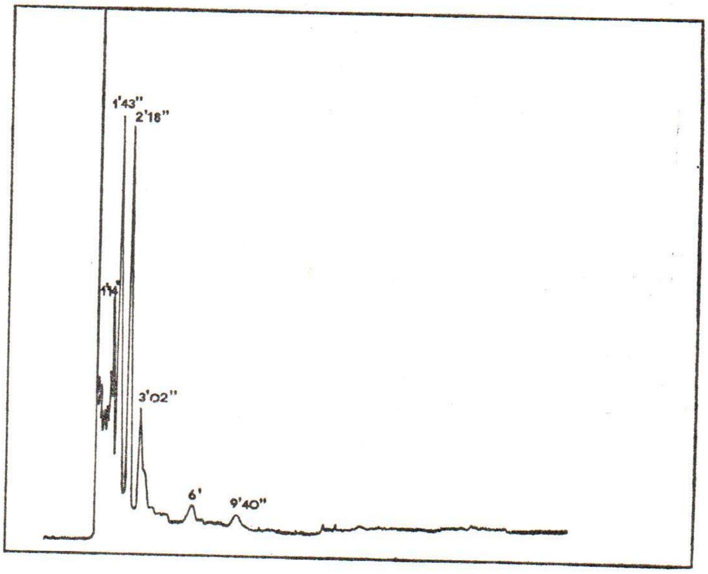

Fig. 4. *Gas chromatogram of the eluate with solvent system isoamyl alcohol+ +n-heptane+benzene (2 + 98 + 400) of activated carbon microcolumn after percolation of 5 l sample of the river Sava*

the identification of individual components by gas chromatographic-mass spectrometric system available. The sensitivity of the system used in these experiments did not reach 50 ppm for a single component.

Contrary to published data (3) organophosphorus compounds were found to be persistent in aquatic environments investigated during a relatively long period of time in accordance with data reported for one order of magnitude lower concentrations (10 μg/l) (10). The only exception was a fast decay of dichlorvos in the water of the Kupa river (Fig. 2). This could hardly be explained by either total carbon or total organic carbon values. Obviously the degradation of this compound was catalysed by the presence of some specific component or otherwise dichlorvos was bound by some product forming in the course of time. However, it was shown that dichlorvos and malathion were not at all adsorbed on the precipitate deposited in the course of the experiment while parathion was found to be adsorbed only in trace amounts.

These findings have incited efforts to accompany the determinations of organophosphorus pesticides with as complete water analysis as possible. Furthermore, systematic investigations of parameters affecting the rate of their hydrolysis were initiated.

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Sažetak

PONAŠANJE PESTICIDA U VODENOJ OKOLINI. I. POSTOJANOST NEKIH ORGANSKOFOSFORNIH PESTICIDA U RIJEČNOJ VODI

Uspoređena je efikasnost akumuliranja organskofosfornih spojeva, koji su kao mikropolutanti prisutni u riječnim vodama, metodom ekstrakcije s organskim otapalima i adsorpcijom na mikrokoloni aktivnog ugljena.

Postupak adsorpcije i eluiranja s kolone aktivnog ugljena primijenjen je za određivanje postojanosti organskofosfornih pesticida — diklorvosa, malationa i parationa — u riječnoj vodi različitog stupnja čistoće. Koncentracija svih dodanih spojeva tokom vremena opada u svim uzorcima riječnih voda, ali na različite načine, dok se stajanjem u redestiliranoj vodi bitno ne mijenja količina niti jednog spoja. Međutim, u usporedbi s objavljenim vremenima poluraspada od 0,7—28 sati spojevi prisutni u koncentracijama 60—100 μg/l su se pokazali relativno postojanima. Vremena poluraspada su u svim uzorcima voda bila dulja od 72 sata s još mnogo sporijim daljnjim opadanjem. Izuzetak je brza razgradnja diklorvosa u vodi rijeke Kupe. Diklorvos nije detektiran ni u filtratu nakon propuštanja vode kroz aktivni ugljen ni u talogu nastalom stajanjem vode.

Totalni ugljik i totalni organski ugljik, određeni kao parametri onečišćenja vode, pokazali su se nedovoljnim za objašnjenje te činjenice.

Razrada postupka za određivanje organskofosfornih pesticida nužno se mora povezati sa sistematskim ispitivanjem svih činilaca koji utječu na stupanj njihove hidrolize i što potpunijom analizom vode.

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