Persistence of endosulfan in selected areas of Kasaragod district, Kerala

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The persistence of organochlorine pesticides in different environmental matrices is a matter of concern as the complete environmental fate of these chemicals is still an unexplored field. Water, soil and sediment samples were collected from selected panchayats of Kasaragod district, Kerala in four different phases to assess the contamination by endosulfan applied on cashew plantations. Endosulfan was detected in only 2 samples out of 22 water samples analysed during the second phase of sampling. Concentration of endosulfan was below detection limit in all the 22 samples analysed during the third phase. A total of 14 sediment samples were analysed and during the third phase, the concentration of endosulfan was below detection limit in all the samples. Out of 13 soil samples, endosulfan was detected in 5 samples during the second phase and during the third phase it was detected in 3 samples. Endosulfan was detected in two soil samples from Panathadi and Muliyar Panchayats during the fourth phase. Also, comparison of results of the analysis of endosulfan during the third and fourth phase showed decrease in concentration in the three soil samples. The findings from the present study provide information on the current residue levels and persistence of organochlorine pesticide endosulfan in water, sediment and soil in selected areas of Kasaragod district. The study shows that combined toxic residues of endosulfan in the sediment and soil samples of selected areas of Kasaragod district were found to be persistent for a period of 1.5–2 years, but the persistence showed variations depending upon the climatic conditions and physico-chemical characteristics like pH, organic matter content and particle size of the soil in the area.

Keywords: Endosulfan, organochlorine pesticides, soil and sediment samples, water.

ORGANOCHLORINE pesticides (OCPs) have been extensively used in India for agricultural purposes. Modern agriculture practices reveal an increase in the use of pesticides and fertilizers to meet the food demand of the increasing population, which results in contamination of the environment. Pesticides have played a major role in achieving maximum crop production, but maximum usage and accumulation of pesticide residues has been highly detrimental to aquatic and other ecosystems[1,2]. Many pesticides are toxic and they persist in the environment for a limited period of time and later are subjected to some chemical processes of degradation, hydrolysis, oxidation, photolysis, etc. by the ecosystem[3,4].

Endosulfan is a persistent, toxic, broad-spectrum organochlorine insecticide and acaricide used on food and non-food crops. Introduced in the 1950s, it emerged as a leading chemical used against a broad spectrum of insects and mites in agriculture and allied sectors. In human health assessment studies, endosulfan has been shown to have high acute oral and inhalation toxicity as well as slightly toxic dermal toxicity. It is an irritant to the eyes and primarily affects the nervous system. Toxic effects observed in animals from acute, subchronic, developmental neurotoxicity, and chronic/carcinogenic toxicity studies showed that endosulfan causes neurotoxic effects, which are believed to result from over-stimulation of the central nervous system[5,6]. According to Bureau of Indian Standards, 2012, the permissible limit of endosulfan in drinking water is 0.4 μg/l. Maximum permissible limit according to the United States Environmental Protection Agency (EPA) for endosulfan in lakes, rivers and streams is 74 μg/l.

Since 1954, the dominant group of pesticides called organochlorine insecticides has been extensively used in India for agriculture as well as in the public health sector[7]. Although the use of most OCPs has been discontinued as a result of their environmental persistence, exposure to OCPs will continue during the coming years too. As a consequence, many OCPs may induce chronic toxicities through long-term exposure, even if their doses are relatively low[8,9].

The time necessary for degradation of pesticides is important to assess whether pollutants are persistent in the environment. The disappearance of these compounds is related to several factors such as pH, temperature, light, oxygen and quantity of organic matter, which alter the kinetics of degradation[10].

Due to its hydrophobic nature, endosulfan tends to get adsorbed to soil particles, resulting in persistence[11,12]. 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 persistent as the parent compound. Pesticide residues in the soil can move from the surface when they dissolve in run-off water, or percolate down through the soil, and eventually reach the groundwater. According to the US Geological Survey[13], at least 143 different pesticides and 21 transformation products have been found in groundwater, including pesticides from every major chemical class. Over the past two decades, pesticides were reported in the groundwater of more than 43 states in USA[14]. During one survey in India, 58% of drinking water samples drawn from various hand pumps and wells around Bhopal

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Table 1. Details of water sampling locations in Kasaragod district

Sample code	Panchayat	Coordinates	Source of sample	Site description
ENM 2	Enmakaje	12°37′14.8″N 075°08′08.0″E	Surangam	Near house – near plantation area
ENM 3	Enmakaje	12°37′45.8″N 075°07′23.8”E	Pond	Water from surangam
KUM 1	Kumbadaje	12°36′49.3″N 075°06′50.2″E	Pond	Clay mining area
PER 2	Pullur Periya	12°23′28.2″N 075°05′59.3″E	Pond	Abandoned pond
MUL 1	Muliyar	12°31′26.3″N 075°05′30.7″E	Surangam	Valley slope
MUL 3	Muliyar	12°30′01.9″N 075°05′08.9″E	Pond	Plantation area
CHE 2	Kayyur Cheemeni	12°13′35.5″N 075°16′00.6″E	Pond	Near temple
AJN 1	Ajanoor	12°23′04.4″N 075°05′09.0″E	Stream	Under bridge
BAD 2	Badiyadukka	12°37.327′N 075°06.279′E	Stream	Near plantation area
KAL 1	Kallar	12°25′10.0″N 075°14′0.9″E	Pond	Pond near Kanhirathody – plantation area
KAL 2	Kallar	12°25′44″N 075°15′27.4″E	Open well	Well in private land – near plantation area
KAL 3	Kallar	12°25′17.7″N 075°13′57.0″E	Open well	Kanhirathody Colony Well – near plantation land
KAL 4	Kallar	12°25′44.5″N 075°14′51.8″E	Open well	Well near plantation quarters
KAL 7	Kallar	12°25′44.5″N 075°14′51.8″E	Open well	Well inside plantation area – Rajapuram estate
PAN 1	Panathadi	12°27′53.8″N 075°23′49.2″E	Plantation tank	Inside plantation area- near helipad site
PAN 2	Panathadi	12°28′34.4″N 075°22′48.3″E	Stream	Near Kallepalli plantation area
KAR 2	Karadukka	12°34.638′N 075°12.128′E	Open well	Well near Minchipadavu plantation office
KAR 3	Karadukka	12°34.571′N 075°12.031′E	Stream	Stream near Minchipadavu plantation office
KAR 4	Karadukka	12°34.717′N 075°11.420′E	Pond	Pond in private land – near Minchipadavu plantation area
BEL 1	Bellur	12°35.289′N 075°10.396′E	Pond	Pond in private land (Megnamana)
BEL 3	Bellur	12°35.532′N 075°10.897′E	Pond	Near plantation area
BEL 4	Bellur	12°35.535′N 075°11.216′E	Pond	Pond near the plantation

was contaminated with organochlorine pesticides above the EPA standards[15].

A survey of endosulfan in Chinese soil was carried out by the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS) in 2005 as part of Chinese Persistent Toxic Substance (PTS) Soil and Air Monitoring Programme, Phase I, in which concentrations of endosulfan were monitored from 141 Chinese surface soils[16]. Endosulfan was found ubiquitous in Chinese surface soil. Occurrence frequencies were high in the 141 soil samples, and 83%, 96% and 91% for α-endosulfan, β-endosulfan and endosulfan sulphate respectively. Concentration of total endosulfan ranged from below detection limit to 19,000 pg/g. In Florida, endosulfan was the third most commonly detected agrichemical in surface waters and was found at concentrations of 22–1861 μg/l (ref. 17). It was also the most commonly detected agrichemical in sediments, at a concentration of 0.7–230 μg/g. A study on the endosulfan residues in cultivated soils in southern India reported that the concentration of α-endosulfan, β-endosulfan and endosulfan sulphate ranged from 0.1 to 29, 0.1 to 167 and 12 to 187 mg/kg respectively[18]. According to Bishnu *et al.*[19], in the tea-growing areas of West Bengal, α-endosulfan, β-endosulfan and endosulfan sulphate ranged from 7.40 to 81.40, 8.50 to 0.256.1 and 55 to 95.9 μg/kg respectively. Previous studies on the effects of endosulfan exposure in Kasaragod district by the National Institute

Table 2. Details of sediment sampling locations in Kasaragod district

Sample code	Panchayat	Coordinates	Source of sample	Site description
ENM1	Enmakaje	12°40′21.8″N 075°08′30.5″E	Pond	Valley
ENM2	Enmakaje	12°37′14.4″N 075°08′07.9″E	Surangam	Surangam near house
ENM3	Enmakaje	12°37′45.8″N 075°07′23.8″E	Pond	Near Galigopura Road
KUM1	Kumbadaje	12°36′49.3″N 075°06′50.2″E	Pond	Clay mining area
MUL1	Muliyar	12°31′26.3″N 075°05′30.7″E	Surangam	Valley slope
MUL3	Muliyar	12°30′01.9″N 075°05′08.9″E	Pond	Plantation area
CHE 2	Kayyur Cheemeni	12°13′35.5″N 075°16′00.6″E	Pond	Near plantation area
AJN 1	Ajanoor	12°23′04.4″N 075°05′09.0″E	Stream	Site under bridge
KAL 1	Kallar	12°25′10.0″N 075°14′0.9″E	Pond	Pond near Kanhirathody plantation area
KAL 6	Kallar	12°25′85.1″N 075°14′60.4″E	Valley	Sediment from valley slope
KAR1	Karadukka	12°34′918″N 075°12′121″E	Pond	Sediment from Kaveri Temple pond
KAR3	Karadukka	12°34.571′N 075°12.031′E	Stream	Stream near Minchipadavu plantation office
KAR4	Karadukka	12°34.717′N 075°11.420′E	Pond	Pond in private land – near Minchipadavu plantation area
BEL 3	Bellur	12°35.532′N 075°10.897′E	Pond	Near plantation valley – near Pallapady

of Occupational Health reported that the concentration of endosulfan residues in water, pond sediment and soil samples ranged from 0.0078 to 0.0667 μg/l, 0.155 to 0.307 μg/kg and 0.372 to 0.988 μg/kg respectively. All these studies prove the highly persistent nature of endosulfan residues in the soil[5].

Endosulfan is known to be an endocrine disruptor and a genotoxin[20]. Because of its persistence in the environment for a long time and its toxicity, endosulfan contamination in the environment is of great concern. Endosulfan was aerially sprayed for many years in the cashew plantations of Kasargod district, though it has now been discontinued. Because of the reported cases of endosulfan problem and related health issues due to aerial spraying of endosulfan in Kasaragod district, a study on the persistence of endosulfan was carried out in 11 selected panchayats of the district in four phases.

The sampling sites were fixed with the help of concerned health inspectors and members of ‘Endosulfan Victims and Remediation Cell’ formed under the coordination of District Medical Officer of Kasaragod district. Details of water, sediment and soil sampling locations are given in Tables 1–3 respectively, and sampling locations are shown in Figure 1. All sampling points were geographically referenced with Global Positioning System.

In the first phase of sampling and analysis, the soil, sediment and water samples were collected from the 11 affected panchayats during March 2010. The second phase of sampling and analysis was conducted during March 2012 and the third phase during September 2012. Since endosulfan was found persistent in three soil samples during the third phase of analysis, sampling was conducted in the fourth phase during April 2013. Some of the water, soil and sediment sampling sites are shown in Figure 2.

The sampling and analysis were carried out according to standard protocol[21,22]. The water samples for the analysis were collected in clean amber glass bottles with Teflon stopper and labelled. The glass bottles were washed well with acid, detergent, tap water, distilled water, acetone and finally with the working organic solvent, i.e. chromatographic grade *n*-hexane. The collected samples were transported in a cool box with ice packs and subsequently stored in a refrigeration at 4°C until further analysis. Samples were also collected from the selected sites to determine the physico-chemical parameters along with OCP analysis. The soil samples were collected at 0–5 cm depth. The soil and sediment samples for the analysis were collected and stored in air-tight, solvent-washed, new glass jars, verified as pesticide-free and sealed with Teflon foil liner fitted with new screw caps. Field samples were preserved at 4°C during transportation and then kept in a deep freeze until solvent extraction.

Analytical grade (AR) chemicals were used. External pesticide reference standards (E. Merck, Germany) were used to compare and quantify the sample concentrations.

Table 3. Details of soil sampling locations in Kasaragod district

Sample code	Panchayat	Coordinates	Source of sample	Site description
CHE 1	Cheemeni	12°14′05.0″N 075°16′41.0″E	Dry pond	Near plantation area
PER 1	Pullur Periya	12°23′32.0″N 075°06′05.6″E	Plantation area	Near plantation area
PER 3	Pullur Periya	12°23′37.8″N 075°05′42.4″E	Inside plantation area	Helipad site
PER 4	Pullur Periya	12°23′39.9″N 075°05′41.0″E	Inside plantation area	Helipad site
PER 5	Pullur Periya	12°23′57.7″N 075°07′11.1″E	Plantation area	Inside plantation area
MUL 2	Muliyar	12°29′59.0″N 075°05′07.3″E	Dry pond	Dry pond
BAD 1	Badiyadukka	12°37′40.0″N 075°06′03.8″E	Plantation – helipad site	Helipad site
BAD 3	Badiyaduka	12°37.327′N 075°06.279′E	Near plantation area	Soil from a private land near plantation area
BAD 4	Badiyaduka	12°37.536′N 075°05.670′E	Near plantation area	Sacred Heart Church compound
KAL 5	Kallar	12°25’0.796′N 075°14.794′E	Plantation compound	Soil from plantation compound
PAN 1	Panathadi	12°27′53.8″N 075°23′49.2″E	Plantation area	Soil and water from plantation tank
BEL 2-Surface	Bellur	12°39.84′N 075°12.45′E	Plantation area	Near Hosanamana – plantation area
BEL 2-depth	Bellur	12°39.84′N 075°12.45′E	Plantation area	Near Hosanamana – plantation area

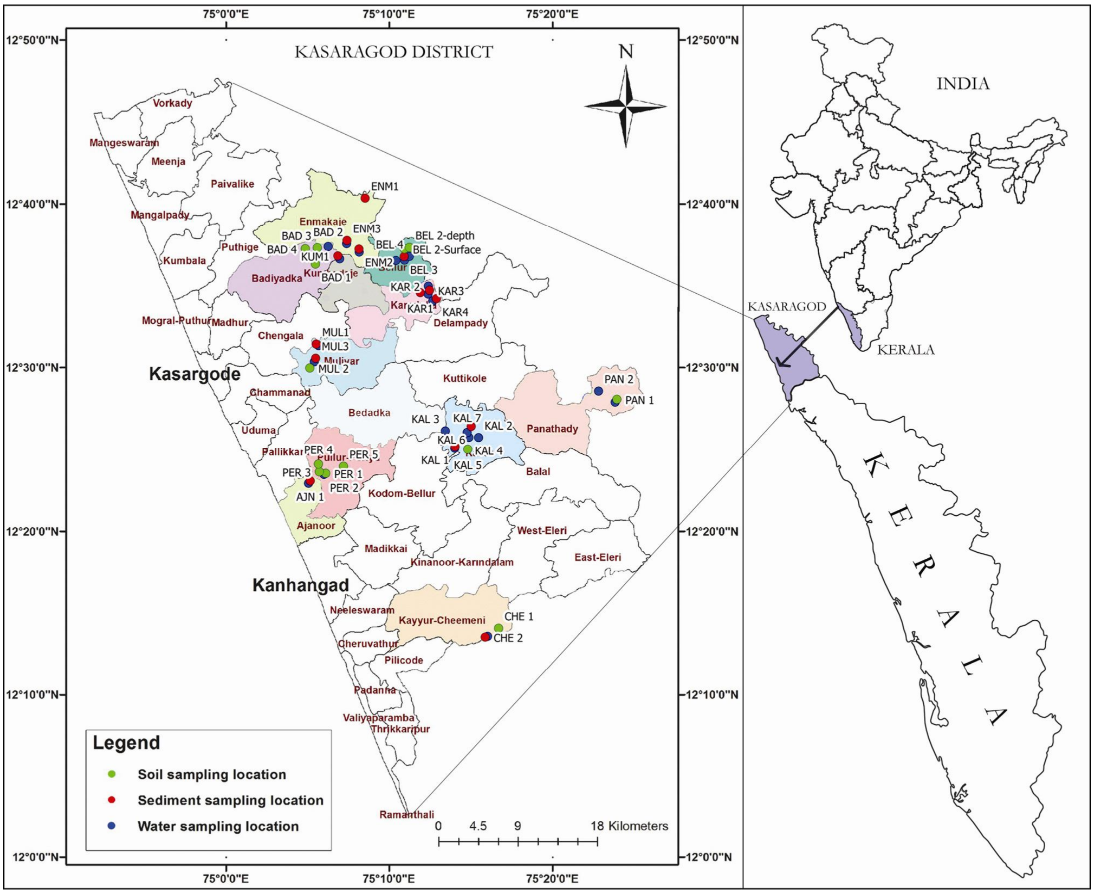

Figure 1. Map showing endosulfan sampling stations in Kasaragod district, Kerala.

Figure 2. Water sampling stations (***a***), sediment sampling stations (***b***) and soil sampling stations (***c***) in selected panchayats of Kasaragod district.

For the extraction of pesticide residues from water, liquid–liquid extraction method was adopted. Extraction of pesticides from soil required a more polar solvent than hexane or dichloromethane alone. Hence a mixed extracting solvent with added acetone was used. Organics were extracted by shaking with a solvent mixture of chromatographic grade *n*-hexane and acetone. Pesticide residues were extracted following standard methods with some modifications. For extraction, the water sample was taken into a separating funnel. It was mixed with 30 g of NaCl and 50 ml of *n*-hexane. The sample was shaken well and hexane layer was separated. This process was repeated thrice and hexane portions were pooled together. The co-extractives were removed from the concentrated extract on an alumina column overlaid with 1 g anhydrous sodium sulphate to remove any remaining water molecules. The extract was concentrated to around 10 ml on rotary evaporator. The concentrated extract was transferred to air-tight, amber-coloured gas chromatography (GC) vials and stored at 4°C until analysis[21–23].

After processing the samples through the different extraction steps, the final concentrated and cleaned-up sample was analysed using gas chromatograph with electron-capture detector, which is specific and highly sensitive for halogenated compounds. A Varian-make CP-3800 gas chromatograph equipped with Ni^{63} ECD electron-capture detector was used to analyse the pesticides. One microlitre of each extract was injected into the injection port using a micro syringe.

WCOT fused silica capillary column of length 30 m, internal diameter 0.32 mm and film thickness 0.25 μm was fitted and efficient temperature programmes were used. Nitrogen was used as the carrier gas and the gas inlet pressure was 80 psi corresponding to a flow rate of 2 ml min^{-1}. The temperature for injector and detector was 250°C and 300°C respectively. The temperature column was programmed from 130°C (hold 1 min) to 200°C at 5°C (hold 10 min) and then from 200°C to 232°C at 1°C min^{-1}. The chromatograms were recorded and integrated using Star Workstation software. External pesticide reference standards (E. Merck, Germany) were used to compare and quantify the sample concentrations. The pesticides detected were compared with those of the standards[24].

Accuracy within-day and between-day precision was assessed using QC samples at three concentration levels, i.e. 50, 100 and 200 μg/l. The samples were all run in triplicate ($n = 3$) on three different days and the RSD and relative error (RE) were calculated for each. The within-day and between-day precisions were found. Acceptable precision was considered to be an RSD of ≤ 15%. The overall accuracy was assessed by subtracting the theoretical concentration of each QC sample from the mean concentration determined from the three days of analysis. Detection (LOD) and quantitation (LOQ) limits were calculated relative to the values for the blank at the retention times of the analytes (10 injections).

Physico-chemical analysis of water was done according to the standard procedure reported by the American Public Health Association[21]. A portion of the collected soil samples was air-dried, sieved and kept in polythene bottles for physico-chemical analysis. Soil pH was measured electrometrically with glass electrode pH meter in water using soil/water ratio of 1 : 10. The soil particle size was determined by hydrometer method. The wet oxidation method of Walkley and Black was used to determine the organic carbon content from which organic matter content was calculated.

The samples were leached with 1N ammonium acetate. The leachate was analysed for exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+). Potassium and sodium in the leachate were determined by flame photometer. Inorganic phosphorus was determined using UV–visible spectrophotometer.

A total of 15 water samples were analysed during the 3 phases of study and the results of the analysis are compared in Table 4. Endosulfan residues in water samples in the 15 sites were found to be below detection limit in all the three phases of sampling. The results show that endosulfan is not present in the water samples. In addition to the 15 samples, 7 new sites were identified where there was a chance of endosulfan persistence and hence water samples were collected from these sites and analysed during second and third phases of study (Table 5). Out of seven water samples, endosulfan was detected in two samples during the second phase (March 2012). During the second phase of sampling, the concentration of endosulfan in water samples ranged from below detection limit to 1.11 μg/l. The maximum value for endosulfan in water was detected in sample PER 2 from Pullur Periya panchayat followed by ENM 2 from Enmakaje panchayat. The values were 1.11 and 1.01 μg/l respectively. The sample with code PER 2 was collected from a pond adjacent to the plantation area; the pond remained undisturbed and was not cleaned for a long period of time. Sample ENM 2 was collected from a surangam near the plantation area. During the third phase of water sampling, endosulfan residues were found to be below detection limit.

Table 4. Comparison of endosulfan residues in water samples during the first, second and third phase of sampling

Panchayat	Sample source	Sample code	Total endosulfan (μg/l) First phase	Second phase	Third phase
Ajanoor	Stream	AJN 1	BDL	BDL	BDL
Muliyar	Pond	MUL 3	BDL	BDL	BDL
Kallar	Open well	KAL 2	BDL	BDL	BDL
Kallar	Open well	KAL 3	BDL	BDL	BDL
Kallar	Open well	KAL 4	BDL	BDL	BDL
Kallar	Open well	KAL 7	BDL	BDL	BDL
Panathadi	Plantation tank	PAN 1	BDL	BDL	BDL
Panathadi	Stream	PAN 2	BDL	BDL	BDL
Karadukka	Open well	KAR 2	BDL	BDL	BDL
Karadukka	Stream	KAR 3	BDL	BDL	BDL
Karadukka	Pond	KAR 4	BDL	BDL	BDL
Bellur	Pond	BEL 1	BDL	BDL	BDL
Bellur	Pond	BEL 3	BDL	BDL	BDL
Bellur	Pond	BEL 4	BDL	BDL	BDL
Badiyadukka	Stream	BAD 2	BDL	BDL	BDL

BDL: Below detection limit; Detection limit: 1 μg/l.

Eight sediment samples were collected and analysed during the three phases of study and the results of the analysis are compared in Figure 3. Among the eight samples, endosulfan detected in samples MUL 3, KAL 6, KAR 3, KAR 4 and BEL 3 underwent 100% degradation during the second phase. The endosulfan detected in sample KAL 1 degraded only 25% during the second phase, but 100% degradation was found during the analysis in the third phase. Six additional sediment samples were also analysed during the second and third phase of study. Comparison of results of analysis of the six samples is shown in Figure 4. Out of 14 sediment samples, endosulfan was detected in 7 samples during the second phase of sampling. The maximum value of endosulfan was detected in the sample ENM-1 (6.24 μg/kg) from Enmakaje panchayat. The source of sediment was a valley slope, where the run-off water from the nearby plantation area got clogged and settled down. Beta-isomer was found to be in higher concentration than the alpha-isomer. Endosulfan sulphate was detected only in one sample collected from Kallar panchayat (KAL 1 = 4.02 μg/kg). The concentration of endosulfan detected from the same site in 2011 was 5.37 μg/kg. During the third phase of sampling, endosulfan residues in sediment samples were found to be below detection limit. Comparison of results of endosulfan analysis of sediment samples indicated that degradation of endosulfan has taken place in majority of the samples. During 2010, traces of endosulfan were detected in many samples. The comparative results show that the highest concentration of endosulfan (6.22 μg/kg) in sediment during 2010 was found in a sample collected from Kallar panchayat. During the study conducted in 2012, endosulfan residues were not detected in any of the sediment samples.

Table 5. Endosulfan residues in seven water samples during the second and third phase of sampling

Panchayat	Sample source	Sample code	Total endosulfan (μg/l) Second phase	Third phase
Enmakaje	Stream	ENM 2	1.01	BDL
Enmakaje	Pond	ENM 3	BDL	BDL
Kumbadje	Open well	KUM 1	BDL	BDL
Pullur Periya	Open well	PER 2	1.11	BDL
Muliyar	Open well	MUL 1	BDL	BDL
Kayyur Cheemeni	Open well	CHE 2	BDL	BDL
Kallar	Plantation tank	KAL 1	BDL	BDL

Detection limit: 1 μg/l.

Eight soil samples were collected and analysed during the three phases of study and the results of analysis are compared in Figure 5. Endosulfan present in soil samples with codes KAL 5, BEL 2 and BAD 4 degraded 100% during the second phase. The maximum concentration of endosulfan detected in Pullur Periya (PER 4) degraded 89% during the second phase and 100% degradation was found during the third phase. In the sample PAN 1, rate of degradation was found to be low; only 56% degradation during the second phase and 67% degradation during the third phase. Five additional soil samples were analysed during the second and third phase of study. Results of the analysis are shown in Figure 6. During the third phase of sampling endosulfan was detected in three soil samples – PER 1 (from Pullur Periya panchayat), PAN 1 (from Panathadi panchayat) and MUL 2 (from Muliyar panchayat). Sampling was continued in the fourth phase (April 2013) also to find out the persistence of endosulfan in the soil samples.

The highest concentration of endosulfan (16.91 μg/kg) in soil was detected in Pullur Periya (PER 4) during 2010 (first phase of sampling). During the second phase of analysis, concentration of endosulfan degraded to 1.93 μg/kg and results of the third phase analysis showed that endosulfan was not present in PER 4. Comparison of results of endosulfan analysis of soil samples showed that out of eight samples endosulfan was detected in five samples during the first phase of sampling. During the second and third phase of sampling endosulfan was detected in three and two samples respectively. Rate of degradation was found to be different in different areas. Endosulfan released to the soil is subject to biodegradation. The biodegradation of endosulfan in soil and water is dependent on climatic conditions and type of microorganisms present. Both biotic and abiotic processes are expected to decrease endosulfan concentration in soil environments. PAN 1 was the only soil sampling location where endosulfan sulphate was detected. The sample was collected from Rajapuram plantation area near the helipad. The site was primarily used for cleaning as well as filling pesticide into the sprayers of helicopter for aerial spraying. This may be the reason for the presence of comparatively high concentration of endosulfan in the area. About 14.85 μg/kg endosulfan was detected from the same site in 2011. The reduction in the concentration may be due to degradation of endosulfan.

During the fourth phase analysis, concentration of endosulfan was found degraded in three samples. In sample PER 1, endosulfan was found to be completely degraded during the fourth phase. In the sample MUL 2, concentration decreased from 5.21 to 3.91 μg/kg. Also, in the sample PAN 1, the concentration decreased from 4.88 to 4.12 μg/kg. The half-lives for the combined toxic residues of endosulfan (alpha endosulfan and beta endosulfan plus endosulfan sulphate) as reported by the EPA range from 9 months to 6 years[6].

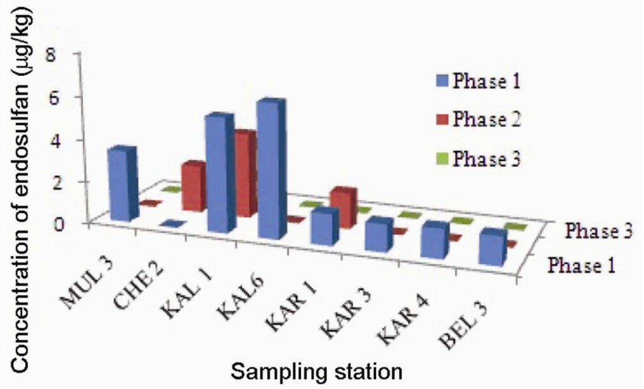

Figure 3. Comparison of endosulfan residues in sediment samples during the first, second and third phase of sampling.

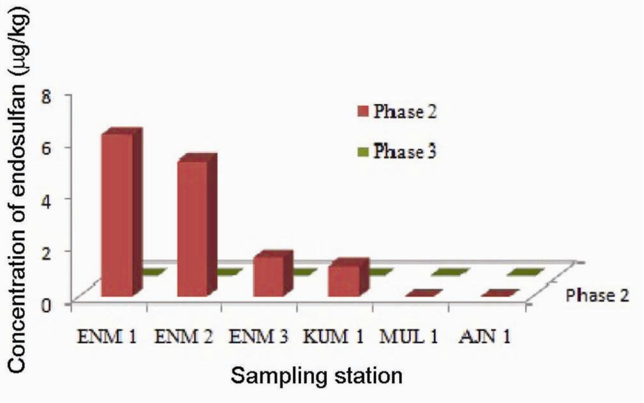

Figure 4. Endosulfan residues in six sediment samples during the second and third phase of sampling.

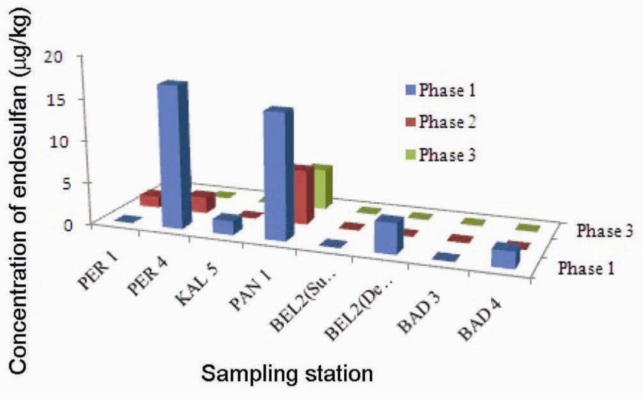

Figure 5. Comparison of endosulfan residues in soil samples during the first, second and third phase of sampling.

The persistence of the residues of endosulfan that cause pollution in the soil is dependent on various factors like soil type, size of soil particles, rainfall, etc.[25]. Other factors that can influence the persistence of endosulfan include meteorological conditions prevalent in the area. Average monthly rainfall data of Kasaragod district during 2009–2012 is given in Figure 7.

In Kasaragod district during 2009–10 and 2010–11 (June–May), the average annual rainfall[26] was 138 and

1213 mm respectively. This low annual rainfall might have helped the endosulfan residues to be persistent in the environment. In 2011–12, the annual rainfall increased to 3105 mm. During the second phase of sampling in March 2012, rainfall was not recorded in Kasaragod and in September 2012 the average monthly rainfall was 315.3 mm; this might have also contributed to reduction in concentration of endosulfan residues in water, sediment and soil samples during the third phase.

The physico-chemical properties of sediment and soil samples from 11 panchayats of Kasaragod district provide an insight into the nature of the samples being studied.

The persistence of the residues of endosulfan that cause pollution in the soil is dependent on various factors like soil type, size of soil particles, organic matter content, etc.[25,27]. Physico-chemical characteristics of the soil samples are presented in Table 6.

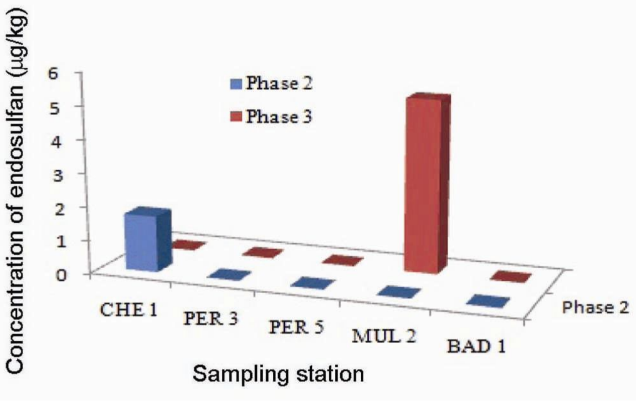

Figure 6. Endosulfan residues in five soil samples during the second and third phase of sampling.

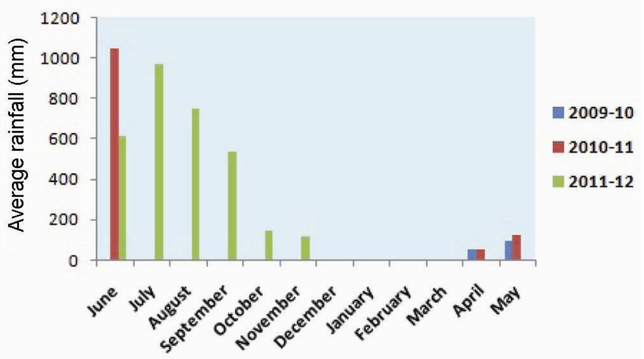

Figure 7. Average monthly rainfall data of Kasaragod district for the years 2009–2012.

Table 6. Pearson correlation of soil and sediment physico-chemical properties with total endosulfan residue concentration

Phase	pH	Organic matter (%)	Sand (%)	Clay (%)	Silt (%)
Soil					
First	–0.2900	0.8768	–0.1008	0.5208	–0.8142
Second	–0.2976	0.7714	–0.8910	0.9420	–0.2756
Sediment					
First	–0.2746	0.8655	–0.0280	0.7155	–0.1561
Second	–0.3440	0.9408	–0.7910	0.8749	–0.0132

The results are in accordance with those of Iraqi and Iraqi[28], who demonstrated that beyond 2% organic matter in soils, the adsorption of pesticides takes place almost entirely on the organic surfaces. The report on the benchmark soils of Kerala by Soil Survey Organization[29], showed organic matter content in Maloth series of Kasaragod district as 6.2%. The study reported five series of soils in Kasaragod district. The minimum and maximum values of organic matter reported in this study ranged from 0.55% to 17.36%. The sites from where soil was collected were areas inside the plantation and there was specific evidence of the presence of large vegetation which had decayed in the area. The decrease in pH of the soil increases the adsorption of endosulfan and the presence of clay and organic matter immobilizes endosulfan in the soil. Soil with low organic matter and heavy rain water will be the best medium for mobility/leaching of endosulfan pesticide. Soil rich in organic matter may retain the pesticides. The organic matter was found to be comparatively high in those soil samples where endosulfan was detected. The result showed that all the soil samples were acidic in nature. Clay contents are known to influence the dynamics and behaviour of both organic and inorganic pollutants in soil. The presence of clay immobilizes endosulfan in the soil. The maximum value of endosulfan was detected in the sample PAN 1 from Panathadi panchayat. The maximum value of clay content was observed at the same site. Majority of the soil samples where endosulfan was detected was high in clay content.

Endosulfan entering into natural water bodies in gaseous or dissolved phase is assumed to rapidly adsorb to suspended matter. Sedimentation of particles or direct partitioning to sediment causes rapid removal from the water body. All the sediment samples were found to be acidic in nature, which was a favourable condition for the persistence of endosulfan in sediments. Majority of sediment samples where endosulfan was detected was rich in organic matter.

Correlation analysis was carried out to examine the relationship between the soil and sediment physico-chemical properties and the quantity of endosulfan residues detected (Table 6). The resulting correlation coefficients between soil physico-chemical properties and total endosulfan residues, revealed significant correlation between the organic matter content and endosulfan residues measured in the soil and sediment throughout the entire study area. This suggests that pesticide residue levels in the soil are possibly more associated with organic matter content of the soil, which could be attributed to the fact that endosulfan molecules have greater tendency of binding to organic carbon in the soil. There was positive correlation between clay content and concentration of endosulfan residues. Clay contents are known to influence the dynamics and behaviour of both organic and inorganic pollutants in the soil. The presence of clay immobilizes endosulfan in the soil. These new minerals are able to hold nutrients and organic molecules to their surfaces. Majority of the soil and sediment samples where endosulfan was detected was high in clay content. Negative correlation was found between pH, percentage of sand, silt with the persistence of endosulfan. All the sites in which endosulfan residues were detected were highly acidic, which indicated negative correlation between pH and persistence of endosulfan.

According to the results obtained by the analysis of endosulfan in water, soil and sediment samples collected from 11 panchayats of Kasaragod district, it can be concluded that concentration of endosulfan has been decreasing over a period of time. The degradation rates of both endosulfan isomers are greatly affected by environmental conditions. The study showed that combined toxic residues of endosulfan in the sediment and soil samples of selected areas of Kasaragod district are found to be persistent for a period of 1.5–2 years, but the persistence showed variations depending upon the climatic conditions and physico-chemical characteristics like pH, organic matter content and particle size of the soil in the area. The results also indicated greater persistence of endosulfan in soil and sediment samples than water samples because of greater adsorption of endosulfan on the sediment and soil than water. Comparatively high concentration of endosulfan detected in the soil is because of the fact that endosulfan is fairly immobile in the soil and is highly persistent.

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