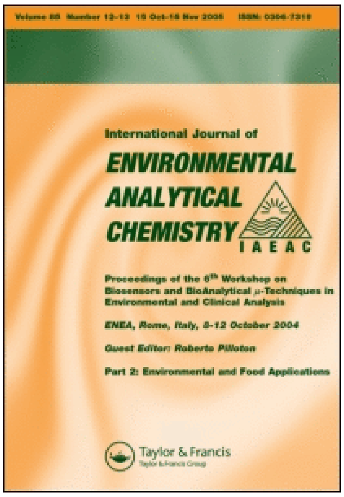

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Drevenkar, V. , Fröbe, Z. , Štengl, B. and Tkalčević, B.(1985) 'An Adsorption Procedure for Determining the Level of Organophosphorus Pesticide Residues in Pond Water', International Journal of Environmental Analytical Chemistry, 22: 3, 235 — 250

To link to this Article: DOI: 10.1080/03067318508076423

URL: http://dx.doi.org/10.1080/03067318508076423

Intern. J. Environ. Anal. Chem., 1985, Vol. 22, pp. 235–250
0306-7319/85/2204-0235 $18.50/0

Printed in Great Britain

An Adsorption Procedure for Determining the Level of Organophosphorus Pesticide Residues in Pond Water

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(*Received January 3, 1985; in final form May 24, 1985*)

A procedure for the accumulation of phosphorus-containing degradation products of organophosphorus pesticides from water by elution of ion-associates of dialkylphosphorus anions with tetraphenylarsonium cation adsorbed onto an activated carbon micro-column is described.

Using a 50 cm^3 sample volume at a concentration of 1 μg cm^{-3} the average accumulation recoveries (% ± S.D.) were 81 ± 11 and 91 ± 8 for diethyl and dimethyl phosphorodithioates, 69 ± 10 and 66 ± 10 for the corresponding phosphorothioates and 33 ± 13 and 13 ± 6 for the analogous phosphates. A decrease in these values was caused by the presence of common inorganic anions and at lower concentrations of the analysed species. At a detection limit of 20 ng cm^{-3} the recovery was 20–30%. Despite of low accumulation recoveries the minimum detectable concentration of these anions was decreased below 0.1 ng cm^{-3} by handling 1 dm^3 sample volumes.

The procedure was applied for the analysis of dialkyl phosphorothioates and dialkyl phosphorodithioates in the water from three ponds located in an apple orchard before and after seasonal application of organophosphorus pesticides.

KEY WORDS: Organophosphorus pesticide residues, dialkyl phosphorothioates, dialkyl phosphorodithioates, activated carbon, water analysis.

INTRODUCTION

In view of the large number of organophosphorus pesticides used and the marked differences in their degradation rates,[1-8] the control of an aquatic environment polluted with this class of compounds should consist not only of the determination of the parent compounds—orthophosphoric, thiophosphoric and dithiophosphoric acid triesters—but also of the degradation products. Therefore adequate procedures for the accumulation of dialkyl phosphates, dialkyl phosphorothioates and dialkyl phosphorodithioates are essential for reliable monitoring of organophosphorus pesticides. Efficient accumulation procedures for these and related compounds based upon adsorption onto Amberlite XAD-4,[8,9] or upon an anion-exchange resin prepared from XAD-4 resin,[10] have been reported. However, in our experience the accumulation of dialkylphosphorus anions using XAD-4 adsorbent was accompanied by serious difficulties in eluting dialkyl phosphorodithioates from the column.[7]

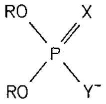
The enrichment of organophosphorus pesticides from an aqueous medium by adsorption onto an activated carbon micro-column has been found satisfactory for parent triesters.[5] A study of the adsorption of organic phosphates onto activated carbon cloth[11] has shown that the adsorption capacity falls from a neutral phosphate, such as triethyl phosphate, to more ionic dimethyl phosphate and even orthophosphate.[12,13]

In this work we attempted to improve the accumulation of dialkylphosphorus anions, formed by hydrolysis of one functional group of organophosphorus pesticides (Figure 1), by eluting their ion-associates with tetraphenylarsonium cation[14] adsorbed onto activated carbon. The study was initiated following the death of sheatfish in three small ponds located in an apple orchard, which was considered to be caused by the presence of pesticides.

EXPERIMENTAL

Materials

Dimethyl phosphate barium salt, $(DMP)_2Ba$, Lot No. 9564, purity 97.3%; diethyl phosphate barium salt, $(DEP)_2Ba$, Lot No. 9209, purity 98%; O,O-dimethyl phosphorothioate potassium salt,



R	X	Y	Symbol
Me	O	O	$(DMP)^-$
Me	S	O	$(DMTP)^-$
Me	S	S	$(DMDTP)^-$
Et	O	O	$(DEP)^-$
Et	S	O	$(DETP)^-$
Et	S	S	$(DEDTP)^-$

FIGURE 1 Dialkylphosphorus anions formed by hydrolysis of organophosphorus pesticides.

DMTPK, Lot No. 5058; O,O-diethyl phosphorothioate potassium salt, DETPK, Lot No. 5056; O,O-dimethyl phosphorodithioate potassium salt, DMDTPK, Lot No. 5057; O,O-diethyl phosphorodithioate potassium salt, DEDTPK, Lot No. 6802, were all obtained from the U.S. Environmental Protection Agency Repository, NC, U.S.A.

Tetraphenylarsonium chloride, p.a., $(Ph_4As)Cl$, and ion-exchanger Amberlite IRA 400 were products from Fluka, Buchs, Switzerland.

Activated carbon "Aktivkohle für Gas Chromatographie nach Dr. Grob", 0.1–0.2 mm, was supplied by Bender und Hobein, Switzerland.

Tris-(hydroxymethyl)-aminomethane (Tris buffer) p.a., ethanol p.a., methanol p.a. and dichloromethane p.a. were purchased from Kemika, Yugoslavia.

N-methyl-N-nitroso-*p*-toluenesulphonamide, Merck-Schuchardt, Germany, was used for the preparation of an ethereal diazomethane solution[15] containing 5–15 mg CH_2N_2 per cm^3.

Apparatus

Varian Aerograph Series 1400 (Column I) and Series 2800 (Column II) gas chromatographs with alkali flame ionization detectors (Rb_2SO_4) were used.

Gas chromatographic columns: glass 1.5 m × 2 mm i.d., packed with 20% Triton X-305 on Chromosorb W/AW DMCS 0.16–0.20 mm (Column I); glass 1.8 m × 2 mm i.d., packed with 4% SE-30

+6% OV-210 on Gas Chrom Q 0.16–0.20 mm, starting with a 10 cm length of Chromosorb W/NAW 0.16–0.20 mm coated with 10% Carbowax 20M (Column II).

Column I was used for analysis of individual dialkylphosphorus compounds and Column II for the mixture of organophosphorus species.

Operating temperatures and gas flow rates were: Column I 155°C, Column II 85°C; injector 200°C and detector 235°C (Varian 1400), injector 200°C and detector 210°C (Varian 2800); nitrogen carrier 30 $cm^3 min^{-1}$, air 235 ± 10 $cm^3 min^{-1}$ and hydrogen 35 ± 3 $cm^3 min^{-1}$.

Methyl derivatives of dimethyl and diethyl phosphorothioates and phosphorodithioates present in the pond water samples were identified with a capillary gas chromatograph-mass spectrometer (GC-MS) system by courtesy of Mr. Christian Schaffner, EAWAG, Dübendorf, Switzerland.

Conversion of $(Ph_4As)Cl$ into $(Ph_4As)OH$

An aqueous $(Ph_4As)Cl$ (80–100 $mg\,cm^{-3}$) solution was percolated through a 1 × 10 cm column of anion exchanger Amberlite IRA 400 (OH^- form) followed by deionized water to provide 50 cm^3 of total volume of the effluent. The $(Ph_4As)OH$ concentration in the final solution was 15–19 $mg\,cm^{-3}$.

Extraction of dimethyl phosphorodithioate from water

The samples were treated according to the procedure described previously.[14]

Accumulation of dialkylphosphorus anions as ion-associates with $(Ph_4As)^+$ on activated carbon

a) Efficiency of accumulation from aqueous solution Dialkyl phosphates, phosphorothioates and phosphorodithioates were dissolved in deionized water (0.2–1000 $ng\,cm^{-3}$). The solutions were adjusted to pH 8 by addition of a Tris buffer solution. To 50 cm^3 and 1 dm^3 aliquots for the concentrations ranging from 20 to 1000 $ng\,cm^{-3}$ and from 0.2 to 20 $ng\,cm^{-3}$, respectively, $(Ph_4As)OH$ was added in an 8-

fold excess. The sample was then percolated through a 0.5 × 0.5 cm activated carbon micro-column prewashed with a Tris buffer solution at pH 8. The elution of dialkylphosphorus anions was made with 3 cm^3 of methanol followed by 7 cm^3 of dichloromethane which was kept in contact with the activated carbon for 10 min. The combined eluates were evaporated to 1 cm^3 under a stream of nitrogen and methylated by addition of ethereal diazomethane solution until a persistent yellow colour appeared. After 10 min the sample was evaporated again to 1 cm^3 under a stream of nitrogen.

In order to control the adsorption efficiency, the water passing through the column was collected and a 0.1 cm^3 aliquot was alkylated with diazomethane in a predominantly ethanolic solution.

Standard samples for quantitative gas chromatographic analysis were prepared by mixing 0.01–0.4 cm^3 of the aqueous solution containing known concentrations of dialkylphosphorus anions with 3 cm^3 of methanol and 7 cm^3 of dichloromethane followed by evaporation and methylation as described above.

b) Determination of dialkyl phosphorothioates and phosphorodithioates in pond water To a 1 dm^3 filtered pond water sample 2 cm^3 of 5×10^{-4} mol dm^{-3} $(Ph_4As)OH$ was added. The sample was adjusted to pH 8 by addition of Tris buffer and percolated through an activated carbon micro-column. Subsequently desorption and methylation procedures described under (*a*) were performed.

Standards for quantitative evaluation were prepared by adding known amounts of dialkyl phosphorothioates and phosphorodithioates to a 1 dm^3 sample of deionized water which had been treated in the same way as the pond water sample.

The effect of anions on dialkylphosphorus anions accumulation efficiency

For the investigation of the effect of chlorides, nitrates, sulphates, tripolyphosphates and dodecylbenzenesulphonates (DBS) on the extraction recovery of $(DMDTP)^-$ from deionized water, aqueous solutions of NaCl (6.57 mg cm^{-3}), $NaNO_3$ (3.15 mg cm^{-3}), Na_2SO_4 (8.86 mg cm^{-3}), $Na_2P_3O_{10}$ (1.14 mg cm^{-3}) and $C_{18}H_{29}SO_3Na$ (1.18 mg cm^{-3}) were prepared. The solutions of anions were added singly, or in a mixture, to 50 cm^3 samples of deionized water containing 1.0 $\mu g\,cm^{-3}$ of $(DMDTP)^-$.

The effect of the same anions on the recovery of organophosphorus anions as associates with $(Ph_4As)^+$ on activated carbon was investigated with 50 cm^3 water samples containing 1.0–1.3 $\mu g\,cm^{-3}$ of dialkylphosphorus anions, 80 μg Cl^-, 10 μg NO_3^- as N, 120 μg SO_4^{2-} and 0.6 μg of tripolyphosphate per cm^3.

Persistence of dialkylphosphorus anions in pond water

Twenty dm^3 of Pond 2 water (pH 7.1, temperature 20°C) was placed in a 41 × 27 × 28 cm glass tank. The silt taken from Pond 2 was added to cover the bottom of the tank in a 2 cm high layer. The water was aerated for 35 days and the decrease in concentrations of the initially determined $(DMTP)^-$, $(DETP)^-$, $(DMDTP)^-$ and $(DEDTP)^-$ was measured during this period by analysis of 1 dm^3 of water every 7 days.

RESULTS

The addition of tetraphenylarsonium chloride promotes, in particular, the extraction of dialkyl phosphorodithioates from aqueous solutions with dichloromethane.[14] These anions are extracted considerably better than dialkyl phosphorothioates while dialkyl phosphates are not extracted at all.

In order to establish the applicability of extraction for the selective control of dialkyl phosphorodithioates in an aquatic environment the dependence of extraction recovery on the compositon of the aqueous phase, i.e., on the interferences of other anionic species common to polluted waters was studied. Chlorides, nitrates, sulphates and anionic detergents, in concentrations listed in Table I, were added to solutions of $(DMDTP)^-$ in deionized water. In order to avoid an additional increase in the concentration of chloride ions, $(Ph_4As)Cl$ was converted into the OH form and then added in a 1:1 ratio to anions and in an 4:1 ratio to $(DMDTP)^-$. Under these conditions chlorides and nitrates present in the water sample either alone or in a mixture with sulphates and anionic detergents decreased the extraction recovery of $(DMDTP)^-$ by 12–13%. The standard deviation of these determinations was 5–10% and therefore

TABLE I

The effect of common anions on the extraction recovery of $(DMDTP)^-$ ion-associate with $(Ph_4As)^+$ from water.[a]

(*a*) *Single anions*

Anion	Concentration in water ($\mu g\,cm^{-3}$)	Percent extraction recovery (no. of determinations) Without anion	 With anion
Chloride	80	85 (3)	72 (3)
Nitrate (as N)	10	85 (3)	73 (3)
Sulphate	120	78 (2)	89 (3)
Tripolyphosphate	1.0	74 (2)	73 (3)
Tripolyphosphate	0.6	74 (2)	73 (3)
DBS	0.6	77 (2)	75 (3)

(*b*) *Anions in mixture*

Anion	Concentration in water ($\mu g\,cm^{-3}$)	Percent (±S.D.) extraction recovery (no. of determinations)
Without anion	—	85±9 (21)
Chloride Nitrate (N) Sulphate	80 10 120	70±8 (14)
Chloride Nitrate (N) Sulphate Tripolyphosphate	80 10 120 0.6	78±5 (10)
Chloride Nitrate (N) Sulphate Tripolyphosphate DBS	80 10 120 0.6 0.6	69±7 (9)

[a] Concentration of $(DMDTP)^-$ in water samples was 1.0 $\mu g\,cm^{-3}$.

we concluded that the presence of chlorides and nitrates decreased the extraction recovery of $(DMDTP)^-$ by approx. 10–15%.

The accumulation of other dialkylphosphorus anions was studied by eluting their ion-associates with tetraphenylarsonium cation adsorbed on an activated carbon micro-column. A flow diagram of the procedure is shown in Figure 2. The average accumulation recoveries and the effect of inorganic anions on the efficiency of accumulation are presented in Table II. The presence of a mixture of chloride, nitrate, sulphate and tripolyphosphate in the water sample caused a decrease in the elution recoveries of $(DMP)^-$ and $(DEP)^-$ to 1–3%, while 13–17% of $(DEP)^-$ was detected in the water that had passed through the activated carbon micro-column. The same anions did

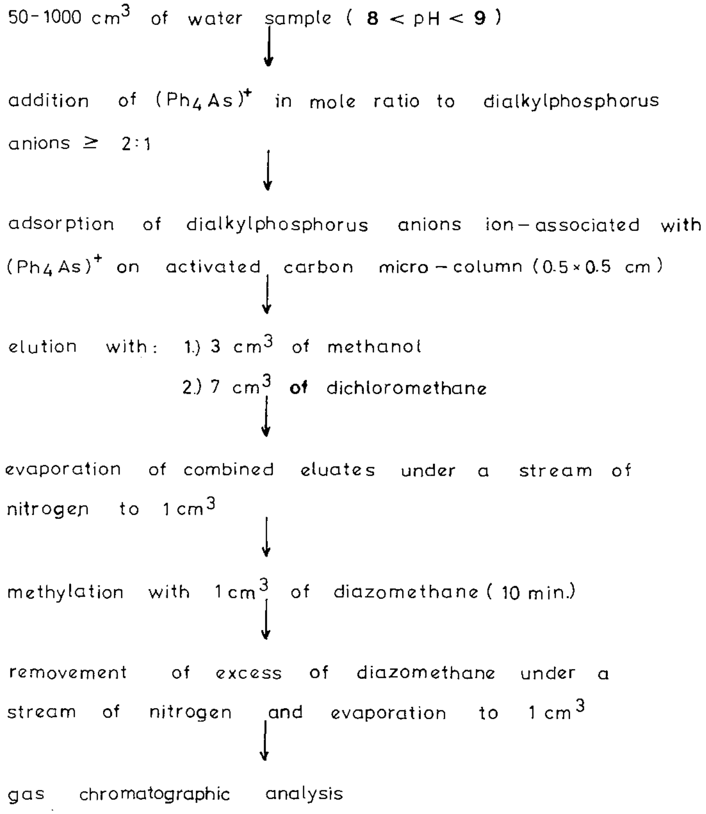


FIGURE 2 Flow diagram showing a procedure for sample preparation.

TABLE II

Efficiency of accumulation from water of ion-associates of dialkylphosphorus anions with $(Ph_4As)^+$ on an activated carbon micro-column.

	Accumulation efficiency, % ± S.D. (no. of determinations)		
		Concentration range (1–1.3 μg cm^{-3})^b	
Compound	Concentration range (0.2–25 ng cm^{-3})^a	Without anions	With anions^c
$(DEDTP)^-$	17 ± 5 (6)	81 ± 11 (12)	82 ± 8 (8)
$(DMDTP)^-$	19 ± 5 (6)	91 ± 8 (12)	86 ± 7 (14)
$(DETP)^-$	33 ± 6 (6)	69 ± 10 (10)	59 ± 10 (10)
$(DMTP)^-$	21 ± 8 (6)	66 ± 10 (10)	39 ± 10 (10)
$(DEP)^-$		33 ± 13 (10)	3
$(DMP)^-$		13 ± 6 (5)	1

[a] Sample volume: 1 dm^3.

[b] Sample volume: 50 cm^3.

[c] Concentrations of inorganic anions in water sample: Cl^-, 80 μg cm^{-3}; No_3^-, 10 μg N cm^{-3}; SO_4^{2-}, 120 μg cm^{-3}; tripolyphosphate, 0.6 μg cm^{-3}.

not interfere to any appreciable extent with the accumulation efficiency of dialkyl phosphorodithioates and in the case of phosphorothioates a reduction was only observed for $(DMTP)^-$.

The adsorption and elution efficiencies of $(DMTP)^-$, $(DETP)^-$, $(DMDTP)^-$ and $(DEDTP)^-$ ion-associates with $(Ph_4As)^+$ were determined as functions of the initial concentration of dialkylphosphorus anions in water sample. The average percentage recoveries in the concentration range from 20 to 1000 ng cm^{-3} increased linearly with increasing concentrations of the ion-associates in the water samples: 20–65% for $(DMTP)^-$, 30–70% for $(DETP)^-$, 20–90% for $(DMDTP)^-$ and 30–85% for $(DEDTP)^-$. The calibration graphs obtained with a series of aqueous samples covering the same concentration range were constructed by taking the sample to standard peak height ratio as the ordinate to eliminate possible variations in gas chromatographic conditions (Figure 3). The detection limit of the procedure with the 50 cm^3 water sample was 20 ng cm^{-3} (signal-to-noise ratio, 4:1).

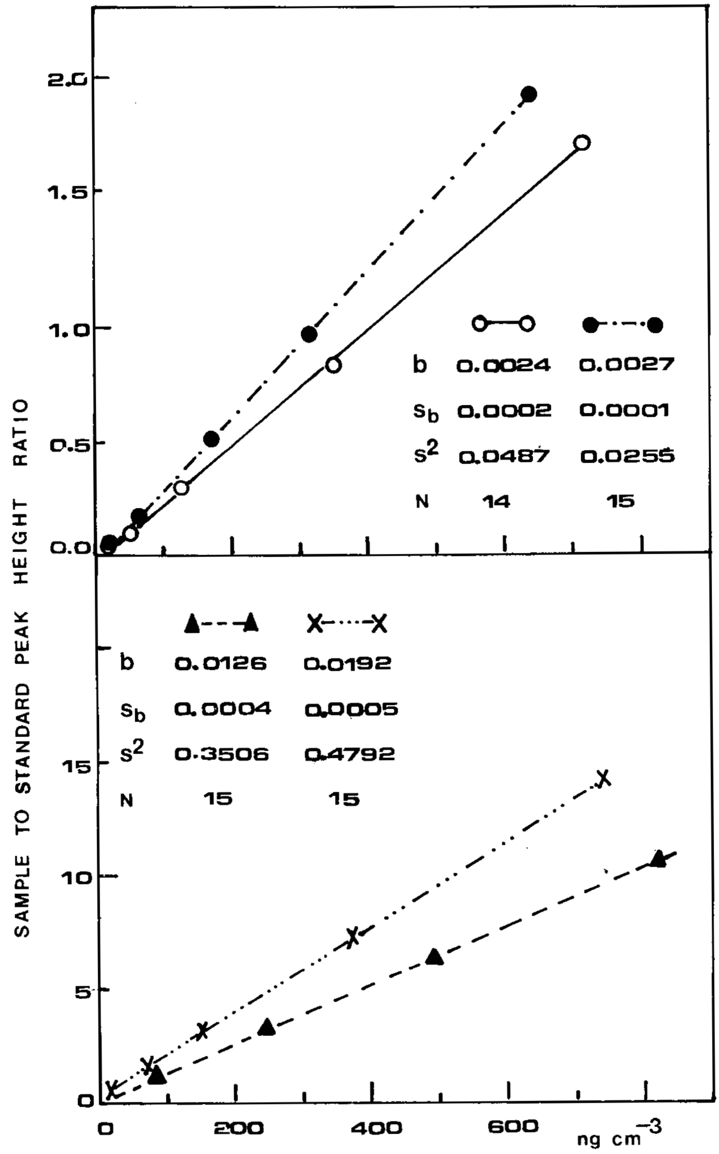


FIGURE 3 Calibration curves for quantitative determination of dialkyl phosphorothioates and phosphorodithioates added to deionized water.

○——○ (DMTP)$^-$; ●—·—● (DETP)$^-$;
▲---▲ (DMDTP)$^-$; ×—···—× (DEDTP)$^-$;

Sample volume: 50 cm^3.

Standards: methanolic solutions of (DMTP)$^-$, 4.49 μg cm^{-3}; (DETP)$^-$, 5.37 μg cm^{-3}; (DMDTP)$^-$, 0.82 μg cm^{-3}; and (DEDTP)$^-$, 0.93 μg cm^{-3}.

b = slope; s_b = standard error of the slope; s^2 = variance of the regression; N = number of determinations.

The sensitivity of the procedure was increased by handling 1 dm^3 volumes of water and the concentration range was extended to concentrations below 20 $ng\,cm^{-3}$. The average recoveries and standard deviations calculated for concentrations ranging from 0.2 to 25 $ng\,cm^{-3}$ are shown in Table II. The minimum detectable amounts were 0.03 $ng\,cm^{-3}$ for $(DMTP)^-$ and $(DETP)^-$ and 0.07 $ng\,cm^{-3}$ for $(DMDTP)^-$ and $(DEDTP)^-$.

The accumulation efficiencies of dialkylphosphorus anions from deionized water and from the water from three ponds located in an apple orchard were comparable. For example, 28% of $(DEDTP)^-$ was recovered from Pond 3 water after addition of 10–20 μg of $(DEDTP)^-$ per dm^3 and 30% from a deionized water sample of the same concentration range. For this test the Pond 3 water collected in September was chosen because of the low concentration of the originally present $(DEDTP)^-$ (Table III). In calculating accumulation recovery, the original $(DEDTP)^-$ concentration was sub-

TABLE III

Concentrations of dialkylphosphorus anions in pond water from an orchard treated with organophosphorus pesticides.

		Concentration, $\mu g\,dm^{-3}$			
Time of sampling	Pond	$(DMTP)^-$	$(DMDTP)^-$	$(DETP)^-$	$(DEDTP)^-$
Before the first treatment					
April	1	0.03	NM	0.08	0.25
	2	0.02	NM	0.11	0.13
	3	0.07	NM	0.19	0.25
July	1	0.32	0.62	0.30	0.20
	2	0.04	0.42	0.15	0.08
	3	0.06	0.83	0.54	0.20
One day after the first treatment					
July	1	0.33	0.55	0.26	0.23
15 days after the last treatment					
September	1	2.08	9.57	1.09	2.45
	2	1.22	11.04	2.78	12.88
	3	3.61	25.32	0.84	0.27

NM = Not measured.

tracted from the concentration determined in the sample to which $(DEDTP)^-$ had been added.

The results of analyses of $(DMTP)^-$, $(DETP)^-$, $(DMDTP)^-$ and $(DEDTP)^-$ in the pond water samples which were collected two months before the spraying of the surrounding orchard with organophosphorus pesticides (April), immediately before and after the first spraying (July), and 15 days after the last spraying (September) are shown in Table III. As no or rather low concentrations of analysed dialkylphosphorus anions were expected in the water samples collected early in the springtime and immediately before the first summer spraying a 1 dm^3 volume of water was passed through an activated carbon column.

The identity of the methylated species isolated from pond water samples after the spraying of the orchard was confirmed by GC-MS analysis of combined and concentrated eluates using a highly efficient capillary column. For identification of components with retention times corresponding to the compounds analysed the mass chromatograms were reconstructed for ions prominent in their scanned spectra. The molecular ion, and two of the most intensive characteristic fragment ions of each compound were chosen (Table IV).

The persistence of dialkylphosphorus anions in the pond water was checked in the experiment carried out with air-circulated Pond 2 water with related silt added. After 35 days there still remained 10,

TABLE IV

Major characteristic fragment ions and molecular ion registered in the mass chromatograms of methylated dialkylphosphorus anions determined in the pond water samples.

Compound	m/z Fragment ions		m/z Molecular ion
$(DMTP)-CH_3$	79	110	156
$(DETP)-CH_3$	111	140	184
$(DMDTP)-CH_3$	93	125	172
$(DEDTP)-CH_3$	97	123	200

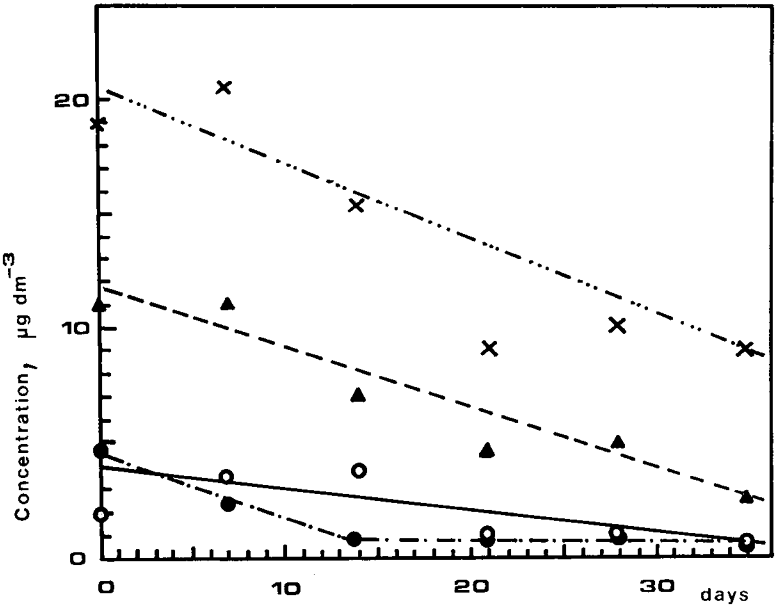


FIGURE 4 Persistence of dialkylphosphorus anions in the air circulated water of Pond 2 with related silt added.

○——○ (DMTP)$^-$; ●—·—● (DETP)$^-$;
▲---▲ (DMDTP)$^-$; ×—···—× (DEDTP)$^-$.

18, 23, and 46% of the initially determined (DETP)$^-$, (DMTP)$^-$, (DMDTP)$^-$ and (DEDTP)$^-$, respectively (Figure 4).

DISCUSSION

The characteristics of tetraphenylarsonium associates with dialkyl phosphorothioates and dialkyl phosphorodithioates were studied in detail previously in order to gain a thorough understanding of the mechanisms of extraction from aqueous solutions.[14] The extraction procedure was found to be selective for the accumulation of dialkyl phosphorodithioates and therefore of an applicability limited to specific cases of pollution control of surface waters.

A possibility of accumulating dialkylphosphorus anions by adsorption on an appropriate adsorbent was investigated in further work.

In spite of nearly quantitative recoveries described in the literature,[8] the accumulation of the phosphorus-containing degradation products of organophosphorus pesticides from water by adsorption on Amberlite XAD-4 resin in our experience does not give satisfactory results.[7] The recovery and reproducibility were high only in the case of $(DEP)^-$ ($95 \pm 10\%$), but we established incomplete and irreproducible desorption of phosphorothioates and phosphorodithioates using 6 g of resin packed in a 15 × 1 cm column and acetone as an eluting solvent. No improvement was obtained by the addition of $(Ph_4As)^+$ to the aqueous solution of $(DEDTP)^-$ before percolating the water through an Amberlite XAD-4 or XAD-2 column; $(DEDTP)^-$ was not detected in the water collected after passing the column. In the dichloromethane eluate about 10% of added $(DEDTP)^-$ was found indicating again a strong adsorption onto the resin.

Very low recoveries (1–13%) were obtained by elution with dichloromethane for dialkyl phosphates, dialkyl phosphorothioates and dialkyl phosphorodithioates adsorbed on an activated carbon micro-column from water. However, in this case the accumulation efficiency was considerably improved by the addition of $(Ph_4As)OH$ to the aqueous phase (Table II). Adsorption-desorption recovery of dialkyl phosphorus anion-associates mixture in the presence of inorganic anions followed the series $(DMP)^- \approx (DEP)^- < (DMTP)^- \approx (DETP)^- < (DMDTP)^- \approx (DEDTP)^-$. The same sequence but considerably lower recoveries of dialkyl phosphorothioates were previously obtained for the extraction procedure in the presence of $(Ph_4As)Cl$.[14]

Compared to the extraction procedure the elution of ion-associated degradation products of organophosphorus pesticides adsorbed on activated carbon presents a certain improvement. The range of species which can be analysed is extended to dialkyl phosphorothioates ensuring at the same time more constant recoveries for $(DMTP)^-$, $(DETP)^-$, $(DMDTP)^-$ and $(DEDTP)^-$ even at concentrations lower than $1\,ng\,cm^{-3}$. A possibility is given for handling larger sample volumes whereby the sensitivity of the method can be enhanced. However, the facts that dialkyl phosphates cannot be determined and that rather poor accumulation recoveries are obtained for all other anions must be pointed out.

Searching for a suitable procedure for simultaneous accumulation of dialkyl phosphorothioates and phosphorodithioates, we applied the procedure described here, despite its serious drawbacks, in an urgent investigation of the effect on fish dying of seasonal treatment of an apple orchard with organophosphorus pesticides for assessing specific degradation products in the water of three adjacent ponds.

To avoid the errors caused by low accumulation efficiencies the standards for these determinations were prepared from a deionized water solution of $(DMTP)^-$, $(DETP)^-$, $(DMDTP)^-$ and $(DEDTP)^-$ treated in the same way as the pond water samples. The concentrations of standards were adjusted so that peak heights in gas chromatograms of the sample and standard were nearly equal. The experimental error caused by a non-quantitative recovery was thus brought to a minimum, although it was not completely eliminated because of possible slight differences between accumulation recoveries from different types of water. Therefore the results of pond water analysis have to be considered only as relative values, whose correlation points to changes in concentration of dialkylphosphorus anions in pond water during a period of time.

From July to September the 320 ha of the orchard area was treated three times with approx. $1500\,dm^3\,ha^{-1}$ of a 0.1% solution of various organophosphorus pesticides, which were all triesters of thio- and dithiophosphoric acid. Traces of $(DMTP)^-$, $(DETP)^-$, $(DMDTP)^-$ and $(DEDTP)^-$ were detected in the samples from all three ponds collected in April and July before the beginning of spraying (Table III). One day after the first pesticide application no great changes in concentrations in Pond 1 water were observed. However, the level of dialkylphosphorus anions measured two months later, i.e. after two more treatments at the end of July and August, increased considerably in all ponds reaching maximum values of $3.61\,\mu g\,(DMTP)^-\,dm^{-3}$, $25.32\,\mu g\,(DMDTP)^-\,dm^{-3}$, $2.78\,\mu g\,(DETP)^-\,dm^{-3}$ and $12.88\,\mu g\,(DEDTP)^-\,dm^{-3}$.

A relatively slow rate of disappearance of dialkylphosphorus anions from the pond water (Figure 4) indicates that these compounds are quite resistant to further degradation. They persist up to several months after spraying and may be detected in trace amounts as long as one year after pesticide application. Therefore a slow, but steady long-term increase in the pollution of the ponds caused by pesticides can be anticipated.

Acknowledgement

The authors are indebted to Prof. Zlata Štefanac for useful discussions and interest in this work.

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