

GAS CHROMATOGRAPHY OF ORGANOPHOSPHORUS PESTICIDES IN SOILS BY INTERNAL STANDARD METHOD

M. A. SATTAR

Department of Soil Science, Bangladesh Agricultural University, Mymensingh, Bangladesh

(Received June 17, 1991; revised November 14, 1992)

Two types of soils treated with seven organophosphorus pesticides were extracted separately with six solvent systems. The recovery yields from the soils were studied by gas chromatographic technique using an internal standard. The data were subjected to statistical analysis. The best solvent system for best recovery is reported.

Key words: Gas chromatography, Organophosphorus pesticides, Solvent systems.

Introduction

Organophosphorus pesticides are widely used in agriculture. They show a varied range of chemical stability towards environmental degradation. Sattar [1] critically reviewed the thinlayer chromatography (TLC) analysis of organophosphorus pesticides present in soils, crops, foods, and other environmental samples. Aoki *et al.* [2] reported the gas liquid chromatography (GLC) method of detecting, some organophosphorus pesticides from rice, wheat, and dried beans with a detection limit from 0.0002 to 0.015 ppm. Cochrane *et al.* [3] reported a GLC method for detection of pesticides from the apple samples. A few organophosphorus pesticides were analysed by Sattar and Paasivirta [4] from soils by gas chromatography (GC) using an external standard method. Numerous other methods are [5-22] also available for analysing organophosphorus pesticides from soils or other environmental samples. Recently, Sattar and Rahman [23] reviewed a large number of articles on GC of organophosphorus, organochlorine and phenoxy herbicide compounds from various environmental samples. The present investigation, describes a simple and sensitive internal standard GC method for analysing 7 organophosphorus pesticides present in an acidic and a neutral soil conditions.

Materials and Methods

Pesticides. Seven commonly used organophosphorus pesticides were used in the study. The general and the chemical names of the compounds are given as follows: (1) Dichlorvos (2,2-dichlorovinyl dimethyl phosphate), (2) Phosdrin (methyl 3-(dimethoxyphosphinyloxy) but-2-enoate); (3) Dimethoate (dimethyl-S-methylcarbamoyl methyl phosphorodithioate); (4) Diazinon (0, 0-diethyl-0-2-isopropyl-6-methylpyrimidin-4-ylphosphothioate); (5) Parathion (0, 0-diethyl -0-4-nitrophenyl phosphorothioate); (6) Malathion (dimethyl-S-1,2-dicarboethoxy ethyl dithiophosphate) and (7) Bromophos (4-bromo-2, 5-dichlorophenyl dimethyl phosphorothionate). The samples (1)–(7) collected

from EPA, USA were reported to be 99 to 100% pure. Phenylphosphonic acid was used as an internal standard. The compounds were prepared as 0.1 % solution in hexane, ethylacetate or dichloromethane.

Soils. A noncalcareous dark grey floodplain (neutral) and a red brown terrace (acidic) soils were used in the experiment. The sampling sites were free from usage of any pesticides. The soils were collected at 0-15 cm depth, dried at room temperature and ground to pass through a 10-mesh sieve. Some of the soil characteristics are reported in Table 1.

TABLE 1. SOIL CHARACTERISTICS.

Characteristics	Noncalcareous dark grey floodplain soil	Red brown terrace soil
Moisture %	2.0	2.8
Sand %	22.8	25.8
Silt %	30.4	58.5
Clay %	46.8	15.7
pH	7.3	7.2
Organic matter %	1.4	1.1
Soil type	Sandy loam	Clay

Soil treatment. Five or ten grams of each soil sample was taken in a 200 ml beaker and each sample 200-500 μ l (for 5g soil) or 500-1000 μ l (for 10 gm soil) of solutions of all the seven pesticides were added by using micro-litre pipettes, and mixed well with a glass rod. Distilled water 1 or 2 ml was added to each sample to make the soils simulating field conditions and the stirring was continued until the mixtures were uniform. Then 2-3 g of anhydrous sodium sulphate was added to each beaker, again mixed well, and allowed to stand at room temperature ($\pm 32^\circ$).

Extraction. The samples were extracted separately with the following solvents:

- (i) Ether: chloroform: dichloromethane (1:1:1),
- (ii) Light petroleum ether: benzene: dichloromethane: 2-propanol (1:1:1:1)

- (iii) Ether: hexane (1:1),
- (iv) Cyclohexane: acetone (7:3),
- (v) Hexane: ether: dichloromethane: 2-propanol (1:1:1:1),
- (vi) Toluene: cyclohexane: acetic acid (7:2:1).

For this, each sample with 100 flask was treated with 50 ml of one solvent and shaken over Griffin flask shaker for 45 min. The solutions were filtered through filter paper having 2-3 g of anhydrous sodium sulphate. Each residue was extracted further with 50 of the same solvent already used. The extracts were combined, evaporated, transferred to volumetric flasks and the volumes were made upto 10 ml with hexane.

Derivatization and analysis. 250 or 500 µl of the soil extracts were transferred to 10 ml glass-stoppered tubes with 25 µl of internal standard (sample No.8) solution, 1 ml of methanol and 2-3 ml of diazomethane ether (to give a permanent yellow colour), mixed well and allowed to stand for

TABLE 2. AVERAGE RELATIVE POSITIONS OF GAS CHROMATOGRAPHIC PEAKS OF EIGHT ORGANOPHOSPHORUS PESTICIDES WITH STANDARD DEVIATIONS (AVERAGE RESULTS FROM 10 CHROMATOGRAMS).

Comp. No.	Pesticides and Int. standard	Position of peak in chart paper	
		Distance from start (cm)	Standard deviation
1.	Dichlorvos	6.82	0.376
2.	Phosdrin	10.30	0.536
3.	Dimethoate	16.70	0.484
4.	Diazinon	18.4	0.550
5.	Parathion	20.82	0.312
6.	Malathion	21.36	0.556
7.	Bromophos	22.42	0.556
8.	Phenylphosphonic acid (Int.standard)	9.814	0.528

TABLE 3. AVERAGE PERCENTAGE RECOVERY YIELDS OF SEVEN ORGANOPHOSPHORUS PESTICIDES (1-7), IN SOILS BY INTERNAL STANDARD METHOD (EACH RESULT FROM AVERAGE OF FOUR CHROMATOGRAMS) AND THE STANDARD DEVIATIONS (S.D.).

Solvent system	1		2		3		4		5		6		7	
	%	S.D.	%	S.D.	%	S.D.	%	S.D.	%	S.D.	%	S.D.	%	S.D.
<i>Red brown terrace (acid) soil (Bhaluka)</i>														
I	95.0	0.11	95.1	0.05	96.0	0.08	93.0	0.09	93.0	0.11	94.6	0.09	95.7	0.08
II	94.1	0.13	91.2	0.21	92.0	0.14	94.3	0.11	95.3	0.10	94.8	0.15	95.2	0.22
III	89.1	0.24	88.1	0.19	91.0	0.23	92.2	0.24	90.0	0.19	89.9	0.23	92.5	0.18
IV	83.4	0.21	83.7	0.23	82.0	0.22	88.1	0.21	85.0	0.20	85.0	0.22	87.7	0.17
V	95.7	0.10	0.1	0.07	97.2	0.05	98.1	0.08	97.5	0.05	95.5	0.07	96.8	0.10
VI	79.1	0.21	80.7	0.17	81.4	0.11	83.4	0.14	85.6	0.11	85.5	0.15	86.0	0.11
<i>Noncalcareous dark grey floodplain (neutral) soil (Bau, Mymensingh)</i>														
I	97.4	0.09	99.2	0.08	99.3	0.07	95.7	0.05	96.8	0.09	98.9	0.08	99.0	0.06
II	96.4	0.11	94.2	0.09	95.7	0.13	97.8	0.12	98.2	0.12	96.9	0.15	98.5	0.10
III	93.3	0.10	94.3	0.10	95.6	0.24	96.6	0.11	94.4	0.08	94.9	0.13	95.0	0.14
IV	88.2	0.17	89.0	0.21	85.0	0.19	91.0	0.21	92.3	0.15	92.3	0.16	94.4	0.12
V	98.8	0.05	98.4	0.06	99.5	0.03	98.7	0.03	98.8	0.07	99.1	0.04	99.3	0.05
VI	80.3	0.15	83.0	0.19	85.3	0.20	86.7	0.14	-	0.18	91.2	0.20	89.4	0.16

40-50 min. at room temperature. The mixture were evaporated with a stream of nitrogen gas. After appropriate dilutions with hexane, the samples were injected (1 µl) to the gas chromatographic equipment. Different suitable concentrations of all the 7 pesticides and the internal standard were mixed and the mixtures were subject to gas chromatographic analysis, and compared with chromatographs of soil samples for calculating percentage recovery of pesticides from samples.

A Perkin-Elmer Sigma 3B gas chromatograph equipped with F₁ detector was used. The 25 m quartz/capillary column was packed with SE-30/Silar-10C. The temperature applied for injector was 250° and that of detector was 270°. A programmed temperature was applied, increasing from 80-220° at the rate of 6°/min.

Results and Discussion

Model compounds. The average positions of 8 compound peaks (No.1-8), standard deviation (S.D.) of the peak distances obtained from 10 chromatograms of the 8 pesticide mixtures were given in Table 2.

The average percentage recovery yields of 7 organophosphorus pesticides (compound No. 1-7) in an acid and a neutral soil samples are given in Table 3. The results varied widely with 2 by the soil samples extracted 6 (I-VI) solvent systems. The solvent No. V gave the best recovery yields of all 7 compounds in both soils, whereas the lowest yield of the 7 compounds were recorded with solvent No. VI. The overall recovery result was higher in neutral (94. 15%) than that of acid type (90.55%) of soil regardless of compounds.

A t-test comparison. The recovery yields of 7 pesticides with I-VI solvent systems were compared by t-test (Table 4.). Most of the result differed significantly within I-VI solvent systems. Maximum variations were recorded when compari-

TABLE 4. T-TEST COMPARISON OF THE RESULTS WITHIN SOLVENT SYSTEMS FROM I-VI (DEGREES OF FREEDOM:6).

Soil type	Solvent system	II	III	IV	V	VI
Acid clay soil	I	3.529	12.389	26.232	4.177	22.696
	II	-	8.859	21.770	5.339	19.903
	III	-	-	13.669	11.819	13.596
	IV	-	-	-	21.505	2.847
	V	-	-	-	-	20.851
Neutral sandy soil	I	3.216	8.977	13.240	4.303	12.686
	II	-	5.838	11.036	7.879	13.893
	III	-	-	6.634	13.821	10.323
	IV	-	-	-	16.138	4.277
	V	-	-	-	-	17.884

sons were done within the following solvent mixtures: I-IV, I-VI, II-VI, II-VI, IV-V and V-VI.

References

- M. A. Sattar, Bangladesh Pesticide Sci. Research Report Series, Report No.5 (1983), pp. 47.
- Y. Aoki, M. Yakeda and M. Uehiyama, J. Assoc. Offic. Anal. Chem., **50**, 1256 (1975).
- W. P. Cochrane, R. Creenha and N. K. Loomney, J. Agri. Sci., **59**, 617 (1976).
- M. A. Sattar and J. Paasivirta, Kemia-Kemi, **12**, 820 (1982).
- S. Grisip and K. R. Tarrant, Analyst, Lond., **96**, 310 (1971).
- R. T. Murphy A. H. Hofberg and A. K. Buser, Assoc. Offic. Anal. Chem., **54**, 700 (1971).
- Z. Masud, V. Batora and J. Kovacicova, Pestic. Sci., **4**, 131 (1973).
- D. M. Coulson, L. A. Cavangh and J. Stuart, J. Agri. Fd. Chem., **7**, 250 (1959).
- G. Ratto, F. Quaranta and L. Sardi, Relata Tech., **4**, 435 (1972).
- H. A. Moye, J. Agri. Fd. Chem., **21**, 621 (1973).
- J. Worniak, A. Tokarz and J. Podlesny, Roczn. Panst. Zakl. Hig., **26**, 191 (1975).
- Y. Aoki, M. Takeda and M. Uehiyama, J. Assoc. Offic. Anal. Chem., **58**, 1286 (1975).
- W. Kriligemen and G. G. Kamp, J. Chromatogr., **117**, 201 (1976).
- M. A. Sattar, Chemospher, **20**, 287 (1990).
- M. A. Sattar, Pak. j. sci. ind. res., **33**, 274 (1991).
- J. J. Karr, J. Assoc. Offic. Anal. Chem., **60**, 862 (1977).
- H. J. Stan, B. Abraham, J. Jung, M. Kellert and K. Steinland, Z. Anal. Chem., **287**, 27, (1977).
- C. E. Johansson, Pestic. Sci., **9**, 313 (1987).
- V. Rus and A. Crainiceann, Rev. Chem., **29**, 673 (1978).
- E. R. Jackson, J. Assoc. Offic. Anal. Chem., **61**, 495 (1978).
- J. R. Miles and C. R. Harris, J. Eco. Entom., **72**, 125, (1978).
- M. A. Sattar, Study of the Residues of Organophosphorus Pesticides in Soils, Paper Presented at Malaysian Chem. Soc. Congress, Kuala Lumpur, Malaysia, Nov. 17-21 (1986).
- M. A. Sattar and M. M. Rahman, Bangladesh Pestic. Sci. Research Series, Report No.,12 (1988), pp.55.