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Analysis of Endosulfan residues in cultivated soils in Southern India.

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Abstract. Endosulfan is a characteristic pesticide having both chlorine and sulphur as functional groups, effective in controlling a large spectrum of pests. It is sprayed as contact insecticide on food crops. Residues of α and β endosulfan have varying half life and persist in air, water and soil along with their degradation products like endosulfan sulphate. The present study aimed at delineating endosulfan residues in soil, representing samples drawn from agricultural fields during winter season. The samples after pretreatment were subjected to enrichment of the residues. The residues were estimated by GC-ECD method. The concentration of α endosulfan ranged from 0.1 mg to 29 mg/Kg , the levels of β Endosulfan ranged from 0.1-167 mg/kg, and that of Endosulfan sulphate ranged from.12-187 mg/Kg respectively. This study once again proves the highly persistant nature of the residues of endosulfan in soil and hence the need to find measures to remove them from the environment.

Keywords: Endosulfan, persistence, Soil pollution**.**

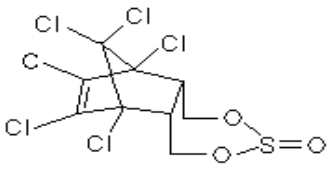
1. Introduction

Endosulfan (1,2,3,4,7,7-hexachlorobicyclo(2.2.1)-2-heptene-5,6-bisoxymethylenesulfite) is a pesticide widely used all over the world, since 1954 when it was first released for commercial use (Maier-Bode, 1958). India is one of the largest consumer of pesticides in South Asia (Agnihotri, 1999). According to the Indian Chemical Council, it is used extensively to control pests in a wide range of crops like cereals, tea, coffee, cotton, cashew, fruits, and vegetables.

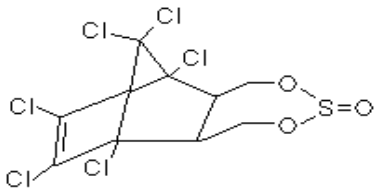
Commercial Endosulfan is synthesized as a mixture of two isomers approximately 70% α-Endosulfan and 30% β-Endosulfan. Endosulfan has been detected in the atmosphere, soil, sediments, surface water, rain water and food materials (USDHH, 1990).

Due to its hydrophobic nature, Endosulfan tends to get adsorbed to soil particles, resulting in persistence (Rao and Murthy, 1980; Leung et al, 1998). The rate of degradation of Endosulfan is rather low and often results in the formation of Endosulfan sulphate which is an oxidative metabolite shown to be as toxic and persistant as the parent compound.

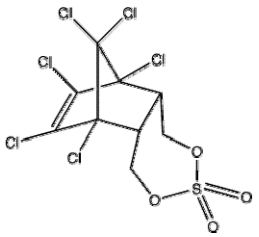
Endosulfan is known to be an endocrine disruptor (Fernandez MF,2007) and also a genotoxin (Fernandez MF, 2007). Because of its persistence in the environment for a long time, and its toxicity endosulfan contamination in the environment is of great concern.



α-Endosulfan



β-Endosulfan



Endosulfan sulphate

2. Materials and methods

2.1 Soil sampling: Soil sampling was done by the quartet method. A 10' x 10' area was cleaned and demarcated into 4 quartets. About 1 kg of the soil was collected from 0-15 cms depth from 2 opposite quartets into a plastic trough. This was then mixed well and again divided into four quartets. The soil from opposite quartets was collected and was further reduced to ½ kg and stored in cotton bags and then placed in polythene covers. 4-6 samples were collected from different parts of the same field.

Table 1:- Sampling sites:

Sl.No	Geographical area	Standing Crop	Soil description
1.	Gejjagaaraguppe,Ramanagara, Karnataka	Bengal gram	Lateritic soil
2.	Field 1,Baalupete, Hassan, Karnataka	Coffee	Lateritic soil
3.	Field 2, Baalupete, Hassan, Karnataka	Coffee	Lateritic soil
4.	Hommagarahalli, HD Kote, Mysore	Paddy	Black loamy soil
5.	Field 1, Badiyadka, Kasargod, Kerala	Cashew	Lateritic soil
6.	Field 2, Badiyadka, Kasargod, Kerala	Cashew	Lateritic soil

The sampling sites were identified in consultation with the Agricultural Officers, pesticide retailers and local farmers. Totally six agricultural fields were identified where there was a history of application of Endosulfan. Site 1 is located about 20 kms interior from the Bangalore-Mysore highway near Ramanagaram. Bengal gram was regularly grown in the field. The field was flanked by road on the east and agricultural fields on all the other sides. This field has seen regular application (at least 3 times) of Endosulfan every year, especially during the flowering of Bengal gram.

Site 2 is located in Baalupate in Kenchammana Hoskote of Hassan District in Karnataka. The field bound by road in the south and Coffee estates on all the other sides. Site 3 is also a coffee estate located in the same area, it is bound by road on the south and surrounded by coffee estates on the other sides. This area is a predominantly coffee growing area where endosulfan was used regularly in the previous years.

Site 4 is Hommagarahalli, a small hamlet located in HD Kote taluk of Mysore District. Soil sample was obtained from a paddy field irrigated by the river Cauvery. The field is bound by State Highway on the South and Kaccha road on the East, and paddy fields on the other two sides. Endosulfan application was done few weeks before the collection of sample.

Sites 5 and 6 are located in Badiyadka, in Kasargod district of Kerala. This region is a predominantly Cashew growing area and has seen aerial application of Endosulfan for many years, though it has now been discontinued. Sites 5 and 6 are bound by road on the South and Cashew plantations on all the other sides.

2.2 Pre-processing: Upon receipt to the lab, the soil sample was air dried at room temperature, powdered in a pestle and mortar and sieved through a 2mm sieve and stored at 4^0C till further analysis.

2.3 Preparation of residues: The technique adopted for preparation of residues was a slight modifications from Jayashree et al, 2007. About 5 grams of the soil was soaked overnight in 40 ml of Hexane: acetone(80:20), in a 250 ml sealed conical flask. The flask was then shaken in an orbital shaker at 70 rpm at room temperature for about 2 hours. The solution was filtered through ordinary filter paper and the soil was re-extracted twice with 30 ml of Hexane : acetone (80:20). The extract was passed through a column of 5 g of Florisil layered on top with 2g of sodium sulphite. The extract was then concentrated in a water cooled condenser and reduced to 0.5 ml.

2.4 GC analysis: The residues were analysed by Gas Chromatography (Agilent) system fitted with an ECD detector on a DB 1701 column (30 m x 0.25) with Nitrogen as the carrier gas with a flow rate of 1ml/ minute . The oven temperature was 280^0C, injection temperature was 290^0C and the detector temperature was 320^0C. Technical grade α, β and Endosulfan sulphate was used as standards.

3. Results and Discussion

GC Analysis:

Table 2: Residues of α, β Endosulfan and Endosulfan sulphate

Location	Sample	α-endosulfan (mg/Kg)	β-endosulfan (mg/kg)	endosulfan sulphate (mg/kg)	total endosulfan (mg/kg)
	A	0.62	1.18	1.62	3.42
	B	0.106	0.18	0.2	0.486
	C	0.116	0.4	26	26.516
1	D	0	0.3	6.26	6.56
	A	0	0.2	0	0.2
	B	0	0	3.2	3.2
	C	0	0	0.124	0.124
2	D	0	0.1	0.95	1.05
	A	0	0	6.2	6.2
	B	0	0	3.52	3.52
	C	0	0	5.26	5.26
3	D	0	0	3.68	3.68
	A	0	0	4.4	4.4
	B	0	0	0	0
	C	0	0	6.14	6.14
4	D	0	0	1.3	1.3
	A	0	0	2.28	2.28
	B	29.34	167.9	186.98	384.22
	C	0.34	0.66	4.9	5.9
5	D	0	0	2.4	2.4
	A	0	0.118	0	0.118
	B	0	0.16	0.336	0.496
6	C	0.168	2.56	1.56	4.288
	D	0	0	2.30	2.30

The retention time for α, β and Endosulfan sulphate was found to be 41.94, 46.64 and 49.82 minutes respectively. The detection limit was 50µg/L.

The levels of α Endosulfan ranged from 0.1 mg to 29 mg/Kg , β Endosulfan mg/Kg from 0.1-167 mg/kg, and Endosulfan sulphate from 0.12-187 mg/Kg. In locations 1 and 5,

high amounts of α and β Endosulfan are seen compared to the other locations. This is due to recent application of the pesticide. In Field 5, very high amounts of residues were observed which could also be due to the presence of the field at base of a hill, which results in tha accumulation of residues from the runoff. Endosulfan sulphate could be seen in considerable quantities in all the locations, owing to its highly persistant nature. Its highest concentration was seen in field 5 (186.98)mg/Kg.

Other reports of endosulfan residue levels in India in paddy fields are α endosulfan- 0.98 mg/Kg, β Endosulfan – 6.39-0.800 mg/Kg and Endosulfan sulphate- 11.8-2.2 mg/Kg. According to Bishnu A(2008), in the Tea grown areas of West Bengal, α Endosulfan ranged from 0.007-0.081mg/Kg, β Endosulfan ranged from 0.008-0.256 mg/Kg, and Endosulfan sulphate from 0.055-0.095 mg/kg.

Our study reports the highest levels of Endosulfan residues from the Southern parts of India.

The persistence of the residues of endosulfan that cause pollution in soil are dependent on various factors like soil type, particle size of soil particles, rainfall etc (M.Zhou, 2003). Other factors can also be due to existing meteorological conditions, soil quality and spraying profile in that area. Endosulfan can contaminate the soil and water in the vicinity of the fields where it is applied by one of the following methods-spray drift, vapour transport, dust transport, and runoff pathways (M.R.Raupach, 2001). Under anaerobic conditions, the half life of Endosulfan in water is reported to be 1-6 months (ASTDR 2000). In soil, the half lives of α, β and total endosulfan under aerobic conditions has been reported to range between 12-39, 108-264 and 288-2241 days respectively (GFEA-U, 2007).

Chronic exposure to endosulfan in humans can cause congenital deformities, long term brain damage, epilepsy, autism, delayed sexual maturity, early menarche, cerebral palsy etc.(Aleksandrowicx, 1979, Quijano 2002, NIOH 2003, Saiyed 2003, Roberts 2007, Venugopal 2008). Endosulfan bioaccumulation can also be seen in a number of terrestrial and aquatic animals. Hence, regulations in the usage of Endosulfan, alternative solutions for pest management and bioremedial measures for the removal of endosulfan residues from the soil are issues that necessitate immediate attention.

4. Acknowledgements

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