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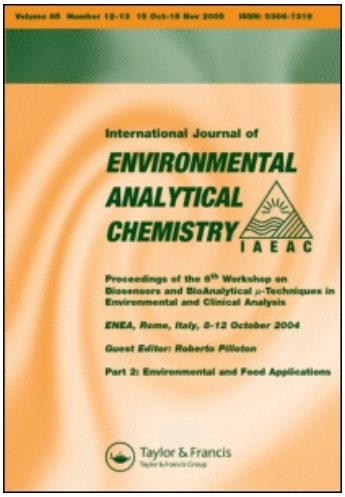

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DETERMINATION OF TRACE LEVELS OF DIAZINON AND PROPETAMPHOS IN WATER AND SEWAGE BY SOLID PHASE EXTRACTION

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An analytical method is described for the determination of the organophosphorus pesticides diazinon and propetamphos in water and in sewage, at levels ranging from 0.01–1.0 mg/L. The method involves solid phase extraction using C-18 Bond Elut cartridges, elution with ether, and solvent change to hexane. Quantification of the pesticide is by temperature programmed capillary gas chromatography using a nitrogen–phosphorus detector. Recoveries of diazinon are between 98–102% from water and between 70–80% from activated sludge biomass. These results are compared with a more polar organophosphate, propetamphos, for which the recovery from both water and biomass is close to 100%.

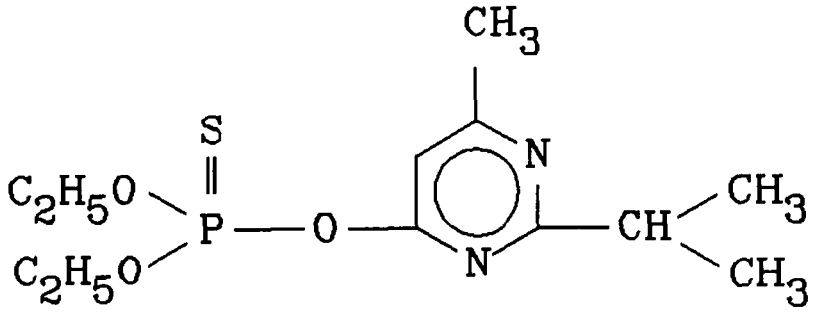
KEY WORDS: Diazinon, propetamphos, organophosphate pesticide, solid-phase extraction, water, sewage, gas chromatography with nitrogen-phosphorus detection, mass balance.

INTRODUCTION

The number of species of insect, mite, and tick resistant to chemical pesticides has increased almost exponentially over the last 30 years, following the extensive use of synthetic organic pesticides[1]. Consequently, newer and more toxic pesticides are being developed to treat such pests. Currently organophosphates (OPs) are widely used industrially and in agriculture for crop protection and for the elimination of ectoparasites[2,3], in preference to the once favoured organochlorines (OCs). This is due to the relatively rapid decomposition and lower persistence of the OPs. However, their high mammalian toxicity[2] makes their fate in the environment a matter of much recent and widespread concern.

As the use of these newer pesticides increases, so too does their occurrence in industrial effluents received at wastewater treatment plants. If such pollutants are not removed during wastewater treatment, they will be discharged to natural waters, where they may have deleterious effects upon the aquatic environment[4]. The fate of polychlorinatedbiphenyls (PCBs) and OCs have been studied in a number of different wastewater treatment plants[5–7].

a



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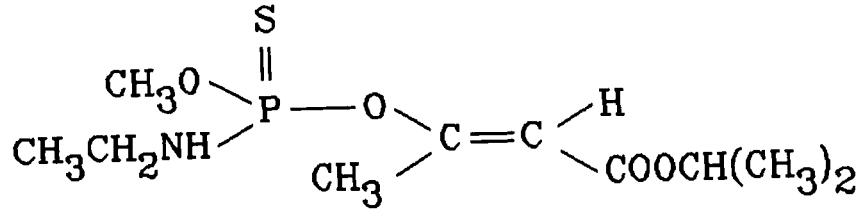

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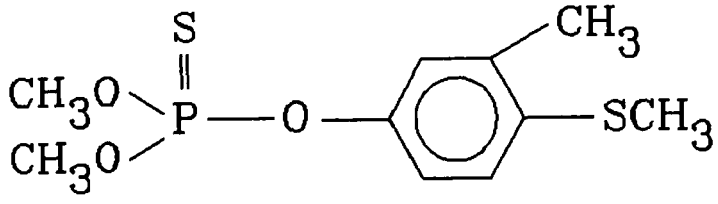

Figure 1 Organophosphorus pesticides: (a) diazinon, (b) propetamphos, (c) fenthion.

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For the OPs, however, there has been little reported on their fate in the treatment process.

OPs form a large class of pesticides with various chemical structures and polarities. Diazinon, an OP of intermediate polarity, has been chosen as a model compound in this study (Figure 1a). The presence of diazinon has been studied in water and wastewater samples[8–15], soils[16], fruits[17,18], vegetables and other foodstuffs[18], and fatty extracts such as olive oil[19,20]. A search of the literature has failed to reveal any reports on the determination of propetamphos (Figure 1b) in environmental samples. The extraction methods used to study diazinon include liquid-liquid extractions using a variety of solvents including methylene chloride[8], dichloromethane and hexane[12,15,16] and solid phase extractions, using amberlite XAD resins[12,13], specially modified diatomaceous earth[18], Extrelut, a Kieselghur–type material[19,20], florosil[21], and silica[22]. Solid phase extraction (SPE) is gradually replacing liquid-liquid extraction for the determination of pesticides in water samples for a variety of reasons, including the wide availability of selective adsorbent materials[23]. In this work, the disposable C-18 Bond Elut cartridge was used to extract diazinon from sewage samples. The C-18 cartridge adsorption technique has been attempted with a number of OP pesticides

and herbicides in lake and pond water[24–26], surface water[27,28], and environmental water samples[14,29], but not with such a complex matrix as sewage.

EXPERIMENTAL

Reagents

The OP pesticides diazinon, propetamphos (Ciba Geigy, Switzerland) and fenthion (Bayer, Germany) were all technical grade. The organic solvents, methanol and ether, were HPLC grade (Ajax Chemicals, Australia) and the hexane was pesticide grade (BDH, Poole, England). Deionised water was prepared using a Milli-Q system (Millipore Corporation, Bedford, MA, USA). The non-ionic surfactant used, Lissapol TN450 is a nonylphenol ethoxylate (ICI, Australia). Bond Elut C-18 cartridges (Varian, Harbor City, CA, USA, 500 mg/2.8mL) were used as the adsorbent in this study and samples were drawn through them by an applied vacuum, using a VacElut vacuum manifold device (Analytichem International, Harbor City, CA, USA). Each Bond Elut cartridge was used only once.

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Activated Sludge

Live activated sludge was collected from the South Eastern Purification Plant, (SEPP), Carrum, Victoria, Australia in well aged high density polyethylene containers (5L) and used within 24 hours of collection. Leaching of contaminants from these containers was negligible compared with concentrations measured in raw sewage in other studies. For example, we have found that typical sewage streams contain 0.001–0.01 mg/L of various phthalates.

Freeze dried activated sludge was prepared by sterilising (autoclaving at 121°C for 15 minutes) live SEPP sludge, snap freezing it in 1L plastic bags (laid flat for greater surface area) and then freeze drying. The process takes approximately 3–5 days for each batch of 25–30g.

Domestic sewage

A 2L sample of totally domestic sewage was collected in a brown glass winchester from the residential catchment at Brushy Creek, Croydon, Victoria, Australia and a portion was filtered by vacuum (Whatman GF/C). The solids were discarded, and the filtrate collected in a Schott bottle. Both the filtered and unfiltered sewage were stored in the dark at 4°C.

Equipment

Sewage was centrifuged in 100mL glass tubes for 15 minutes at 3000 rpm. The wrist-action

shaker used was a Griffen flask shaker, able to accommodate 8 flasks at once. All glassware was cleaned according to the procedure described in the US EPA Method 614[30].

Recommended method

Standard solutions

Stock solutions of diazinon and propetamphos (10 mg/L) in hexane were used to prepare standards (0.1–1.0 mg/L) by pipetting appropriate volumes into 10mL standard flasks, adding 1mL of the internal standard, and making them up to volume with hexane. The internal standard, fenthion (Figure 1c), was a 10 mg/L solution prepared in hexane. Standards were prepared every two to three weeks and stored at 4°C in glass stoppered pyrex flasks in the dark.

Aqueous standards were prepared in deionised water from stock solutions of the pesticides in methanol (10 mg/L).

A stock solution (2000 mg/L) of surfactant was used to prepare standards of 0.0, 0.2, 2.0, 20, and 200 mg/L in deionised water. All standards were spiked with diazinon so that the concentration of the pesticide in each was 1.0 mg/L.

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Extraction of diazinon from water and domestic sewage

The Bond Elut cartridges were conditioned prior to use with one volume (2.8mL) of diethyl ether, one volume of methanol, one volume of 60:40 methanol:water, and one volume of water. This served to wet the C-18 packing and minimize any organic contaminants.

Sample volumes of 10mL for the aqueous standard solutions or 100 mL for domestic sewage samples were passed through pretreated Bond Elut cartridges, by vacuum, at a rate of approximately 1mL/min. The cartridge was then dried under vacuum for a further 1 hour to minimize any residual water. The adsorbed diazinon was then eluted with 2×1.0mL of diethyl ether. The eluate was collected in a 10mL standard flask and evaporated under N_2 until a few droplets remained. 1.0mL of the internal standard solution was added, and the sample was diluted to volume with hexane.

Extraction of diazinon from reconstituted sewage sludge

A 10mL sample of spiked activated sludge biomass, prepared from freeze dried activated sludge, was centrifuged, the supernatant was decanted and analysed according to the procedure outlined for water. The sludge was placed into a 25mL pyrex screw-top test-tube and 1mL of ether was added. The thread of the test-tube was wound with teflon tape to help reduce evaporation of the ether and the closed tube placed in an ultrasonic bath for 1hr. The ether solution was collected in a 10mL standard flask and the ether extraction procedure was repeated. The ether extracts were combined, evaporated to a small volume under N_2, mixed with internal standard, and diluted to the mark with hexane.

Chromatographic analysis

Most analyses were performed using a Hewlett Packard 5890A gas chromatograph fitted with a nitrogen-phosphorus detector (NPD) and a 5% diphenyl dimethyl siloxane (BP5, Scientific Glass Engineering, Ringwood, Australia) capillary column: 25m × 0.32mm i.d., film thickness, 1.0μm. Temperature program: 50°C (3 mins), 20°C/min to 250°C, held for 5 minutes. Splitless injection, vent open after 3 minutes. Injector temperature, 250°C, detector temperature, 270°C. Column pressure, 10 psi. Injection volume, 1μL.

For comparative purposes, flame photometric detection (FPD- phosphorus mode) was also used to analyse some samples. This detector was in a Varian 3400 gas chromatograph fitted with a 3% OV225 packed column. Temperature program: 180°C, 10°C/min to 220°C, held for 5 minutes. Injector temperature, 250°C, detector temperature, 300°C. Column pressure, 36 psi. Injection volume, 10μL.

RESULTS AND DISCUSSION

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Calibration

A standard curve for diazinon using nitrogen-phosphorus detection is shown in Figure 2. The concentration range shown is only between 0.0–1.0 mg/L, although it was found that the calibration graph was linear over three orders of magnitude—i.e. 0.01–10 mg/L using nitrogen-phosphorus detection. Quantitation was by peak area ratio diazinon:fenthion. The correlation coefficient was greater than 99.9% (n = 6 points) with a gradient of 1.067 and an intercept of -0.001. The detection limit was 0.001 ppm using the NPD.

The flame photometric detector (FPD) was also used to analyse diazinon standards in hexane and spiked water samples, but due to its poorer sensitivity compared to the NPD, it was not used for any further analyses.

The OP fenthion was chosen as the internal standard, since it was well resolved from diazinon under the chosen conditions, it eluted just after the pesticide, and it had a good response in the nitrogen-phosphorus and flame photometric detectors.

Extraction from water

In order to determine the efficiency of the C-18 Bond Elut cartridge for the removal of diazinon from water samples, a diazinon standard in methanol (10 mg/L) was used to prepare 0.1–1.0 mg/L solutions of diazinon in deionised water. The stock solution was prepared in methanol to help minimize both adsorption of diazinon onto the glass walls of the standard flask as well as hydrolysis of the pesticide[13]. The aqueous solutions were passed through the Bond Elut cartridges at approximately 1mL/min, and the cartridges were then eluted twice with a variety of solvents.

Ether was found to be the best eluent, giving 99% recovery, followed by hexane (70%), methanol (53%), and 60:40 methanol: water (35%). While diazinon is readily soluble in

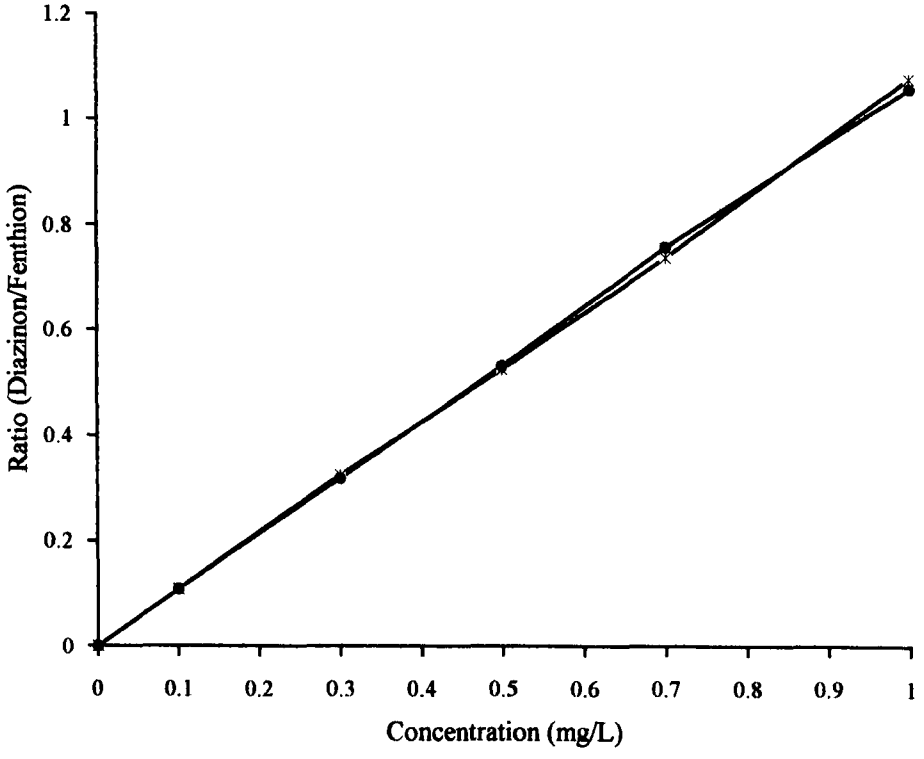

Figure 2 Calibration graphs for diazinon
—×— Diazinon standards in hexane (fenthion internal standard = 1.0 mg/L)
—•— Extraction of aqueous diazinon standards onto Bond Elut followed by elution with ether (fenthion internal standard = 1.0 mg/L).

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methanol, this solvent gave low recoveries and direct injection caused a greatly diminished response. Ether gave the best recoveries, however, a solvent change to hexane prior to injection was necessary because ether also reduced sensitivity of the NPD. (Ethyl acetate has also been found to ruin detector response[31].) The ether was easily evaporated under a stream of nitrogen, but maintaining the N_2 flow after dryness (which was approximately 10 minutes) led to large losses of diazinon; 45% after an additional 10 minutes and 84% after 50 minutes.

The recovery of diazinon from aqueous standards using the recommended method is illustrated in Figure 2. The curve obtained was not significantly different to the standard curve obtained with hexane solutions. The correlation coefficient (r^2) for this line was also greater than 99.9% (n = 6 points). Its gradient was 1.060 and its intercept 0.002. The ratio of the gradients gave the overall recovery of diazinon, which was calculated to be 99.3%. Recoveries of the individual aqueous diazinon solutions over a concentration range from

0.1–1.0 mg/L vary from 98.1–103.0%, with a mean of 100.0% and relative standard deviation (r.s.d.) of 1.8%. These data show that the presence of up to 10% v/v methanol in the aqueous standards had no effect on the extraction efficiency of the Bond Elut cartridges or the sensitivity of the NPD.

The precision obtained using the NPD was estimated from seven replicate analyses of two diazinon solutions at 1.0 and 0.1 mg/L. The relative standard deviations were 4.4% for 1.0 mg/L and 5.8% for 0.1 mg/L.

Propetamphos was analysed by capillary gas chromatography using NPD. The calibration graph obtained for this pesticide was, like diazinon, linear over three orders of magnitude (i.e. 0.01–10 mg/L) and the recoveries from spiked water samples, were between 95.6–102.0% (mean, 99.0%, r.s.d., 2.1%). The correlation coefficient (r^2) for this standard graph was 99.87% (n = 6), with a gradient of 0.821 and an intercept of 0.006.

Extraction of diazinon from water containing non-ionic surfactant

The recovery of diazinon from water samples containing surfactants was measured to determine whether they may interfere in the analysis of environmental samples. Detergents could interfere in the analysis in three ways: by competing for adsorption sites on the C-18 extraction cartridges, by making the aqueous phase more attractive to diazinon, or by interfering in the chromatographic quantitation process. The concentration range prepared (0.2–200 mg/L) included surfactant levels which were higher than those typically found in sewage (ca 10 mg/L). In initial experiments, it was shown that concentrations of detergent up to 20 mg/L in the final hexane extract had no effect on GC quantitation.

The recoveries of diazinon from the aqueous solutions containing up to 200 mg/L of surfactant are shown in Table 1. These recoveries decreased with increasing surfactant concentration. To increase the amount of C-18 packing available, two 500 mg cartridges were connected in series and the standard was passed through both. The cartridges were eluted separately and the eluates combined. This improved the diazinon recoveries considerably (Table 1). Whilst the mechanism for the surfactant effect is still uncertain, it is recommended that two cartridges in series be used if the surfactant concentration is believed to be greater than 20 mg/L.

Table 1 Diazinon (1.0 mg/L) recovery from aqueous surfactant solutions using (a) one Bond Elut and (b) two Bond Elut tubes in series

Surfactant	*% recovery of diazinon*	
(mg/L)	*(a)*	*(b)*
0.0	100	102
0.20	99.0	100
2.0	80.0	101
20	61.0	90.0
200	35.0	65.0

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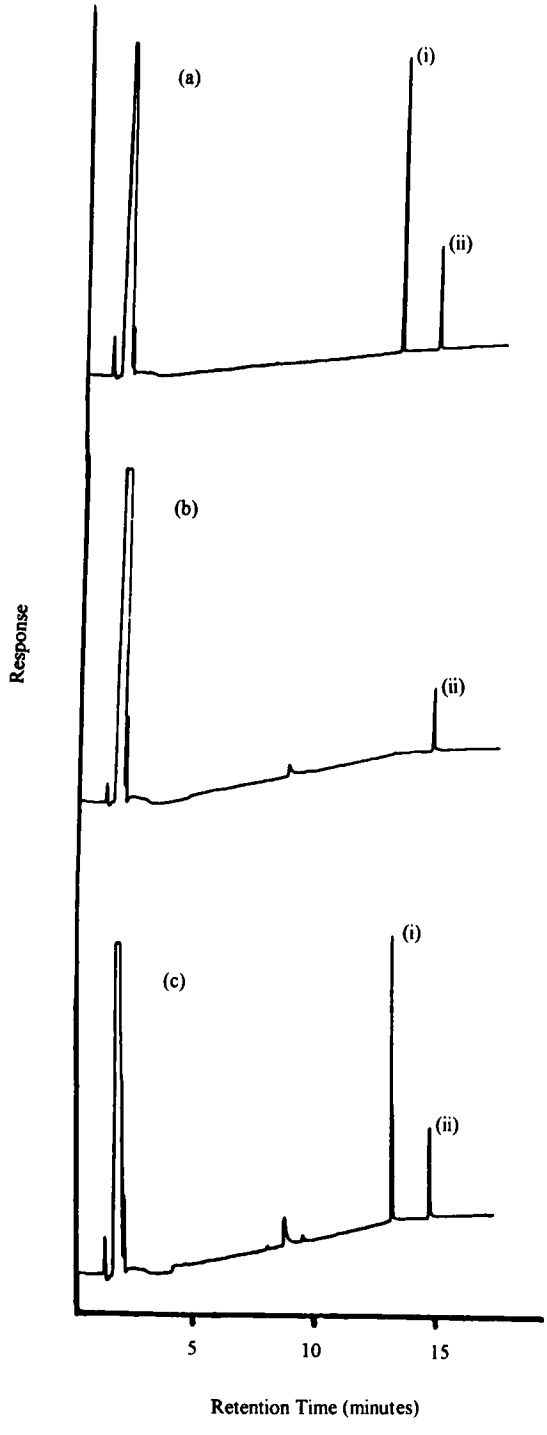

Figure 3 Gas chromatograms of (a) diazinon standard in hexane (1.0 mg/L), (b) sewage blank, and (c) extraction of 1.0 mg/L of diazinon from a spiked sewage sample. (i) represents the diazinon peak and (ii) the internal standard, fenthion, which was added to each sample (1.0 mg/L).

Extraction from sewage supernatant and sewage sludge

Using two 500 mg Bond Elut columns in series, diazinon was extracted from a sample of spiked totally domestic sewage from Brushy Creek. The sample was opaque and frothy which was indicative of the presence of surfactants and the suspended solids concentration was quite low (500 mg/L). A blank was run prior to spiking and no diazinon was detected in the sewage. The recovery of diazinon from both filtered and unfiltered sewage was between 89–100% (Figure 3).

As with other studies[32–35], initial experiments were performed comparing live sludge (biomass) and freeze dried biomass. Both sets of data were similar, indicating that for the present study, freeze dried sludge was able to be used in the place of fresh sludge. This is contrary to the results obtained by Dobbs[36] for the adsorption of dyes onto both viable and freeze dried activated sludge. He found that the organics did not adsorb onto the freeze dried sludge as well as they did onto the live biomass. Since adsorption of diazinon is unaffected by the freeze drying process, and since having a large batch of prepared freeze dried sludge was more convenient and time effective than collecting live sludge for each experiment, the freeze dried sludge was used for recovery studies.

To determine the recovery of diazinon from activated sludge biomass, a series of diazinon standards (0.0, 0.1, 0.5, 1.0 mg/L) were prepared in deionised water and the freeze dried sludge was added to them to give a suspended solids level of 3000 mg/L. This level is comparable with sewage from the SEPP. The samples were placed on a wrist action stirrer and allowed to shake for 6 hours, the average residence time of sewage in the treatment plant. Blank solutions containing diazinon (0.0–1.0 mg/L) but no sludge were also subjected to the same treatment.

The total recovery of diazinon from the supernatant and sludge was lower than the original amount added (Table 2). It appeared that some of the pesticide was very tightly bound to the biomass and unable to be extracted by ultrasonication. About 50% of the diazinon is adsorbed to the sludge. Most of this was extracted into the first 1mL portion of ether. A second extraction, however, recovered only another 5–10% from the sludge, giving a total recovery (from the supernatant and sludge) of 70–80% of the pesticide. Further ether extractions contained only trace amounts of the pesticide. Additions of surfactant to the ether (up to 2000 mg/L) increased the overall recovery from 70 to 78%. We are currently investigating reasons for the less than optimal recoveries of diazinon from sludge and supernatant.

Table 2 Mass balance of diazinon and propetamphos in the sludge-water system

Pesticide	*Concentration (mg/L)*	*% found*			
		Supernatant	*Extract 1*	*Extract 2*	*Total*
Diazinon	0.1	40	20	10	70
	0.5	44	20	10	74
	1.0	53	15	8	76
Propetamphos	0.1	70	30	-	100
	0.5	66	36	-	102
	1.0	71	35	-	106

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Recoveries of propetamphos from the biomass were much better (Table 2). Recoveries near 100% were obtained for all three concentrations of the pesticide. As propetamphos is less hydrophobic than diazinon, a larger proportion of it was found in the aqueous phase—70% compared with 45% for diazinon. Similarly, it appears to be bound less strongly to the biomass and is able to be desorbed from sewage sludge quite readily with only single treatment of ether.

CONCLUSION

The determination of the organophosphorus pesticides, diazinon and propetamphos in water and sewage by solid phase extraction provides an alternative to the preparation of samples by other prolonged extraction methods. Whilst recoveries from water samples are excellent for both pesticides, those from sludge biomass demonstrate that better extraction processes are required for diazinon. The specific nitrogen-phosphorus gas chromatography detector allows quantitation of the samples at low and sub-mg/L levels of the organophosphates. Studies of the partitioning of the pesticides between the aqueous phase and activated sludge has shown that the amount of pesticide in the aqueous phase is dependent upon its polarity. We believe that the analytical methods described in this paper will serve as a basis for further studies on the partitioning behaviour of similar pesticides in sludge matrices.

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