Bull. Environ. Contam. Toxicol. (1991) 47:711-716

Bulletin of Environmental Contamination and Toxicology

Fate and Interconversion of Endosulfan I, II and Sulfate on Gram Crop (*Cicer arietinum* Linn.) in Subtropical Environment

Parm Pal Singh, Raminderjit Singh Battu, Balwinder Singh, and Rajinder Lal Kalra

Department of Entomology, Punjab Agricultural University,
Ludhiana-141 004, India

Endosulfan (6,7,8,9,10,10-hexachloro-1, 5, 5a, 6, 9, 9a hexahydro-6, 9-methano-2,4,3-benzodioxathiepin 3-oxide) is a broad spectrum insecticide and acaricide widely used in agriculture and forestry throughout the world (Hartley and Kidd 1983; Polyk 1989). Due to its favourable environmental properties and safety to a large number of beneficial organisms, it is one of the few organochlorine pesticides that are still allowed to be used on crops. Technical endosulfan consists chiefly of two stereoisomers i.e. approximately 70% endosulfan I and about 30% endosulfan II, both of which possess biological activity. Endosulfan sulfate (6,7,8,9,10,10-hexachloro-1, 5,5a,6,9, 9a-hexahydro-6, 9-methano-2, 4,3-benzodioxathiepin 3,3-dioxide) is the major metabolite of endosulfan on plants and is almost as toxic as technical endosulfan to the rats (Goebel et al. 1982). In addition, interconversions of endosulfan I, II and sulfate under certain environmental conditions have also been reported. Accordingly, maximum residues limits for endosulfan residues in various food items have been recommended as the sum of endosulfan I, II and sulfate (FAO/WHO 1986).

Various appraisals of the environmental fate of endosulfan residues reveal that most of the studies on this aspect have been conducted in temperate zones and virtually no information on their metabolic or environmental transformations under sub-tropical or tropical field conditions is available (Menzie 1974; Goebel et al. 1982; Aizawa 1982). Moreover, almost all the work on environmental behaviour of endosulfan residues has been carried out by using technical endosulfan and only Chopra and Mahfouz (1977) have investigated this topic by treating plants separately with endosulfan I, II and sulfate. Since agroecosystems of sub-tropical and tropical regions are different

---

Send reprint requests to P.P.Singh at the above address from that encountered in temperate zones in many ways, the need for studying the chemodynamics of pesticides under different agro-climatic conditions has been stressed so that their possible side effects on the biosphere can be assessed more comprehensively (Geissbuhler et al. 1983). Keeping this in view, the present study was undertaken to investigate the fate of endosulfan I, II and sulfate on gram, a major pulse crop, under sub-tropical field conditions at Ludhiana, India.

MATERIALS AND METHODS

Endosulfan I (99%), II (97.8%) and sulfate (analytical standard grade) used in this experiment were obtained from Environmental Protection Agency, Research Triangle Park, North Carolina, USA. Seventy mg of each compound were dissolved separately in 5 ml xylene and after adding 1 ml of Triton-X-100 (Romali, Bombay, India) as emulsifier to each solution, the volumes were made to 100 ml with distilled water to form aqueous emulsions of 0.07% concentrations. Using kitchen garden sprayer, the emulsions thus obtained were sprayed separately upto the point of run off on gram crop (*Cicer arietinum* Linn., variety GL 1014) raised in three plots measuring 3 m^2 each to simulate the recommended field application rate (Anonymous 1987). In addition, gram crop grown in a similar manner was treated with emulsion prepared only from xylene and emulsifier to serve as control.

Endosulfan residues from representative samples of leaves of gram crop (20 g) obtained from each plot at different intervals were extracted twice with 50 and 25 ml portion of acetonitrile by blending for 3 minutes each time. The combined extracts were transferred to a separating funnel, diluted with 300 ml of 10% aqueous sodium chloride and partitioned with two 50 ml portions of hexane. The aqueous phase was discarded and pooled hexane phases were dried over anhydrous sodium sulfate and concentrated to about 5 ml using a rotary vacuum evaporator. The cleanup was performed on 10 g silica gel (60-120 mesh) activated for 2 hours at 130°C and packed in glass column (30 cm x 1.2 cm i.d.). After prewashing the column with 100 ml hexane, sample extract was added to it and eluted with 100 ml benzene. The residues in the eluate were estimated on Packard Becker GLC model 417 fitted with ^{63}Ni source electron capture detector and glass column (1 m x 2 mm i.d.) packed with 1.5% SP-2250 + 1.95% SP-2401 on 100-120 mesh Supelcoport. The operating temperatures (°C) were: column oven 200, injection port 210 and detector 220. The carrier gas (nitrogen) flow rate was 60 ml min^{-1}. The identity of the residues was confirmed by micro-alkali derivatization (EPA, 1980). The recoveries obtained by following the above mentioned procedure for gram leaves fortified with endosulfan I, II and sulfate at levels of 0.1 and 0.5 kg^{-1} each ranged from 82 to 93% and residue values reported have not been corrected for recovery. The suitability of all the solvents and reagents for residue analysis was ensured by running reagent blanks.

RESULTS AND DISCUSSION

Endosulfan I, II and sulfate residues in samples of gram leaves from the control treatment were below detectable limit (less than 0.01 mg kg^{-1}) throughout the period of study. Even though the plants were treated with only one chemical out of endosulfan I, II or sulfate, low levels of the compounds which had not been sprayed on the plants were detected in all the samples collected 2 hours after the application (Table 1). GLC analysis of reference compounds used in the study revealed that this was due to the presence of small amounts of impurities in them.

Out of the three compounds studied, endosulfan I was the least persistent while endosulfan II and sulfate had similar and higher persistence. The respective half-life values of these compounds calculated by the procedure given by Hoskins (1961) were 1.30, 2.83 and 2.81 days. However, in the only published study in which crop was treated separately with endosulfan I, II or sulfate, trend of dissipation of these compounds on tobacco leaves under temperate field conditions of Chinqua Penn, NC, USA was endosulfan I $>$ endosulfan II $>$ endosulfan sulfate (Chopra and Mahfouz 1977). Other workers who have studied the fate of technical endosulfan on plant surfaces have also reported that endosulfan I dissipates more rapidly than endosulfan II (Goebel et al., 1982).

The per cent loss of each compound observed in the present study was much higher than that found by Chopra and Mahfouz (1977). While only less than 1% of endosulfan I and nearly 4% of endosulfan II and sulfate were left after 12 days of the treatment during the present investigations, the average corresponding levels after 24 days as calculated from the figures given by Chopra and Mahfouz (1977) work out to be approximately 8, 16 and 44%, respectively. These differences may be due to higher temperature and stronger sunshine in the sub-tropical region as compared to the temperate zone. The weather parameters for the period of the study being reported are given in Table 2, but this information for the investigations carried out in temperate environment is not available for comparison. However, on the basis of present investigations, it cannot be commented whether the greater loss of endosulfan residues in sub-tropical conditions is due to

Table 1. Residues of endosulfan I, II and sulfate on leaves of gram crop treated separately with these compounds

Interval after application (days)	Mean residue levels (mg kg^{-1}) and range		
	Endosulfan I	Endosulfan II	Endosulfan Sulfate
	Treatment with Endosulfan I		
0(2 hours)	26.03±4.58	Trace*	Trace
2	5.50±2.30	Trace	1.25±0.29
4	2.68±0.63	0.12±0.03	0.82±0.18
8	1.32±0.34	0.05±0.02	1.10±0.54
12	Trace	Trace	0.21±0.12
	Treatment with Endosulfan II		
0(2 hours)	0.06±0.02	20.53±3.99	Trace
2	Trace	9.84±2.86	0.88±0.06
4	Trace	4.66±0.73	0.55±0.18
8	Trace	2.66±0.53	2.32±0.42
12	Trace	0.90±0.15	0.47±0.14
	Treatment with Endosulfan Sulfate		
0(2 hours)	0.05±0.01	Trace	23.75±4.11
2	Trace	Trace	18.09±1.72
4	Trace	Trace	13.47±1.77
8	Trace	Trace	7.80±2.42
12	Trace	Trace	1.03±0.42

*Trace = between 0.01 and 0.04 mg kg^{-1}

Table 2. Mean and range of various weather parameters from February 23 to March 7, 1989

Temperature (°C)		Relative humidity (%)	
Minimum	Maximum	Minimum	Maximum
8.7(4.0-14.8)	24.6(21.6-28.1)	30(24-40)	93(84-98)

Sunshine (hours)	Solar radiation (Langley)	Rainfall (mm)
10.6(5.8-11.6)	491(400-601)	0(0-0)

photolysis or just because of greater volatalization. Moreover, difference in the nature of crop in the two studies is also likely to have affected the rates of dissipation of these compounds. Both endosulfan I and II were observed to get transformed into endosulfan sulfate (Table 1). However, conversion to endosulfan sulfate was relatively rapid in the case of endosulfan I sprayed plants and 2 days after the treatment, about 18% of the total endosulfan residues were constituted by endosulfan sulfate. In contrast, rate of conversion of endosulfan II into endosulfan sulfate was initially slow and picked up only after 4 days. The level of endosulfan I and sulfate in endosulfan I treated plants reached almost equal levels in 8 days and endosulfan sulfate residues were higher than endosulfan I after that. However, in endosulfan II treated plants,endosulfan II level was greater than endosulfan sulfate level upto 12 days. Similar differences in rates of conversion of endosulfan I and II into endosulfan sulfate were also observed by Chopra and Mahfouz (1977) and were considered to be due to the involvement of different enzyme systems in these two processes. Small amounts of endosulfan II and I in gram plants treated with endosulfan I and II, respectively, were also detected (Table 1). This indicates the interconversion of these two isomers on a limited scale. This phenomenon has been reported to be more extensive on tobacco plants in temperate environment (Chopra and Mahfouz 1977).

In endosulfan sulfate treated crop,endosulfan residues were constituted mainly by the parent compound and endosulfan I and II were not found to exceed 0 day levels during the 12 days sampling period. In contrast, Chopra and Mahfouz (1977) reported that on tobacco crop grown under temperate conditions, endosulfan sulfate gets converted into endosulfan I but not into endosulfan II.

Thus, endosulfan I or II applied to gram crop grown under sub-tropical conditions were transformed into endosulfan sulfate. They were also interconvertible on a limited scale. The rate of formation of endosulfan sulfate from endosulfan I was relatively rapid. However, no indication regarding the conversion of endosulfan sulfate into endosulfan I or II was obtained. The trend of dissipation of these compounds was endosulfan I > endosulfan sulfate = endosulfan II.

Acknowledgment. This study was financed in part by Indian Council of Agricultural Research, New Delhi under 'All India Coordinated Research Project on Pesticide Residues'. The authors gratefully acknowledge the cooperation of Dr B.S.Kooner in conducting the field experiments and Professor-cum-Head, Deptt. of Entomology for providing the necessary analytical facilities.

REFERENCES

Aizawa H (1982) Metabolic Maps of Pesticides, Academic Press, New York, p.78

Anonymous (1987) Protocol for conducting supervised trials for endosulfan residues on gram crop. All India Co-ordinated Research Project on Pesticide Residues, Indian Agricultural Research Institute, New Delhi, p.1

Chopra,N M, Mahfouz A M (1977) Metabolism of endosulfan I, endosulfan II, and endosulfan sulfate on tobacco leaf. J Agr Food Chem 25:32-36

EPA (1980) Section 12D(1). In: Watts R R (ed) Analysis of pesticide residues in human and environmental samples. US Environmental Protection Agency, Research Triangle Park, North Carolina

FAO/WHO (1986) Codex maximum limits for pesticide residues. Food and Agriculture Organization of the United Nations, Rome, p.32-IV

Geissbuhler H, Muller U, Pachlakto J P, Waespe H (1983) Biorational design of chemicals. In: Shemilt LW (ed) Chemistry and World Food Supplies: The New Frontiers. Pergamon Press, Oxford, p.643

Goebel H, Gorbach S, Knauf W, Rimpau R H, Huttenbach H (1982) Properties, effects, residues and analytics of the insecticide endosulfan. Residue Rev 82:1-174

Hartley D, Kidd H (1983) The Agrochemicals Handbook. Royal Society of Chemistry, The University, Nottingham p.A175

Hoskins W M (1961) Mathematical treatment of loss of pesticide residues. FAO Pl Prot Bull 9:163-168

Menzie C M (1974) Metabolism of pesticides : An update. US Department of Interior, Fish and Wildlife Service, Washington DC, p.192

Polyk J (1989) Farm Chemicals Handbook. The Meister Publishing Company, Willoughby, OH, Section C, p.118

Received November 4, 1990; accepted December 26,1990.