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Review Article

Survey and Estimation of Endosulfan in Milk from Prone Areas in the State of Kerala

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Abstract

The industrialization of the agricultural sector is increasing, but many times it caused a burden on natural systems, processes, and people. Endosulfan posed many problems to mankind and caused many neurological disorders, DNA damage, characteristic liver changes, and so on. Pesticides after spraying will stay for some time in the soil and if plants and animals are raised on the land, definitely absorb the pesticide left over on the soil. These pesticide residues will get metabolized in the body of the animals and converted into metabolic products and excreted through natural secretions. The pesticide residues will also definitely get excreted through the milk and when the milk is converted into products it also may contain the pesticide residues. An effort was made to analyze the milk samples for endosulfan in Endosulfan-prone areas in Kasargod District, Kerala, India. Forty samples were analyzed and in all the samples the levels of α-Endosulfan, β–Endosulfan, and Endosulfan sulfate were absent at 1ppb level.

Keywords: Endosulfan; Pesticide; Organo Chlorinpesticidece; Pesticide Residue in Milk; Endosulfan in Milk in Kasargod; Kerala

Introduction

A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest (US EPA). They belong to diverse groups and are widely used to control insects, weeds, fungi, and rodents.

Pesticides are important in modern farming and will remain indispensable in the future to produce enormous quantities of food that are required to feed the Indian growing population [1] The use of pesticides in food production has provided numerous benefits in terms of increasing production and quality. Since chemical control of pests is successful, there has been an explosive expansion in the development and consumption of synthetic organic pesticides but, at the same time, consumers were exposed to pesticides that pose a threat to public health by entering into the food chain and are now omnipresent in air, water, soil, vegetables, fruits, food grains, animal feeds, meat, milk, and milk products [2].

Pesticides after spraying will stay for some time in the soil and if plants and animals are raised on the land, definitely absorb the pesticide left over on the soil. These pesticide residues will get metabolized in the body of the animals and converted into metabolic products and excreted through natural secretions. These pesticide residues will also definitely get excreted through the milk and when the milk is converted into products it also may contain the pesticide residues. The milk and milk products when consumed by people, the metabolites are stored in the adipose tissue of the body and may produce severe health hazards, congenital abnormalities in newborns, and neurological disorders. Adverse health effects are not expected from consuming water with pesticides below the maximum residue limits. Maximum residue limits for parent OC pesticides have been set by several organizations such as FAO, Codex Alimentarius, and European Union.

Endosulfan is an insecticide and acaricide. It was introduced to the market in the 1950s and it was a continuously used pesticide for decades even after the discontinuation or removal of most of the other members of the cyclo diene group from the market because of their toxicity, bioaccumulation, and environmental persistence. Its primary use was for the control of pests in agricultural land. Although endosulfan is off-patent and is being phased out in many nations around the world, it was reportedly used in India until the Supreme court temporarily banned it in 2011. A lot of research work was undertaken on pesticides like DDT and BHC and their

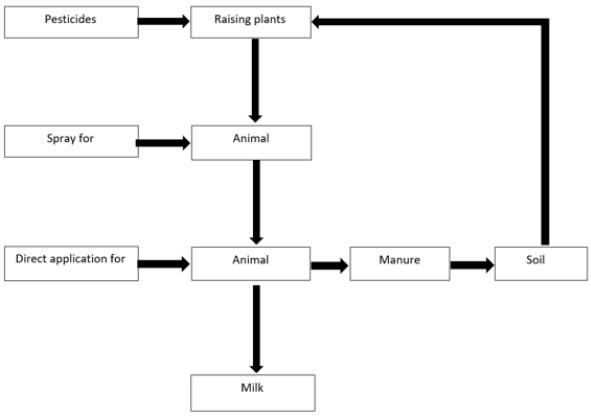
analogue's residual effect on human health through milk, meat, and grains in relation to different production systems. Endosulfan poisoning was observed in cattle where the owner applied the insecticide topically as ectoparasitic control [3] however there were no studies being done on its level in milk in the marked areas of endosulfan spraying and exposure. Many years of aerial spraying on cashew plantations in has left many with mental and physical disorders. Many studies have established the connection between the aerial spraying of the pesticide and the growing health disorders in the Kasaragod district. Hence, the present investigation was carried out with the objective to estimate the presence of endosulfan in milk obtained from the Kasargod district of Kerala, India.

Review of Literature

Pesticide residues

Pesticide residue means any specified substance in food, agricultural commodities or animal resulting from the use of pesticides. The term includes any derivative, such as conversion into metabolites, reaction products and impurities to be of toxicological significance. The pesticide residues may be divided into bound residues and conjugated residues. Bound residues may be defined as chemical species originating from pesticides usage that cannot be extracted by the methods used in the analysis. Conjugated residues are products of secondary metabolism which involve reaction of the pesticide or its metabolites with indigenous substances such as sugars, glucose, amino acids [4].

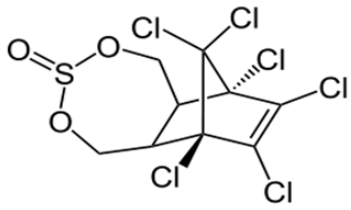
Excretion of pesticide residues through milk



Endosulfan residues

Structure of Endosulfan

Endosulfan is a synthetic cyclodiene non-systemic insecticide and acaricide with both contact and stomach activity. Endosulfan consists of 2 isomers that differ in the configuration of the 7-membered dioxothiepin-oxide ring. These isomers are known as alpha endosulfan and beta endosulfan. The ratio of alpha endosulfan and beta endosulfan is approximately 2:1.



- **Common Name:** Endosulfan
- **IUPAC Name:** 6,7,8,9,10,10-hexachloro-1,5,5ª,6,9,9ª-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin-3-oxide
- **Molecular formula:** C9H6Cl6O3S
- **Molecular mass:** 406.96 g/mol
- **Boiling point:** 290 to 350°C.
- **Relative density:** 1.745g/cm^3 at 20 °C

The Environmental Protection Agency (EPA) outlined the characteristics of Endosulfan such that it is a semi-volatile and persistent cyclodiene pesticide that can migrate over a long distance through various environmental media such as air, water, and sediment. Once Endosulfan was applied to crops it can either persist in soil as a sorbed phase or be removed through several physical, chemical and biological processes. The pure compound was a cream to brown coloured solid that may appear in the form of crystals or flakes. It has a smell like Turpentine but does not burn. It does not occur naturally in the environment.

Exposure to endosulfan

It was reported that exposure to Endosulfan occurs mostly from eating contaminated food but may also occur from skin, breathing contaminated air or drinking contaminated water [6]. It affects the function of the central nervous system.

Materials and Methods

Selection and sampling

Study area

Five areas namely Nhandadi, Nidumba, Pothamkandam, Pannikkunnu and Periya of Kasargod district in Kerala, were selected to monitor the Endosulfan residues in milk.

Sampling

Forty raw cow milk samples were collected from individual dairy farmers residing in the five study areas.

Block	Village Panchayat	Area	No. of Samples
Nileswar	Kayyur-Cheemeni	Nhandadi	5
		Nidumba	5
		Pothamkandam	10
Kanhangad	Pullur - Periya	Pannikkunnu	6
		Periya	14

Table 1: Details of Sampling of Milk.

Location of GC analysis

- The milk samples were analysed in the Central Instrumentation Laboratory of College of Veterinary and Animal Sciences, Mannuthy (Thrissur district).
- Chemicals and glassware
- Chemicals of analytical grade and glasswares of Borosil Glass Works Ltd. were used for the analysis.
- Gas chromatography.

Sl. No.	Equipment	Specification		
1	Name	Trace 1300 Gas Chromatograp [Model: Trace 1300 Series] [Make: Thermo Scientific		
2	Detector	MSMS [Thermo Scientific DynaMax XR Detection System]		
3	Length of the column	30 Meters		
4	Diameter of the column	0.25mm		
5	Temperature programme of column oven			
		Rate (°C/min)	Temperature(°C)	Hold Time (min)
	Initial	-	60	1
	1	12	280	5
6	Injector temperature	280 °C		
7	Detector temperature	230°C		
8	Carrier gas	Helium (UHP grade 99.999%)		
9	Flow rate	1.2 ml/min		
10	Min. limit of detection	1 ppb		
11	Min. limit of quantification	1 ppb		

Table 2: The Specifications of the Equipment Used for Analysis.

Endosulfan standard solution

An endosulfan standard solution of Series 5 OC Pesticide Mix # 1 at a concentration of 100 µg/mL in acetone solvent and at a purity of 99% (Catalog#:32412; Lot#: A0106142) manufactured by Restek Corporation, Bellefonte, Pa. 16823 was used as a standard for the analysis.

Multiresidue procedure

The procedures below are based on AOAC Official 2007.01 Method [4].

Result and Discussion

Profile of Study Area

Kerala, the southern state of India in the West Coast is known as Gods Own Country and Kasargod, the northern district of this state. Kasargod had never witnessed industrial development and traditional farming was their main occupation. The Plantation Corporation of Kerala (PCK) started using pesticides in mid-seventies and the helicopter that came circling the villages with showers of pesticide was a curiosity for many villagers and all children [2]. Plantation Corporation of Kerala has 4696 hectares of Cashew Plantations in Kasaragod district. It is distributed in 3 sectors spread over 20 villages.

- **Kasaragod Plantations:** 2190.00 hectares
  - **Muliyar division:** 367.86 hectares
  - **Perla Division:** 783.14 hectares
  - **Adhur division:** 749.00 hectares
  - **Periya division:** 290.00 hectares
- **Rajapuram Plantations:** 1526.00 hectares
- **Cheemeni Plantations:** 980.00 hectares

Results

The results obtained after the analysis of 40 samples are presented in table 3. The presence of α-Endosulfan, β-Endosulfan, and Endosulfan sulphate were not detected in any of the raw milk samples.

Discussion

The result of the analysis states the absence of α-Endosulfan, β-Endosulfan, and Endosulfan sulfate in all 40 milk samples. But as per the specifications of the equipment used for analysis, the

Sl No.	Sample No.	Data File	Endosulfan I (in ppb)	Endosulfan Sulphate(in ppb)	Endosulfan II (in ppb)
1	1	Data15	N/A	N/A	N/A
2	2	Data16	N/A	N/A	N/A
3	3	Data17	N/A	N/A	N/A
4	4	Data18	N/A	N/A	N/A
5	5	Data19	N/A	N/A	N/A
6	6	Data20	N/A	N/A	N/A
7	7	Data21	N/A	N/A	N/A
8	8	Data22	N/A	N/A	N/A
9	9	Data23	N/A	N/A	N/A
10	10	Data24	N/A	N/A	N/A
11	11	Data26	N/A	N/A	N/A
12	12	Data27	N/A	N/A	N/A
13	13	Data28	N/A	N/A	N/A
14	14	Data29	N/A	N/A	N/A
15	15	Data30	N/A	N/A	N/A
16	16	Data31	N/A	N/A	N/A
17	17	Data32	N/A	N/A	N/A
18	18	Data33	N/A	N/A	N/A
19	19	Data34	N/A	N/A	N/A
20	20	Data35	N/A	N/A	N/A
21	21	Data37	N/A	N/A	N/A
22	22	Data38	N/A	N/A	N/A
23	23	Data39	N/A	N/A	N/A
24	24	Data40	N/A	N/A	N/A
25	25	Data41	N/A	N/A	N/A
26	26	Data42	N/A	N/A	N/A
27	27	Data43	N/A	N/A	N/A
28	28	Data44	N/A	N/A	N/A
29	29	Data45	N/A	N/A	N/A
30	30	Data46	N/A	N/A	N/A
31	31	Data48	N/A	N/A	N/A
32	32	Data49	N/A	N/A	N/A
33	33	Data50	N/A	N/A	N/A
34	34	Data51	N/A	N/A	N/A

35	35	Data52	N/A	N/A	N/A
36	36	Data53	N/A	N/A	N/A
37	37	Data54	N/A	N/A	N/A
38	38	Data55	N/A	N/A	N/A
39	39	Data56	N/A	N/A	N/A
40	40	Data57	N/A	N/A	N/A

Table 3: Concentration of Endosulfan in Raw Cow Milk Samples Obtained from Different Places in Kasargod (Annexure 1).

Nb: 1. Endosulfan I is alpha endosulfan and Endosulfan II is beta endosulfan.

2. Endosulfan sulfate is a product of oxidation containing one extra O atom attached to the S atom [7].

minimum level of detection is 1ppb. So, it can be inferred that the concentration of residues if present will be less than the minimum level of detection. Moreover, as per Codex standards for milk, the maximum residual limit (MRL) of endosulfan is 10ppb (0.01mg/kg). The result clearly indicates that the samples confirm the codex standards for endosulfan.

The result obtained is expected to be the outcome of several measures adopted by the government of Kerala in eliminating endosulfan from Kasargode. One among them is the ban of use and sale of endosulfan in Kerala by the Kerala High Court in 2002 and by the Kerala state government in 2003.

Moreover, in aerobic conditions, the half-life of endosulfan in soil ranges from 9 months to 6 years [8]. As this study is conducted after 15 years, there are chances of degradation of endosulfan residues during this period. Also, though in the Indian scenario, a cow has a life span of about 26 years it is usually culled at an age of 6-8 years [9] and this might be the reason for the result obtained. The schemes introduced by the department of dairy development; Government of Kerala also might have helped in eliminating endosulfan residues from milk. The schemes like Milk Shed Development Programme granted a subsidy to farmers only if cow/buffalo is purchased from neighboring states of Kerala [10]. This might have helped in the creation of a new population of cattle that are not exposed to endosulfan.

Conclusion

The endosulfan's use is phased off from spraying onto cashew crops but a few investigations were carried out to detect the levels of endosulfan in milk. The milk samples were collected particularly from the prone areas in Kasargod, Kerala and it is clear from the analyses that the milk is free of the three major variants of endosulfan.

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