Research Article

Stability and Presence of Pesticide Residue Sample Extracts of Soil and Vegetable: Eloor & Edayar Region, Kerala, Industrial Hub Nearer to Arabian Sea

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Abstract

Eloor-Edayar, (latitude 9º 3'N and 10º 6'N and longitudes 76º 18'E and 76º 30' and an area of 14.21km²) the landmass situated on the banks of River Periyar, is known as the industrial backbone of Kerala. The previous reports reveal this region is highly contaminated by heavy metal from industrial effluents. The present study focuses on pesticides in vegetables (Ladies finger, Papaya, Kachil- yam, Guava, Tapioca, Ginger) and related soil extracts when kept in cold conditions and their presence after a long period. The samples collected in May 2008 pre-monsoon, the environment when the soil and vegetables were free from volatile organic components, accelerates the adsorption of pesticides and high temperature. The samples shoot vegetable ladies finger, edible root vegetables Kachil-Yum, Tapioca and Ginger, fruits like Papaya and Guava and the sediments nearer land. The sample extracts analyzed in 2019 after keeping in the cold as well as the usual conditions. The Analysis report shows the pesticides present in the vegetables and soil are α , β , γ BHC Aldrin, Dicofol, α, β, Endosulfan, Dieldrin, OPDDT and PPDDT. Aldrin, Dicofol and BHC are the related forms in ladies Finger contains y BHC, a, b, Endosulfan, Dieldrin, Aldrin, PPDDT. Ginger added α , β , γ BHC Aldrin, Dicofol, α , β , Endosulfan, OPDDT and PPDDT. Tapioca carried α , β , γ BHC, Dicofol and PPDDT. Kachil-Yum absorbed α , β , γ BHC Aldrin, Dicofol, α , β , Endosulfan, OPDDT and PPDDT. Papaya contains α and γ BHC. Guava captivated α , γ BHC Aldrin, Dicofol, α Dieldrin OPDDT and PPDDT.

Keywords: Eloor-edayar; Organochlorine pesticides; Endosulfan; DDT

Introduction

The "Green Revolution" initiated in the 1960s made India No. 1 manufacturer of pesticides in Asia and 12th globally. Due to uncontrolled use, Indian foods and vegetables have the highest residues in the world. At the national level in India, Kerala is the highest [1] among in districts Kasaragod [2] and Palakkad [3].

Environmental bioaccumulation potential and associated health issues, most of the OCL pesticides categorized as environmental hazards and banned by The Stockholm Convention [4-6]. WHO reports that at present, in Developing countries, organochlorine pesticides used for farming [7] even though Developed countries have declared them as primary pollutants [7-11]. Microorganisms, invertebrates, plants, birds like the peregrine falcon, sparrow hawk and bald eagle, fish and blood plasma of agrifarmers affected badly by OCLs [12-18].

Among Humans, effects of pesticide contamination causes Neuromuscular disorders, stimulation of drug and steroid metabolism [19,20], potential risk factor for gallstone disease [21], vitamin D deficiency [22] and also affects endocrine-disruption activity in patients with neonatal thyroid hormone status. Endosulfan residues in humans bioaccumulated through plants and animal foods and Gastrointestinal absorption of it damages CNS-central nerve system causing acute inhalation toxicity [23,24]. Dialdrin is partly responsible for risk increment of Parkinsons disease. Thyroid hormone levels of the newborn are affected by β -HCH, HCB and DDT residues. Heptachlor bring mitochondria-mediated cell death by spoiling electron transport chain complex III and become neurotoxicant and in patients with Parkinson's disease [25]. In the research on passing from one species to its offspring it seemed Pesticide residue are seen present in eggs of sea birds [26] and humans in Korea, Guerrero, Mexico, China and India transferred *via* maternal cord sera, blood, and the placenta and breast milk [27].

Chemical compounds that terminate insects, fungi, bacteria, herbs or rodents are generally known as Pesticides. Pesticides are classified based on their nature, application, and targeted pests. By nature, they are organochlorine (DDT, Dieldrin, lindane, Endosulfanetc), organophosphorus (Parathion, Malathion etc.). It is applicable for Agriculture, Public health, and Domestic purposes. It targets pests as insects -insecticide, fungi- fungicide, herbs-herbicide and rodentsrodenticides [28]. At the application of organochlorine pesticide group (DDT, DDD, Dicofol, Eldrin, Dieldrin, Chlorobenziate, Lindane, BHC, Methoxychloro Aldrin, Chlordane, Heptachlor, Endosulfan, Isodrin, Isobenzan, Toxaphene, Chloropropylate) is well known than the rapidly hydrolyzed degradation of the environmental organophosphorous [29,30]. Organochlorine pesticides persist for days to years in the environment, Endosulfan $C_9H_6C_{16}O_3S$ has a halflife of $35(\alpha$ -isomer) to $150(\beta$ -isomer) days, and Dichloro Diphenyl

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Trichloroethane (DDT) $C_{14}H_9C_{15}$ has a half-life of 2 to 15 years [4,31].

The study region Eloor-Edayar, in Ernakulam district, is the Industrial Area of Kerala and is a hot spot categorized under Green peace [32]. A partial pesticide manufacturing unit, which was closed by Govt due to the local public's protest during the period of sample collection. Many studies conducted here showed that pesticides contaminate the area. A series of pesticide studies from 1990 to 1999 on water and sediment from the Periyar River line was done by the Department of Chemical Oceanography, CUSAT. Menon et al. 2000 [33] studied macro Benthic, Benthic fauna, Prawn, Fish, mollusc and Polychaaetens in this region. Further studies on the survived species were carried out and revised by Martin et al. 2011 [34].

Previous studies focused on the water and sediment samples near estuary or estuarine sediments. The presence of organo phosphorous pesticides Malathion and Methyl Parathion and organo chlorine pesticide Endosulfan samples of Periyar side has been reported by Sujatha et al. 1999 and 1994 [35-37].

This study focused on the baseline data of organochlorine pesticide stability, degradation or pesticide residues in the extracts of vegetables from the land area located at the river end.

Materials and Methods

Study area

Eloor is an industrial area-north of Kochi in Ernakulam District in Kerala in India situated between north latitudes 9° 3'and 10° 6' and east longitudes 76° 18' and 76° 30'. This island has an area of 14.21km² formed between two rivers Periyar distributaries and is the largest industrial belt in Kerala. Most of the industries, (70% approximately 250 companies) of Kerala state in this region, including chemical, engineering, food, drug, paper, rayon, rubber, textiles, and plywood industries. At the time of sample collection in 2008, Eloor, a Panchayat, now turned to Municipality. During the sampling period survey of Department of Industries Govt. of Kerala and Eloor Grama Panchayat had 20 wards of population density 2425/Km². The panchayat is house to 4.2% of industrial company workers. The vegetarian and non-vegetarian comprise 3.9% and 0.1% of the population.14.4% people from Eloor utilized their land for cultivation of food including grains 3.88%, vegetables 1.48%, fruits 1.292%, coconut 16.17% and roots 0.25%. 95.93% of water in wells is contaminated. The sampling was during May 2008 Pre Monsoon period (Figure 1 and Table 1).

The soil samples and vegetables were collected and transferred to the laboratory in glass bottles. pH and Eh of the soil analyzed by **Table 1**: Sampling site and Sample Description.



APHA methods [38].

Extraction of pesticides

About 2g wet weight of vegetables or 10gm soil/sediment was taken in a 250ml glass-stoppered Erlenmeyer flask and converted to dry weight data. The sample was extracted with 150ml acetone for 24h on a mechanical shaker. The acetone extraction was repeated twice for each sample. The combined supernatant was evaporated to dryness and dissolved into 10ml hexane. The hexane extract was dried by passing it through a layer of anhydrous sodium sulfate and then concentrated to 2ml by using a Kuderna-Danish (KD) concentrator. A 2ml of the KD extracts of soil/sediment was subjected to Florisil column chromatography (Florisil PR: Floridin Co., 10g) cleanup and fractionation. The Florisil gel was activated at 130°C for 12h, before the fractionation with 120ml of 100% hexane and again concentrated to 2ml.

Stability analysis of extract

The extracts were fractionated with 100% hexane and concentrates was kept in different temperature from -20°C in a cold stored to room temperature for 10 years (2008 to 2018). It was made up to 2ml and analyzed for pesticides using GC-ECD. The GC conditions are as follows: injection port temperature 250°C, detector temperature 350°C, oven temperature program: 110°C (5min) at 5°Cmin⁻¹ to 190°C (2min) at 15°Cmin⁻¹ to 280°C (10min).

	Sampling site	Soil colour	Vegetable/Fruit									
S1	Eloor panchayat colony (10.084686N; 76.291281E) near to Panachithodu (10.08815N; 76.290820E)	Blackish	Kachil-Yam (root vegetables)									
S2	Kanjirakkuzhi (10.086123N; 76.291994E)	Yellow	-									
S3	Kuzhikkandamthodu (10.04508N; 76.17301E)	Blackish	-									
S4	Periyar, Muttinakamkadavu (10.085290N; 76.283535E)	Reddish- brown	-									
S5	Near Periyar (10.084686N; 76.291281E)	Reddish- brown	Guava									
S6	Depot road (Agricultural land) (10.085316N; 76.17201E)	Slight blackish	Tapioca and Ginger (root vegetables), ladies finger (shoot vegetables)									
S7	Opposite to HIL (10.079591N; 76.301873E)	Blackish	Papaya (Fruit)									



Result and Discussion

The soil's pH in this area varied from 5.24 and 8.39 and Eh of soil -288mV to 245mV (Figure 2). pH and Eh of soils affect plant metabolism and catabolism [39], by influencing nutrient and ion toxicity transport [40,41]. The optimum pH and Eh for plants is 6.5 to 7, +400 to +450 mV, and favorable conditions for plant growth are between pH 5.5 and 8. Furthermore, Eh greater +350mV [42]. The soil samples collected from Kuzhikkandamthodu (Eh -197mV & pH 7), Panachithodu (Eh -288 mV & pH 7.15), Muttinakamkadavu (Eh -159mV & pH 7.29), Eloor Panchayat colony (Eh 0.012mV & pH 8.39) under the category of highly reduced soils whereas the soils from the area of Depot road (Eh 245mV & pH 5.24) and Kanjirakkuzhi (Eh 242mV & pH 6.54) were found to be moderately reduced. The soil analyzed categorized four types as followed.

Aerated soils over: > +400mV

Moderately reduced soils: +100mV - +400mV

Reduced soils: -100mV - +100mV

Highly reduced soils: -100mV - -300mV [43]

The study report, Eh indicated the soils in these locations are moderately reduced [44,45], the soil in between approved limits of -300mV to +900mV. 1979, Bressy [46] reported the soil-related stress of pH and oxidative stress pesticides acts as oxidants. Fewer distances between sampling sites of Eloor Panchayat shows Eh and pH variations in the soil, which came to an understanding of the other soil scientific reports [42,47]. The residue of (α, β, γ) BHC, Aldrin, Dicofol, (α, β) Endosulfan, Dieldrin OPDDT and PPDDT analyzed as dry basis from Shoot vegetable ladies finger, edible root vegetables Kachil-Yum, Tapioca and Ginger, fruits like Papaya and Guava along with the sediments with different locations (Figure 3a and 3b).

 $\alpha,$ BHC high concentration in soils 689µgm/gm (Kuzhikkandamthodu) to ND (in Kanjirakkuzhi & Panachithodu). The root vegetables 112µgm/gm (Tapioca) and lower in 2µgm/gm (Ginger).

 β , BHC in the soils 690 μ gm/gm (Kuzhikkandamthodu) to ND (Eloorpanjayath colony, Kanjirakkuzhi & Panachithodu) and only in root vegetables and a high value of 92 μ gm/gm (Tapioca).

 γ , BHC detected high 671µgm/gm (Kuzhikkandamthodu) to ND (Eloor panjayath colony and Kanjirakkuzhi) and the fruits 163µgm/gm (Guava) to ND (Papaya).

Aldrin residues present 676µgm/gm (Kuzhikkandamthodu) to lowest 17µgm/gm (Kanjirakkuzhi) high 78µgm/gm in (Guava) to ND (Papaya).

Dicofol high 678µgm/gm (Kuzhikkandamthodu) present low concentration in the soil Eloor panjayath colony and Depot road, vegetables 17µgm/gm (Guava) present root vegetables tapioca and ginger and ND.

 $\alpha, Endosulfan concentration in 631 \mu gm/gm (Kuzhikkandamthodu House) and present Kuzhikkandamthodu, Periyar Muttinakamkadavu and Depot road whereas in vegetable <math display="inline">3.8 \times 10^3 \mu gm/gm$ (Tapioca) and

Destisides in Osil	Pesticides in Vegetables									
Pesticides in Soil	α BHC	β, ΒΗC	ү ВНС	Aldrin	Dicofol	α endosulphan	β endosulphan	Dieldrin	OPDDT	PPDDT
α BHC	-0.173	-0.313	0.078	0.122	-0.18	-0.266	-0.308	-0.307	-0.492	-0.178
β, ΒΗC	-0.456	-0.417	-0.244	-0.192	-0.295	-0.489	0.314	-0.479	-0.681	-0.541
γ BHC	-0.398	-0.446	-0.196	-0.128	-0.28	-0.462	0.17	-0.394	-0.697	-0.534
Aldrin	-0.227	-0.242	-0.04	-0.011	-0.296	-0.259	-0.204	-0.329	-0.44	-0.246
Dicofol	-0.171	-0.24	0.042	0.071	-0.245	-0.224	-0.353	-0.281	-0.394	-0.151
α endosulphan	0.183	-0.438	0.723	0.787	0.61	-0.17	-0.217	-0.421	-0.685	0.293
β endosulphan	0.368	-0.275	0.863(*)	0.896(*)	0.983(**)	0.001	0.124	-0.344	-0.457	0.547
Dieldrin	-0.18	-0.612	0.143	0.253	0.391	-0.447	0.57	-0.354	-0.871(*)	-0.358
OPDDT	-0.367	-0.308	-0.158	-0.128	-0.337	-0.38	0.041	-0.44	-0.536	-0.38
PPDDT	-0.037	-0.421	0.421	0.475	0.219	-0.271	-0.264	-0.444	-0.65	0.06

*Correlation is significant at the 0.05 level; **Correlation is significant at the 0.01 level (2-tailed).





Figure 3b: Concentration of pesticide in the soil samples collected from Eloor-Edayar region.

ND (Papaya).

 β , Endosulfan sensed 861µgm/gm (Periyar Muttinakamkadavu) ND (Eloor panjayath colony Kanjirakkuzhi & Panachithodu) and in vegetable 554µgm/gm (Kachil-Yum) and the other presence in Tapioca.

Dieldrin, the highest concentration of all pesticides 7187µgm/gm (Kuzhikkandamthodu House) and lowest 65µgm/gm (Panachithodu) and the fruit 292µgm/gm (Papaya) to 19µgm/gm (Kachil-Yum).

OPDDT showed high in 805µgm/gm (Kuzhikkandamthodu) and lowest 4µgm/gm (Depot road) and only in root vegetables 554µgm/ gm (Tapioca) and 22µgm/gm (Kachil-Yum).

PPDDT highest in 871µgm/gm (Kuzhikkandamthodu) and lowest 6µgm/gm (Panachithodu) contained as 40µgm/gm (Guava) to ND (Papaya).

The Papaya fruit and root vegetable Ginger had the least presence of pesticides. High metal polluted industrial waste and soil temperature might have led to the decomposition and low residue presence. The water channels which carry industrial effluents and reach the River Periyar, carried these residues. In the seasonal wise studies on DDT in industrial river line area, the pesticide is not observed in the monsoon

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period36, which revealed the effect of temperature and water runoff.

Correlation between decomposed residues of pesticides in the soil and vegetables is shown in Table 2. The correlations showed that β BHC, OPDDT strong negative, Dialdrin moderate, strong negative and Dicofol week negative. These studies emphasized the earlier monitoring study of pesticide's effect on organism lipid level by Sujatha et al. 1995 [48]. The soil in the Industrial Area is contaminated with organic and inorganic components, which affect the pH and Eh. Furthermore, Sujatha et al. 1991 [49] studied the equilibrium/ partition model on the fate of pesticides in the soil, which depends on clay materials, hydrous oxides, organic matter, redox stands, pH of soil system, and climate. This study strongly recommends removing the pesticides from soils of agricultural areas.

Conclusion

The current study is the Baseline for the pesticide pollutants in the industrial area and their persistence after years in the extraction of sediments and vegetables. The samples collected from the Eloor -Edayar region, the industrial zone of Kerala, indicated significant pesticide levels in the soil and vegetables. The presence of pesticide residues in vegetable extract showed the transport of pollutants from sediment to primary producers, which raises the question of the health of the people lives in that region.

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