Bull. Environm. Contam. Toxicol. 26, 116-123 (1981)

Analysis and Incidence of Organophosphorus Compounds in Sewage Sludges

A. E. McIntyre, R. Perry and J. N. Lester

Public Health Engineering Laboratory, Civil Engineering Department, Imperial College, London, SW7 2BU, United Kingdom

Contamination of the environment by organochlorine insecticides has been widely reported (EDWARDS 1973; MORIARTY 1975) and it is evident that residues of these compounds will persist for a number of years. The use of non-persistent organophosphorus (OP) insecticides in place of many organochlorines has also resulted in their detection in a range of environmental media (BURCHFIELD & STORRS 1975; ASKEW et al. 1969; IVEY & CLABORN 1971). In addition to the great number of OP insecticides available, other OP compounds (principally alkyl phosphate esters) find uses in many industrial applications as flame retardants (FISHBEIN 1977).

A number of analytical methods have been developed for the determination of OP compounds in water (RUZICKA et al. 1967) soil and crops (SHELL RESEARCH 1974) but there is a general paucity of information with regard to their occurrence and analysis in waste waters and sewage sludges. With the present concern over the disposal, whether to land, sea or by incineration, of sewage sludges containing low levels of both organic and metallic micro-pollutants (GOVERNMENT OF GREAT BRITAIN 1978), the development of suitable analytical methods may be necessary to monitor sludge disposal operations.

The work reported here describes the investigation of analytical procedures for the determination of OP in sludges and a survey of sewage sludges obtained from twelve U.K. sewage treatment works.

MATERIALS AND METHODS

After pretreatment of sludge samples using an Ultra-Turrax homogeniser (Scientific Instrument Co. London, U.K.) to ensure sample uniformity, subsamples were taken for analysis by the following procedures.

Separating Funnel Extraction. Subsamples (50mL) were extracted with 150 mL dichloromethane/hexane (1:1 mixture) by shaking in a 250 mL separating funnel for 3 min. After phase separation, the solvent extracts were transferred to 250 mL round-bottomed (r.b.) flasks and concentrated to 1.0 mL using rotary evaporation at 30° C under reduced pressure.

0007-4861/81/0026-0116 $01.60

Ultra-Turrax Extraction. Aliquots (50 mL) of sludge were extracted with 150 mL dichloromethane/hexane by mixing with the Ultra-Turrax at 50% full revolutions for 3 min. After phase separation in a 250 mL separating funnel, the solvent extracts were transferred to 250 mL r.b. flasks and concentrated to 1.0 mL using a rotary evaporator.

Disperser Extraction. Subsamples (5 mL) were extracted with 20 mL dichloromethane/hexane in 50 mL centrifuge tubes using the disperser (Scientific Instruments Co.) at 60% full revolutions for 5 min. After centrifugation to effect separation, the solvent extracts were transferred to 25 mL r.b. flasks and reduced in volume to 1.0 mL using rotary evaporation.

Cleanup Procedures. Column chromatography with alumina (Woelm neutral, 5% w/w H_2O) as the stationary phase and dichloromethane as mobile phase was used to purify solvent extracts. For the separating funnel and Ultra-Turrax extracts, 10 g alumina and 50 mL dichloromethane were used, whilst for the disperser extracts, 2 g alumina and 15 mL dichloromethane were used. After removal of solvent from the column eluents using rotary evaporation, residues were redissolved in 0.5 mL dichloromethane.

Analysis. A gas chromatograph equipped with a flame photometric detector was used to analyse for OP compounds in purified extracts.

Columns used in the chromatograph were glass, 2 m x 3 mm i.d. packed with 1.5 % OV-17 + 1.95 % QF-1 on 100/120 mesh Supelcoport and 5 % phenyldiethanolamine succinate on 80/100 mesh Gas Chrom Q. (Phase Separations Ltd., Queensferry, U.K.). These were maintained at 200° C with a nitrogen carrier gas flow of 50 mL min^{-1} through each column during analysis. Injection port and detector temperatures were 250 and 300°C, respectively. Weights of the determinands present in sample extracts were calculated from previously constructed calibration graphs.

Extraction Efficiency. To determine percentage recovery of OP from sludge samples, aliquots of homogenised sludge were fortified with known amounts of OP compounds, shaken and allowed to stand for 4 h prior to extraction and analysis.

RESULTS

Standard solutions of the three OP insecticides selected for study were carried through the two cleanup procedures to assess recovery, the results are shown in Table 1. Recovery from the cleanup columns was considered to be quantitative, within the bounds of experimental error, although the variation in recoveries from the 10 g alumina column was found to be greater than that of the 2 g column, as can be seen by the relative standard deviations.

Table 1. Recoveries of organophosphorus insecticides from alumina cleanup columns.

Compound	Column Size (g)	Weight applied (ng)	Mean Recovery* (%)	RSD (%)	Range (%)
Diazinon	2	10	98.8	1.4	97.0-100.0
	10	10	95.4	4.4	89.5- 98.6
Malathion	2	10	98.5	1.2	96.7- 99.4
	10	10	98.1	2.8	94.6-101.0
Parathion	2	10	98.0	2.3	96.0-101.0
	10	10	97.8	3.9	92.4-102.0

* of four replicates.

Comparison of Separating Funnel and Ultra-Turrax Extraction Procedures. Samples of mixed primary and surplus activated sludges, of total solids contents 48.3 and 7.9 g L^{-1} respectively, were collected from Hogsmill Valley sewage treatment works (Thames Water Authority) and were homogenised using the Ultra-Turrax. Two sets of four subsamples were taken of each sludge; one was extracted using a separating funnel method, the other using the Ultra-Turrax extraction method. No OP compounds were detected in any of the subsamples from both sludges. Two further sets of four subsamples, taken from each sludge were fortified with a standard solution of diazinon, malathion and ethyl parathion to give concentrations in each sludge of 1.0 and 0.1 mg L^{-1}. The sets of fortified subsamples from each sludge were then extracted using the two procedures. Results are indicated in table 2.

Recoveries of OP compounds from the sludges using the separating funnel were generally poor with some degree of scatter, whilst use of the Ultra-Turrax resulted in higher average recoveries and less variation, although the relative standard deviations were quite high (>10%).

Extraction of OP insecticides from sewage sludge using the disperser. Although the overall extraction efficiencies obtained using the Ultra-Turrax extraction procedure may be considered adequate, an alternative method using smaller volumes of sample and solvent and extraction using the laboratory disperser was investigated. It was considered that this method would achieve at least comparable extraction efficiencies.

A sample of mixed primary sludge, of total solids content 40.5 g L^{-1} was collected from Hogsmill Valley sewage treatment works and was homogenised using the Ultra-Turrax.

Table 2. Recovery of Organophosphorus Insecticides from sewage sludges by two extraction procedures.

Compound	Sludge type	Concentration (blank) mg L^{-1}	Concentration added mg L^{-1}	Mean Percentage recovery* %		RSD %		Range mg L^{-1}	
				SF	UT	SF	UT	SF	UT
Diazinon	MPS[a]	ND[3]	1.0	47	50	20	12	0.32-0.36	0.44-0.56
	MPS	ND	0.1	39	62	18	15	0.03-0.046	0.05-0.07
	SAS[b]	ND	1.0	30	72	12	12	0.26-0.34	0.68-0.76
	SAS	ND	0.1	18	59	20	20	0.01-0.02	0.05-0.06
Malathion	MPS	ND	1.0	20	70	9	10	0.19-0.22	0.63-0.77
	MPS	ND	0.1	15	68	13	7	0.01-0.02	0.06-0.07
	SAS	ND	1.0	35	93	12	5	0.31-0.39	0.88-0.97
	SAS	ND	0.1	31	98	11	2	0.02-0.03	0.09-0.10
Parathion	MPS	ND	1.0	30	65	10	11	0.27-0.33	0.58-0.72
	MPS	ND	0.1	25	74	9	10	0.02-0.03	0.07-0.08
	SAS	ND	1.0	29	94	13	4	0.25-0.33	0.90-0.98
	SAS	ND	0.1	30	97	14	2	0.02-0.03	0.09-0.10

a. mixed primary sludge
b. surplus activated sludge
* of four replicates

1. Separatory funnel
2. Ultra-Turrax
3. Non-detectable

Three sets of four subsamples were taken; one set was extracted and analysed using the disperser procedure; the other two sets were fortified with diazinon, malathion and ethyl parathion at concentrations of 100 μg L^{-1} and 10 μg L^{-1} respectively and extracted and analysed using the same procedure. No OP compounds were detected in the extracts. Results from the analysis of the fortified subsamples are indicated in table 3.

Table 3. Recovery of organophosphorus insecticides from sewage sludge using disperser extraction procedure.

Compound	Concentration added μg L^{-1}	Mean Recovery* %	RSD %	Range μg L^{-1}
Diazinon	100	71.7	8.1	64.6 -80.0
	10	74.3	17.1	6.18- 9.47
Malathion	100	80.8	9.9	70.3 -89.2
	10	63.3	5.6	5.83- 6.66
Parathion	100	80.7	12.5	68.8 -95.8
	10	54.9	7.3	5.0 - 6.05

* of four replicates.

Use of the disperser procedure yielded results of comparable values to those of the Ultra-Turrax method, although with a marginally smaller degree of scatter. These recoveries, however, were still considered to be incomplete and hence not indicative of an efficient analytical method.

Survey of OP Insecticides in selected UK Sewage Sludges. To gain an appreciation of the extent of contamination of sewage sludges by OP compounds, sewage sludge samples were collected from twelve UK sewage treatment works. These were extracted and analysed using the disperser procedure. Results of the survey are indicated in table 4.

Table 4. Concentrations of OP compounds in sewage sludges.

Compounds	Sample No. (μg L^{-1})											
	1	2	3	4	5	6	7	8	9	10	11	12
Reofos 95*	ND[1]	ND	ND	6000	750	800	ND	ND	ND	ND	ND	ND
Other	ND	ND	D[2]	ND	ND	ND	ND	ND	ND	ND	ND	ND

* concentrations not corrected for extraction efficiency.

1 non-detectable

2 detected but not identified.

In the greater majority of the samples, no OP compounds were detected. However, in samples 3, 11 and 12, distinct peaks appeared on the chromatograms and did not match up with any of the 16 standard materials which were co-chromatographed in an attempt at identification. It is possible that these were breakdown products of parent OP compounds. In samples 4, 5 and 6 moderately high concentrations of OP compounds were detected and these were eventually tentatively identified as commercial flame retardants, the most similar chromatographic profiles being obtained from the flame retardant 'Reofos 95', a mixture of isopropyl phosphate esters of substituted phenols (figure 1). Other chemicals used in flame proofing applications, Tri(2-chloroethyl) phosphate, tri-n-butyl phosphate and trichloropropyl phosphate were also chromatographed, but did not coincide with any unidentified peaks.

The concentrations of 'Reofos 95' in samples 4, 5 and 6 were estimated on the basis of the peak heights of peak 3, 4, 5 and 6 in the mixture (figure 1) and were estimated as 6000, 750 and 800 µg L^{-1} for the three samples, respectively. No account was taken of the percentage recovery of these compounds from sewage sludge.

DISCUSSION

Of the three extraction procedures investigated for the isolation of OP compounds from sewage sludges, the disperser method in conjunction with an alumina column cleanup step and analysis by flame photometric gas-liquid chromatography achieved the highest recoveries, but the results still exhibited some degree of scatter.

A study by AHRENS et al.(1979) investigated the release of Fyrol FR2 (Tris(2,3-dichloropropyl)phosphate) from flame-proofed clothing and concluded that approximately 37% of the compound could be lost by successive washings. Goldfish exposed to 30 mg L^{-1} of Fyrol FR2 died after 3 h. Another recent investigation (SAEGER et al.1979) related environmental fate studies on eleven trialkyl-,alkyl-,aryl- and triaryl phosphate esters, including tests for water solubility. The study concluded that aqueous solubilities ranged from 0.36 mg L^{-1} for tricresyl phosphate to approximately 1000 mg L^{-1} for Tris (2-ethylhexyl) phosphate and that microbial degradation was the principle mechanism for the degradation of these flame retardants in the environment, although a moderate ability to bioaccumulate was detected. It appears likely that varying quantities of these types of materials may be discharged to sewers from industries involved in textile manufacture, a source which has been previously identified (FISHBEIN 1977). The three sludge samples in which these materials were detected during this study were taken from sewage treatment works in an area noted for textile production.

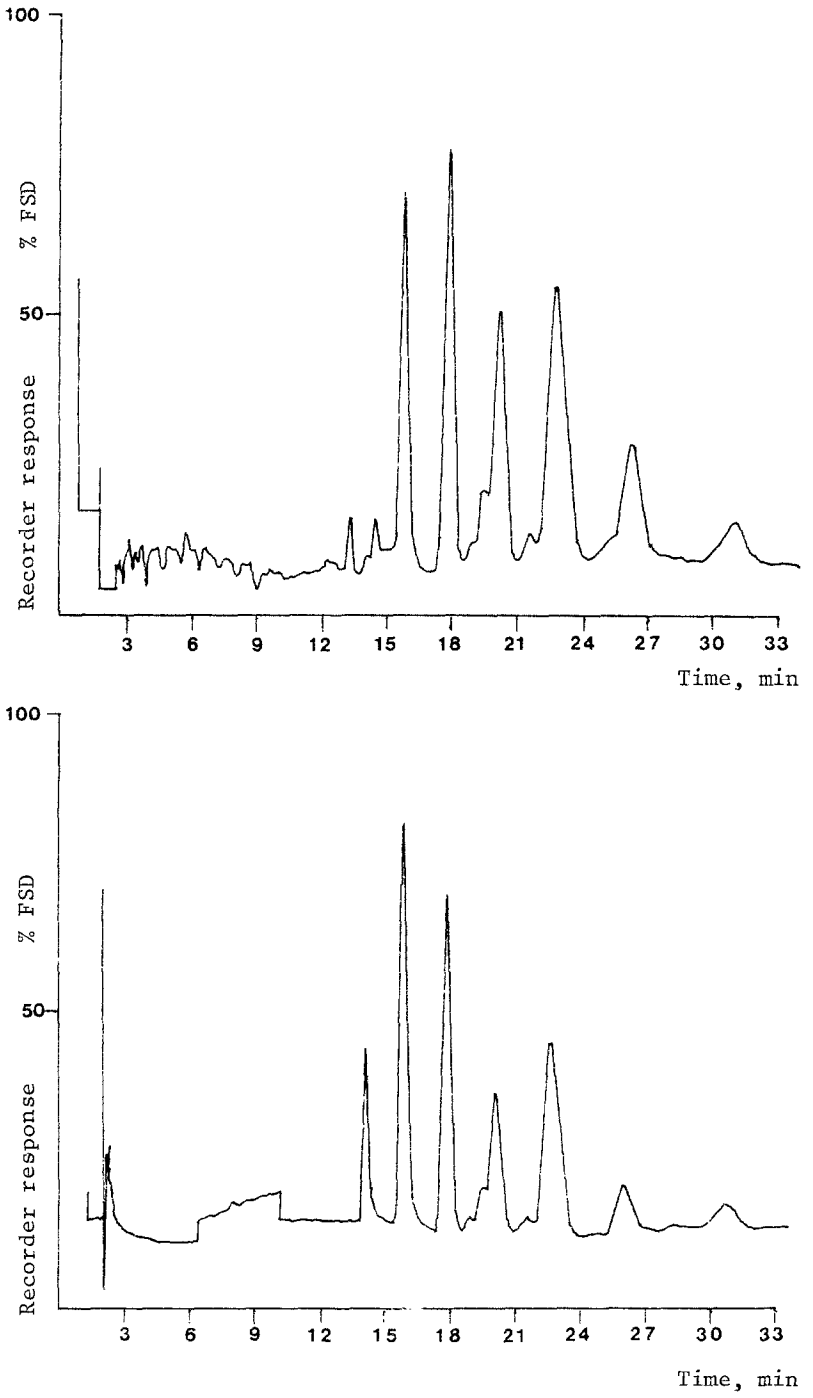

Figure 1. Chromatograms of sewage sludge sample (upper) and flame retardant formulation Reofos 95 (lower)

It is evident that the analytical procedures investigated yielded recoveries of OP which were both variable and incomplete. This may, in part, have been due to degradation of the dosed compounds in sewage sludge samples during the time lag between fortification and analysis. It appears, that from the results of the survey, OP are not commonly-occurring micro-pollutants in sewage sludges.

Acknowledgement

We acknowledge the financial support from and approval for publication by the Department of the Environment.

REFERENCES

AHRENS, V.D., G.A. MAYLIN, J.D. HENION, L.E.St.JOHN, D.J. LISK: Bull.Environ.Contam.Toxicol. 21, 409 (1979).
ASKEW, J., J.H.RUZICKA, B.B.WHEALS: Analyst 94, 725 (1969).
BURCHFIELD, H.P. and E.E.STORRS: J.Chromatog.Sci. 13, 202 (1975).
EDWARDS, C.A.: Persistent Pesticides in the Environment. 1ed. Cleveland, Ohio: CRC Press 1973.
FISHBEIN, L.: U.S.Nat.Tech.Inf.Ser.PB-273-229 (1977).
GOVERNMENT OF GREAT BRITAIN: Sewage Sludge Disposal Data and Reviews of Disposal to Sea. 1ed. London, H.M.S.O. 1978.
IVEY, M.C. and H.V. CLABORN: J.Agr.Food Chem. 19, 1256 (1971).
MORIARTY, F.: Organochlorine Insecticides: Persistent Pollutants. 1ed. London, Academic Press 1975.
RUZICKA, J.H., J.THOMSON, B.B.WHEALS: J.Chromatog. 31, 37 (1967).
SAEGER, V.W., O.HICKS, R.G. KALEY, P.R. MICHAEL, J.P.MIEURE, E.S. TUCKER: Environ.Sci.Technol. 13, 840 (1979).
SHELL RESEARCH LTD.: Determination of Birlane Insecticide in Crops and Soil. 1ed. Sittingbourne, UK, Shell Research 1974.