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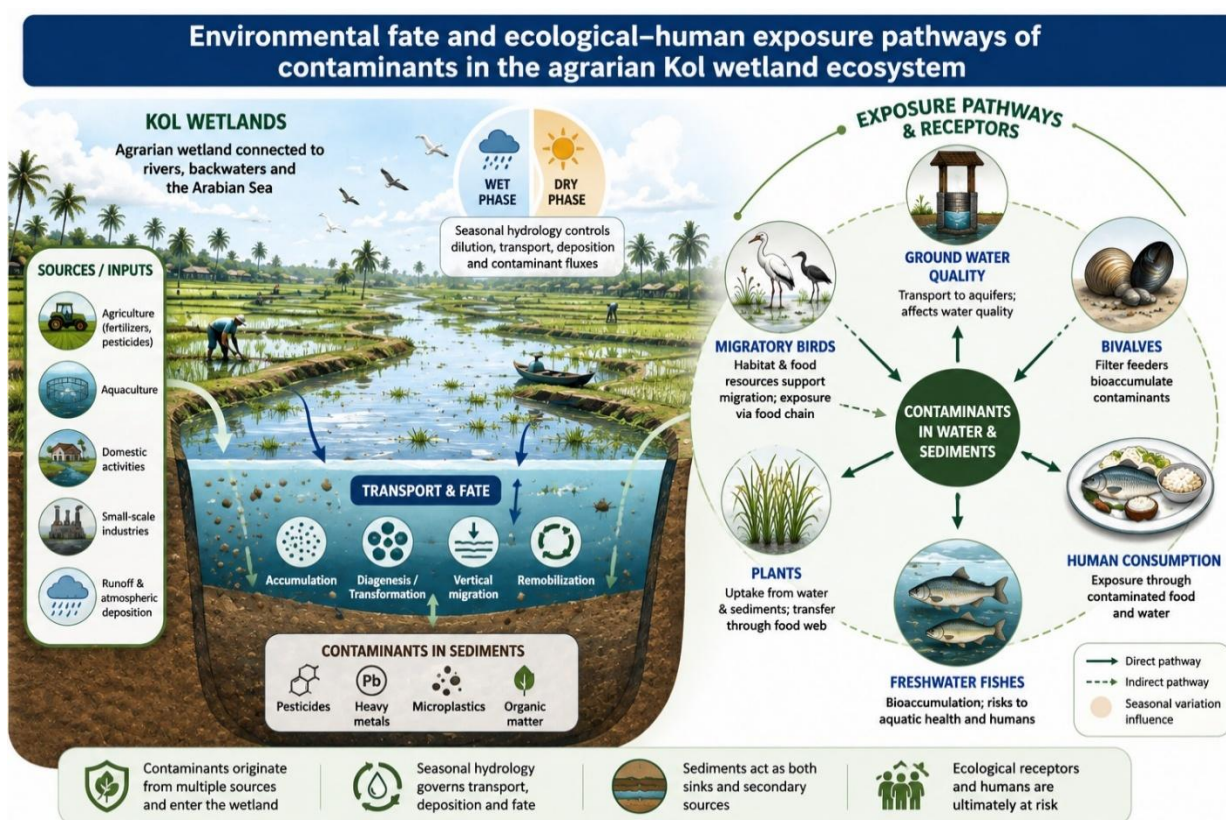
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Sedimentary Fate, Sources, and Ecotoxicological Risk of Persistent Pesticides in the Kol Ramsar Wetland, Southwest India

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Abstract

The agrarian Kol wetland, a Ramsar-listed wetland ecosystem on the southwest coast of India, is subjected to intensive agricultural activities and seasonal inundation, potentially facilitating the transport and accumulation of pesticide residues in sediments. This study investigated the occurrence, seasonal distribution, vertical transport, persistence, potential sources, and ecotoxicological significance of pesticide residues in surface and sediment-core profiles of the Kol wetland. Organochlorine pesticides (OCPs), including HCH isomers, DDT and its metabolites,

dicofol, and butachlor, together with organophosphate pesticides (OPs), including profenofos, ethion, and chlorpyrifos, were detected in surface sediments during wet and dry seasons. The concentrations of $\sum$ DDT were higher during the dry season (31.74 $\mu\text{g/kg}$) than during the wet season (18.62 $\mu\text{g/kg}$), with DDE > DDD > DDT indicating substantial transformation and persistence of historical DDT residues. The α -HCH/ γ -HCH ratio remained below 3 in both seasons, suggesting additional local inputs of lindane or lindane-related sources. Vertical profiles revealed the occurrence of β -HCH, butachlor, and chlorpyrifos in deeper sediment layers, indicating downward transport and burial associated with seasonal inundation and sediment mixing. Sediment quality assessment identified moderate ecological risks at several surface-sediment sites, while elevated $\sum$ DDE concentrations exceeded the Interim Sediment Quality Guideline at selected locations, indicating potential pressure on benthic organisms. Correlation and positive matrix factorization further indicated mixed anthropogenic sources, including contemporary agricultural inputs, historical pesticide deposition, and monsoonal transport. Overall, the findings demonstrate that pesticide residues persist across the sediment profile of the Kol wetland and may undergo redistribution between surface and deeper sediment compartments. The study highlights the need for systematic pesticide monitoring and improved agricultural management to protect the ecological integrity of this Ramsar wetland.

Keywords: Pesticides; wetlands; agriculture; seasonal variations; sediment depth.

1. Introduction

Agricultural practices in wetland habitats have become increasingly important in the growing global demand for food security (McCartney et al., 2010). Multiple uses of wetland habitats are one step toward sustainable wetland management goals. However, development has led to unintended and undesirable consequences, including chemical use, habitat destruction, and flow modification in biodiversity hotspots (Revenga et al., 2005; Nisari & Sujatha, 2021). Unscientific agricultural practices can introduce toxic substances directly into environmental food components through percolation, land erosion, accidental spills, terrestrial runoff, and infiltration (Isman, 2006; Tournebize, 2013; Pal et al., 2024). These processes involve sorption and desorption, chemical reactions, degradation mechanisms, photodecomposition, and microbial activities (Schreiner et al., 2021; Van et al., 2003), and significantly alter the whole prescribed Ramsar criteria (Gardner & Davidson, 2011). Therefore, understanding the ecotoxicological potential of these contaminants

within this heterogeneous Ramsar landscape is crucial for sustainable production (Ericksen et al., 2009).

The alluvial landscape pattern and surface runoff from non-point sources facilitate the transport and dispersion of contaminants that adversely affect agricultural productivity in low-lying fields. Pesticides, fertilizers, herbicides, insecticides, and fungicides are used as agrochemicals and marketed under various commercial brands in new formulations. However, these ubiquitous pesticide residues interact, persist, and accumulate between lithospheric moieties in these low-lying agroecosystems. These agrochemicals induce drastic changes in growth, survival, reproduction, and morphological adaptation within aquatic biotic systems (Seymour, 2005; Kenko et al., 2023; Mu et al., 2023). Moreover, their physicochemical structural features have been considered an indicator of bioaccumulation potential (Chopra et al., 2011; Buah et al., 2018; Osinuga et al., 2023). Consequently, the current evidence suggests that the biomagnification of these micropollutants in the food chain is a significant phenomenon that endangers diverse species in natural Ramsar systems. As a result, anthropogenic contamination has become a major driver of the global deterioration of wetland quality.

Interaction with these harmful pesticides reduces dissolved oxygen levels, impairs water quality, and adversely affects freshwater biota (Akhil & Sujatha, 2018; Sathick et al., 2019; de Souza et al., 2020; Tahir et al., 2021; Ghorbanzadeh et al., 2023; Knauer et al., 2024). Furthermore, organochlorine insecticides have been detected across terrestrial food chains, particularly at higher trophic levels (Rodríguez-Jorquera et al., 2017). Such contamination threatens the survival of rare freshwater flora and fauna, thereby contributing to biodiversity decline (Nowell et al., 2024). In humans, prolonged exposure to organochlorine compounds has been associated with altered enzymatic activity in blood plasma and various organs (Khan et al., 2023). Several organochlorine pesticides are recognized as endocrine-disrupting chemicals that interfere with hormonal regulation and normal physiological functions (Ramzi & Chandramohanakumar, 2020). Chronic exposure to water induces a wide range of biochemical and physiological alterations and increasing the risk of genetic mutations and chromosomal abnormalities (Abdel et al., 2019). Comprehensive investigations of agrochemical contamination in the Ramsar wetland agroecosystem are therefore essential for developing effective mitigation and management practices. Comprehensive investigations into pesticide contamination and its implications for key environmental quality

parameters remain scarce. The present findings establish a baseline for understanding contaminant dynamics and provide a scientific basis for developing targeted management and ecological restoration strategies to safeguard the wetland's long-term ecological integrity.

Environmental Sustainability Index (ESI) rank of India reflects substantial environmental pressures associated with intensive agricultural practices, including the widespread use of agrochemicals (Maggi et al., 2021). According to Zhang (2018), India is among the world's largest consumers of pesticides, highlighting the growing concern over the environmental consequences. However, the extensive application of pesticides in conventional agricultural practices poses considerable challenges to sustainable crop production (Pathak et al., 2022). Several synthetic pesticides have been banned in India; their persistent residues and transformation products can remain sequestered in sediments, where they persist and contribute to long-term environmental contamination (Chakraborty et al., 2023). Strengthening regulatory frameworks, promoting farmer awareness, and implementing standardized guidelines for pesticide application are essential for conserving these ecologically valuable and highly productive agro-ecosystems (Monirith et al., 2003; Sathishkumar et al., 2021). Effective wetland mitigation strategies should therefore integrate protection of existing wetlands, restoration of degraded wetlands, and creation of new wetland habitats. In this context, the sustainable management of these Ramsar wetland agroecosystems is imperative to preserve their ecological integrity while ensuring long-term economic viability and socio-cultural benefits.

The Kol wetland ecosystem, situated within a river system originating in the Western Ghats, represents one of the country's most productive and ecologically significant wetland agroecosystems. Water-based agricultural practices in the Kol wetlands were initiated by local farmers in the 17th century (Srinivasan, 2012). Kol wetlands also provide habitat for numerous resident and migratory bird species, as documented and reported by the Kol Birders group (Praveen et al., 2022). The tropical freshwater ecosystem supports several threatened fish species, including endangered taxa listed in the Red Data Book (Bijukumar et al., 2013; Raghavan et al., 2016; Rodríguez-Jorquera et al., 2017). Exposure to toxic pesticides has been shown to impair reproductive performance, reduce offspring survival, and consequently contribute to population declines in aquatic organisms (Tian et al., 2024). Sediment and water quality undergo degradation due to multiple natural and anthropogenic stressors (Nisari & Sujatha, 2021; Varier et al., 2024;

Nisari & Sujatha, 2024). The monsoon flooding in the Kol field causes complete inundation for six months of a year, and agricultural practices start with ploughing. This is the major reason for the bottom sampling conducted after the continuous surface sediment study. In this context, the present study provides the first baseline assessment of pesticide residues in sediment cores collected from Kol wetlands. Sediment samples were sectioned into discrete depth intervals to characterize the vertical distribution.

The current research plan aims to achieve the following goals. (1) To investigate the spatio-temporal analysis of Organochlorine (OC) and organophosphate (OP) pesticide residual concentrations in the Kol wetlands in eight surface sediments of both the wet and dry seasons. (2) To determine the pesticide residues in the Kol area in the selected bottom portions of two sites in the wet and dry seasons. (3) To analyze the pesticide contamination level of surface and bottom sediments by exploring the pollution indices. Examine the potential ecological risk associated with pesticide residual constituents.

Simultaneously evaluate contamination status, ecological risk, spatial variability, and source contributions through an integrated approach of indices, statistical tools, and Positive Matrix Factorization (PMF) modelling. This work establishes a robust geochemical baseline for the basins and differentiates anthropogenic and geological origins. Furthermore, the receptor-based source determination explains the importance of sustainable agrarian practices in a Ramsar wetland ecosystem.

2. Materials and Methods

2.1 Briefing on the Kol Wetland of Kerala

The Kol agrarian wetland ecosystem is an integral part of the Vembanad- Kol Ramsar site (Ramsar ID: 1214), the second-largest wetland in India. This internationally recognized wetland comprises the Vembanad freshwater lake and the agriculturally productive Kol ecosystem. Both are hydrologically interconnected through the Periyar River and its tributaries (Jayson & Sivaperuman, 2005). This is situated between river systems descending from the Western Ghats, extending from 10°20' and 10°40' S latitudes and 75°58' and 76°11' E longitudes. During the southwest monsoon, six major river tributaries transport large quantities of water and sediments into the Kol floodplains; the interconnected rivers, canals, and backwaters ultimately discharge

into the Arabian Sea (Srinivasan, 2012). The average rainfall in the tropical Kol wetland area was denoted as ≈ 2763 mm (Sarath et al., 2017). The monsoon months from June to December support agricultural activities in the system during the next six months. Water levels typically reach an average depth of 3 meters during the monsoon season. The dry (January to June) and wet (June to December) seasons are the two distinct seasonal variations in the Kol. These traditional community-based water management practices represent a sustainable wetland management system that predates modern agricultural technologies and has been recognized as a model of indigenous ecological knowledge (Aravindh et al., 2019; Panikkaveetil et al., 2020; Kumar & Kunhamu, 2021; Ahaljith et al., 2023; Bonny, 2024).

Agricultural production in the Kol wetlands is closely synchronized with the seasonal monsoon cycle, enabling highly productive rice cultivation during the post-monsoon period (December-May), locally renowned for its “bumper yield”. Following rice harvest, the inundated fields support diverse livelihood activities, including freshwater aquaculture, animal husbandry, duck rearing, vegetable cultivation, lotus farming, medicinal plant collection, and pulse cultivation (Euphrasia & Madhusoodana, 2004; Safnamol et al., 2022; Anusree et al., 2023). Seasonal flooding also sustains an abundant freshwater fish population, and fish auctions are a supplementary income source for local farming communities (Salin et al., 2009; Kumar & Sneha, 2021). Beyond its agricultural significance, the Kol wetland constitutes a biodiversity hotspot along the Central Asian flyway and provides critical habitat for numerous resident and migratory waterbird species, including several taxa listed under the IUCN Red List. Consequently, the ecosystem plays a pivotal role in regional biodiversity conservation while simultaneously supporting the socioeconomic well-being of surrounding communities (Sivaperuman & Jayson, 2000; Greeshma & Jayson, 2020; Chandran et al., 2021; Siji et al., 2021; Kitty & Sajeevan, 2022; Praveen et al., 2022).

2.2 Description of Sampling Stations and the Adopted Procedures

Eight Southern and Northern locations were selected for the present study as surface sampling locations. Surface sediment (S) was retrieved in the wet (W) and dry (D) seasons of September 2018 and April 2019. Duplicate samples were collected from each of the eight sampling sites for environmental replication. Samples were collected from consecutive wet and dry seasons (September 2018, April 2019) according to agricultural activities. These are the two middle months of agrarian and non-agrarian periods of the Kol ecosystem. The continuous ploughing and the

water infiltration change sediment characterization in each monsoon. This dynamic process affects up to a particular depth in the Kol sediment. Two bottom sediments were also collected in September 2019 (W) and April 2020 (D) from Muriyad (M) and Tholur (T) basins to analyze the notable characteristics of the dynamic bottom sedimentary phase in the Kol wetland. The samples were collected using a pushing iron corer (80 cm long with a diameter of 6.3 cm) and an iron corer (60 cm long with a diameter of 8 cm). The depth sampling sites represent the agriculture-based Muriyad and city-oriented Tholur. The three representative core sections identified for the movement of pesticide concentration in to the depth sediment [S1 (0–3 cm), S5 (12–15 cm), and S9 (24–27 cm)]. Collected duplicate bottom samples from the two sites for replication. Surface sediment samples from these selected sites are illustrated in Figure 1. A detailed description of the sample location is provided in Table 1.

2.3 Pesticide Residues in Sediment

10 g of powdered fine sediment was extracted with a hexane: acetone (1:1) mixture (HPLC grade, Glano, Mumbai, India). The extract was subjected to elution through a florisil column (60 cm × 22 m). The extract of the sediment solution was concentrated in a rotary evaporator at 50-60°C. Further analysis and separation were performed using a GC-MS/MS (Thermo Scientific 8000). The GC was equipped with a DB-5 MS capillary column (60 m × 0.25 mm, internal diameter of 0.25 µm, Agilent Technologies, USA). The mass spectrometer's inlet was maintained at 250 °C, and samples were injected in a splitless mode (2 µL injection volume, with a splitless time of 2 min). The GC operated with a constant helium flow rate of 1 mL/min, and the ion source was kept at 260 °C. Electron ionization energy ranged between 40 and 45 eV, with an ionization current of 500 µA. The oven's temperature was programmed as follows: held at 80 °C for 1.5 min, increased at 25 °C per minute until reaching 160 °C, held at 160 °C for 5 min, further increased at 10 °C per minute to 300 °C, and held at 300 °C for 10 min 23 OCPs were analyzed in this study: The GC was calibrated with a standard solution mixture of organochlorine (OC; Mix AD20 and Mix AI21, Italy) and organophosphorus (OP; Mix A33 and Mix E36, Italy) prepared in n-hexane (HPLC grade). Solvent blanks were used to identify external pesticide residues, and duplicate measurements ensured analytical reproducibility. The analyte concentration resulted in a peak with a signal-to-noise ratio (S/N ratio) of 3, and the minimum detection limit was also determined. The OC revealed an efficiency of 97 to 103%, and the OP ranged from 97 to 102%. Relative recovery

was 97%, and the relative standard deviation was < 3.0%. The GC-MS/MS conditions were maintained as follows: injection port temperature 250°C, detector temperature 350°C, oven temperature program: 110°C (5 minutes) at 5°C min⁻¹ to 190°C (2 minutes) at 15°C min⁻¹ to 280°C (10 minutes). 2 µL of the aliquot sample was injected into the column (Akhil & Sujatha, 2014; ShibiniMol et al., 2015). The standardization chromatogram of the pesticide residue is shown in Supplementary Figure 1.

2.4 Persistence and Ecological Risk Assessment

The potential risk of the Pesticide is calculated using the Sediment Quality Guideline Quotient.

$$PELQ_i = MEC_i / PEL$$

MEC_i is the contaminant of the ith constituent, and the PEL is the Probable Effect Level. The risk of pesticides is calculated as the sum of the PELQ_i.

$$SQGQ = \sum_{i=1}^n PELQ_i / n$$

The potential risk is sorted by biological effects of pesticide residues; SQGQ < 0.1 is unimpacted, 0.1 ≤ SQGQ < 1 is moderately impacted, and ≥ 1 is highly impacted (Wang et al., 2017; Deng et al., 2021).

2.5 PMF modelling of data analysis

The PMF model was implemented using EPA (Environmental Protection Agency) PMF 5.0. Positive Matrix Factorization (PMF), developed by Paatero and Tapper (1994), defines the sample matrix as the product of unknown factor matrices and a residual matrix. Positive matrix factorization (PMF) is used for analyzing pollution sources more effectively than other statistical tools that handle uncertainty and mixed sources. This method is helpful for unknown trace metal contamination sources in wetland fields. PMF can effectively deconvolute the contributions of different sources based on observational environmental data. The equation is expressed as:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij}$$

In this equation, represents the concentration of the j th species in the i th sample, g_{ik} denotes the particulate mass concentration from the k th source contributing to the i th sample, f_{kj} is the mass fraction of the j th species from the k th source, e_{ij} is the residual associated with the j th species concentration in the i th sample, and p is the total number of independent sources. In this particular study, three factors were analyzed ($R^2 = 0.94$). In our study, factor number ranging from two to eight were analysed, ultimately leading to the selection of a three-factor solution, as it yielded clear and physically meaningful results. In addition, the three-factor solution gives excellent correlation. This was varied by running the model from various starting points for a specific number of factors and confirming that all runs converged to the same solution. The three factors selected from the ten total seed runs showed an increasing standard deviation. Seventeen types of pesticides two different seasons of sixteen surface and twelve bottom samples were used to raw data for the analysis.

2.6 Statistical analysis

The relationship between water and sediment quality parameters was analyzed using the Statistical Package for Social Sciences (SPSS) version 25 (IBM Corporation). Pearson correlation was calculated to find the sources of these parametric factors. A correlation coefficient > 0.05 is considered the limit, and the dataset was normalized to reduce bias (Khodse & Bhosle, 2013; Cao et al., 2021; Gopal et al., 2023).

2.7 Quality Assurance and Quality Control

Quality Assurance and Quality Control (QA and QC) for pesticide analysis were as follows: surface sediment was also collected separately using metal samplers, and the surface samples were transferred into glass bottles to reduce plastic contamination. The bottom sediments were collected with an iron corer. The samples were frozen at -20°C and stored until analysis. A nickel spatula was used to collect and reduce external contamination. The freeze-dried samples were powdered in an agate mortar (ASTM 230) for the lab analysis. Milli-Q ($18.2\text{ M}\Omega\text{ cm}$) water used to prepare reagents and standards was analytical reagent and ultrapure grade (Merck). The concordant titration values were used. All the materials used in the analytical methods were washed with acid and deionized water (Milli-Q). The Pesticide residue standard was calibrated using an organochlorine mixture (Mix AD20 and Mix AI21, Italy) and an organophosphorus mixture (Mix A33 and Mix E36, Italy) prepared in n -hexane (HPLC grade). The chemicals and solvents were obtained from Merck (India/Germany). All laboratory procedures were carried out to prevent

external contamination during OCP analysis under controlled conditions. Glassware was thoroughly rinsed with acetone and n-hexane before use. All analytical standards were obtained from Sigma-Aldrich. One procedural blank was included for every batch of 10 samples to monitor potential laboratory contamination. The limit of detection (LOD) was determined based on a signal-to-noise ratio (S/N) of 3:1 for each target analyte. Instrumental detection capability was evaluated using GC–MS/MS response characteristics, while laboratory background contamination was assessed through the analysis of procedural blanks. The limit of quantification (LOQ) was established using the laboratory validation criteria based on the variability observed in procedural blanks. Method detection limits (MDLs) for the target OCPs ranged from 0.001 to 0.0028 ng g⁻¹ dry weight (dw). Concentrations below the corresponding MDLs were reported as non-detectable. Surrogate recoveries for 2,4,5,6-tetrachloro-m-xylene (TCMX) ranged from 85 to 110%, indicating satisfactory analytical performance. Therefore, no recovery correction was applied to the reported OCP concentrations.

3. Results and Discussion

3.1 Spatio-temporal Distribution of Pesticide Residues in Surface Sediment

The study investigates the agricultural practices scenario on the Kol ecosystem, specifically focusing on commonly used pesticides, including HCH and its isomers, as well as DDT and its metabolites. The organochlorine classes: Σ HCH (α -HCH, β -HCH, γ -HCH, and δ -HCH), DDT (p, p'-DDD, o, p'-DDD, p, p'-DDE, p, p'-DDT, and Dicofol), and Butachlor were detected in the surface sediment (S). Organophosphates (Profenofos, Ethion, and Chlorpyrifos) were detected in eight surface sediment samples from Kol during both the wet (WS) and dry (DS) seasons. The different isomers of HCH (α -HCH, β -HCH, γ -HCH, and δ -HCH) are illustrated in Figure 2.

The dry seasonal variation of Σ HCH isomers is illustrated in Figure 2 (b). The city-oriented Tholur (DS8) denotes that the isomers of Σ HCH are α -HCH (0.19 μ g/kg) and γ -HCH (0.25 μ g/kg). Different agrochemicals from terrestrial runoff add lindane (γ -HCH) to the low-lying fields (Tadesse et al., 2021). The total concentration in all sampling sites decreased in the order of α -HCH > γ -HCH > β -HCH > δ -HCH. Photooxidation and microbial activities are the major reactions that produce the toxic substituents of such pesticides (Doong et al., 2002a). The highest α -HCH was detected in the Muriyad region during the wet season. Among the HCH isomers, α -HCH easily

diffuses into the air and is transported over long distances. In contrast, β -HCH is more resistant to hydrolysis and degradation. Hence, they are more persistent in the sediment (Barakat et al., 2013). The connected Kol area enhances the chances of transporting and dispersing the chemicals to other fields. The presence of migratory birds, phytoplankton, and freshwater fishes directly impacts the OC components (Biggs et al., 2007; Costa et al., 2011; Bhat et al., 2022; Hatamleh et al., 2022). The δ -HCH isomer is the only moiety present at the Dry Pullu-S4 site, indicating the history of HCH use in the particular region. The low vapor pressure of β -HCH is the main reason for the persistence of specific components present in the sediment. Based on the half-life of the predicted persistent group of chlorinated hydrocarbon insecticides (Yang et al., 2005a).

The DDT and its metabolites in the dry and wet surface sediments are delineated in Figure 3. The penetration of DDT into leaves under various pressure conditions raises concern over Ramsar sites (Guo et al., 2014; Mitton et al., 2016). The different metabolites of DDT are represented as Σ DDT, which includes o, p'-DDT, p, p'-DDT, p, p'-DDE, o, p'-DDD, p, p'-DDD, and Dicofol. The oxidation of DDT leads to the formation of dicofol, and dehydrochlorination results in the addition of dichlorodiphenyldichloroethylene (DDE), resulting in dichlorodiphenyldichloroethane (DDD). The formation of reductive dichlorination generates DDD in sediments (Connell & Miller, 2022). The presence of these banned insecticides signifies the persistence of pesticides in the sediments and their accumulation properties. These various degradation products present in surface sediments during two different seasons are explained here. The wet-season Σ DDT in the surface sediment is illustrated in Figure 3 (a), and the dry-season Σ DDT constituents are graphed in Figure 3 (b). A higher Σ DDT was detected in the dry (31.74 $\mu\text{g/kg}$) than in the wet (18.62 $\mu\text{g/kg}$) season sediments. The total concentration of each metabolite decreases in the order of DDE > DDD > DDT, in both the wet and dry seasons. The high DDE concentration was also reported in the Mekong Basin (Triet et al., 2013). The persisting characteristics of DDT and sub-components enhance the toxicity level in the ecosystem (Hoffman et al., 2002). The high levels of DDT during dry seasons increase deposition in the tissues of migratory birds in Kol (Senthilkumar et al., 2001; Hooper et al., 2002; Yohannes et al., 2017). The penetration of DDT in leaves under pressure variations was pointed out for the Ramsar sites (Guo et al., 2014; Mitton et al., 2016).

Seasonal variations in butachlor herbicides in the surface sediment are illustrated in Figure 4. During the dry season, butachlor was detected at Muriyad (DS1) at a concentration of 0.40 $\mu\text{g/kg}$,

whereas concentrations at Parappukara (S2) were below the detection limit, suggesting limited herbicide use in the predominantly residential farming area. Overall, elevated butachlor concentrations were observed in the agrarian Kol wetland during the dry season. The persistence of butachlor in wetland sediments may be attributed to the environmental characteristics, which can reduce photodegradation and promote the retention of toxic organic compounds. Herbicides are easily degraded under different atmospheric conditions, and their persistent nature causes harmful effects on aquatic organisms (Linz et al., 1997; Edge et al., 2020; Vonk & Kraak, 2020; Tyohemba et al., 2021). Because butachlor can persist under certain environmental conditions, its presence in aquatic ecosystems may pose risks to aquatic organisms (Yu et al., 2018; Yuan et al., 2018). The mean concentration of organophosphate (OP) in the Kol wetlands is illustrated in Figure 5. The photolysis, hydrolysis, and oxic-redox cyclic process of the physico-chemical characteristics of sediments and water depend upon the genesis of organophosphates in the wetland sediments (Cupples et al., 2000). Chloropyrifos, Profenofos, and Ethion are the major OPs determined in the Kol surface sediment. The wet-season OP in surface sediments is incorporated in Figure 5 (a). The dry-season OP in the surface sediment is illustrated in Figure 5 (b). The high decomposition factor and high enzymatic activities are the reasons for the absence of Profenofos in the dry-season samples (El-Bouhy et al., 2023). Systematic detection of the OPs and their impact assessment is a serious issue considering the aquatic environment. The hydrogeological variations and community structure variations in the soil organisms are the most important causes of these synthetic chemicals. The moderate action of the cell membrane production and photosynthesis directly affects the diminishing of plant species. These toxic substances from the water and sediment phases bioconcentrate and bioaccumulate in the food chain from lower to higher trophic levels.

3.2 Spatio-temporal Distribution of Pesticide Residues in Bottom Sediment

Human interaction and surface runoff enhance the transport of the contaminants and their settling in the bottom sediments (Nisari & Sujatha, 2021). These enhance the mixing of pesticides in the sediment layers of agrarian Kol lands (Zeng & Chen, 2011; Divya et al., 2021). Agricultural activities and alluvial deposition point to the dynamic nature of the surface area and the importance of studying the bottom sedimentary profile of the Kol layers. This preliminary baseline assessment

of the bottom portions concentrates on the upper, middle, and bottom portions of the Southern Muriyad (M) and Northern Tholur (T) samples in the wet (W) and dry (D) seasons.

The pesticide residue concentration in the core is illustrated in Figures 6 and 7. The two bottom sediments [Muriyad (M) and Tholur (T)] were selected from the eight surface sediments. The three subsections of each depth core between dry [D1 (0–3 cm), D5 (12–15 cm), and D9 (24–27 cm)] and wet seasons [W1 (0–3 cm), W5 (12–15 cm), and W9 (24–27 cm)]. Two types of OC and one OP pesticide were detected in the wet season bottom sediments. The detected pesticide in Muriyad during the wet season is graphed in Figure 6 (a). During the wet season, the upper (0–3 cm) portion of Muriyad (WM1) samples detected the chlorpyrifos (1.99 µg/kg) concentration. In the middle portion, Butachlor (0.46 µg/kg) and chlorpyrifos (4.96 µg/kg) were detected. In the bottom WM9 portion, butachlor (0.33 µg/kg) and chlorpyrifos (3.56 µg/kg) were found. The pesticide residue concentration in Wet Tholur samples is illustrated in Figure 6 (b). β-HCH (0.25 µg/kg) and chlorpyrifos (2.28 µg/kg) were detected in the Tholur surface sample (WT1, 0–3 cm). The middle portion (WT5, 12–15 cm) denotes the concentration of Butachlor (0.25 µg/kg) and Chlorpyrifos (4.02 µg/kg), and in the bottom layer (WT10, 24–27 cm), β-HCH (0.20 µg/kg), Butachlor (0.45 µg/kg), and Chlorpyrifos (3.70 µg/kg) were recorded. The presence of β-HCH in the bottom portions indicates the residue from past application of HCH, which moved with the water into the inner layers of the Kol sediments. The higher OP in the Kol sediment denotes the usage of these pesticides (Piao et al., 2004). The OP affects the ecological cycle and interlinked biotic systems (Wee & Aris, 2017; Zarei-Choghan et al., 2022; Hu et al., 2024). However, the pesticide profiling of the environmental niche has become a major concern for the public.

Compared with the dry samples, various types of pesticides were detected in the Kol sediment samples. The distribution of pesticide residues in Muriyad samples during the dry season is illustrated in Figure 7 (a). α-HCH (0.23 µg/kg), β-HCH (0.41 µg/kg), Dicofol (1.23 µg/kg), o, p'-DDD (0.56 µg/kg), p, p'-DDE (3.34 µg/kg), and chlorpyrifos (3.72 µg/kg) were detected in the dry Muriyad DM1 portion. In the middle portion (DM5) of the Muriyad area, the presence of p, p'-DDE (0.30 µg/kg) and chlorpyrifos (1.57 µg/kg) was noted. The bottom portion (DM9) of the Muriyad samples α-HCH (0.24 µg/kg), β-HCH (0.28 µg/kg), p, p'-DDE (0.36 µg/kg), and chlorpyrifos (3.51 µg/kg) were recorded. The dry seasonal Tholur samples are included in Figure 7 (b). In Tholur, the surface samples (DT1), β-HCH (0.38 µg/kg), p, p'-DDT (0.34 µg/kg), and

chloropyrifos (2.66 $\mu\text{g/kg}$) were determined. The second portion (DT5) of the Tholur area was detected with Butachlor (0.45 $\mu\text{g/kg}$), p, p'-DDT (0.33 $\mu\text{g/kg}$), Ethion (0.36 $\mu\text{g/kg}$), and Chloropyrifos (6.89 $\mu\text{g/kg}$). The detected pesticide residue in the bottom portion (DT9) of the Tholur samples was Butachlor (0.31 $\mu\text{g/kg}$), p, p'-DDT (0.23 $\mu\text{g/kg}$), Ethion (0.31 $\mu\text{g/kg}$), and Chloropyrifos (5.32 $\mu\text{g/kg}$).

Studies on the residual level of pesticide accumulation in wetland sediments are limited. Generally, the vaporisation mechanism is faster in wet sediments than in dry seasonal sediments due to the variation in adsorption rates, capillary movement, and sediment solution dispersion on the bed surface. The inverse relationship between the organic matter content, Lindane, and dieldrin has been reported in earlier studies (Calvo et al., 2021; Sahin & Karpuzcu, 2020). The transformation of pesticides, including biodegradation, detoxification, and related metabolism, is the subject of extensive investigation. The comparison of pesticide concentrations with worldwide wetlands is incorporated in Table 2. The ΣDDT s of the Kol wetlands (0.25 to 20.25) are higher than the Hugli Estuary (Guzzella et al., 2005) and lower than Cochin estuary (Akhil & Sujatha, 2014). The ΣHCH concentration was detected as similar to Hugli Estuary (Guzzella et al., 2005), Vietnam Estuary (Hong et al., 2006), and Maryut Lake, Egypt (Barakat et al., 2002).

3.3 Persistence

The $\alpha\text{-HCH}/\gamma\text{-HCH}$ ratio reveals the relative stability, resistance to microbial activities, and persistent character in wetlands. The ratio chart is shown in Figure 8. The $\alpha\text{-HCH}/\gamma\text{-HCH}$ ratio of Kol wetlands indicates that the $\alpha\text{-HCH}/\gamma\text{-HCH}$ ratio in both dry and wet seasons was below 3, showing new additional input from the frequent local usage of lindane or its substitutes in the surface sediments of the ecosystem (Chen et al., 2011; Akhil & Sujatha, 2014; Qian et al., 2020). These earlier findings support the re-emission of lindane, corroborating the results of Doong et al., 2002 and Wang et al., 2009.

The ratios of different metabolites of DDT are used to detect the anaerobic and aerobic processes of addition (Yang et al., 2005b; Akhil & Sujatha, 2014). The ratio of DDE + DDD / DDT is illustrated in Figure 9. The DDE+DDD/DDT ratio varied from 0.20 (WS4) to 4.98 (WS3) in the wet seasonal samples, and in the dry season, it ranged from 0.75 (DS2) to 6.98 (DS5). The ratio content in the Wet season is <1 in the WS4 (0.20), WS5 (0.63), and WS8 (0.88) samples and the

DS2 (0.75). The high values indicate the presence of aged and weathered DDT compounds in the aerobic processes of the Kol sediment. This evidence supports the aerobic process and the use of DDT in the same Kol surface sediment samples in the past.

3.4 Ecotoxicological Significance

The biological effects of the sediment OC residue are shown in Figure 10. The SQGQ for the surface sediment explains the ecological impacts of pesticides on the Kol ecosystem. The surface sediment samples and the dry depth samples have concentration levels and PEL values, which enable calculation of the risk factor for the particular Kol ecosystem (Costa et al., 2011; Deng et al., 2021). The biological effects of the concurrent detection limits on surface wet sediment samples vary from 0.007 to 0.23, and the ecological risk coefficient of dry samples ranges from 0.02 to 0.30. The sediment quality guideline method shows that the WS1, WS3, and WS7 wet surface sediment samples indicated a moderate potential risk to organisms. The dry surface sediment samples pose a moderate risk to biological organisms in four sampling sites, namely DS3, DS5, DS6 and DS7.

The Sediment Quality Guideline Quotient (SQGQ) for bottom sediment is illustrated in Figure 11. In the bottom sediment samples, the surface of Muriyad has a moderate ecological risk. The moderate risk in an ecosystem always suggests a risk to ecosystem conservation and management practices. Previous reports indicate the presence and impacts of pesticides in Kerala (Akhil & Sujatha, 2012; ShibiniMol et al., 2015; Gopalan & Chenicherry, 2018; Krishnan & Sujatha, 2020; Divya et al., 2021). The surrounding locale is also constantly using agrochemicals to enhance crop productivity. The comparison of OCP concentrations in the Kol wetlands with the standard quality guidelines from the Canadian freshwater and the USEPA protocols is presented in Table 3. The guidelines of Canada and USEPA denote different levels of concentrations termed ISQG (Interim sediment quality guidelines), PEL (Probable Effects Level), and TEL (Technical Equivalent Level) (Long & MacDonald, 1998; CCME, 2002; USEPA, 2003; Costa et al., 2011; Tian et al., 2013). The minimum and maximum values are listed and compared with the standard values. The γ -HCH, $\sum$ DDT, and $\sum$ DDD concentrations of the Kol wetlands were below the standard values. The source determination and degradation pattern of each pesticide moiety revealed that the present contamination levels were likely from historically bioaccumulated sources. The detection level of

pesticide residues indicates that the possibility of cancer risk through human exposure to such an environment cannot be negligible.

Σ DDE results are illustrated in Figure 12. The Σ DDE concentration was higher than the Interim Sediment Quality Guidelines (ISQG), indicating the risk of the DDE (> 1.42) component in the WS3, WS7, DS1, DS3, DS5 and DS7 surface sediments. The high risk of sediments imposes potential ecological pressure on the benthos and related environments. The Threshold Effect Level (TEL) of the Σ DDE in the sediment is $3.16 \mu\text{g/kg}$. The concentrations of WS3, DS3, DS5, and DS7 is higher than the threshold limit, which justifies that these areas are exposed. The use of banned organic chlorines (OC) and their counterparts was well evidenced from these recorded results. Leaching and runoff through agricultural fields could elevate the concentration levels of pesticides. Agricultural farming is one of the major primary sources of persistent organic moieties (ShibiniMol & Sujatha, 2015; Buck et al., 2020). New trends in agricultural scenarios have become a causative factor for the increasing trend in pesticide residues in the aquatic system, altering the sustainable wetland criteria (Gardner & Davidson, 2011).

3.5 Interlinkage and source

The α -HCH, organophosphates and organochlorides were correlated with each other (Figure 13). The α -HCH with γ -HCH ($.809^{**}$), o, p'-DDD ($.651^{**}$), p, p'-DDE ($.700^{**}$), p, p'-DDD ($.621^{*}$), and dicofol ($.784^{**}$). Interrelation between the chemicals indicates the scavenging of pesticides in the Kol sediments. The DDT metabolites have a similar interaction with γ -HCH ($.536^{*}$ to $.690^{**}$) and dicofol ($.658^{**}$), which was noted. The relation implies the freshly added organophosphorus pesticide constituents with the DDT metabolites. Factor 1 was primarily composed of chlorpyrifos (83%) and α -HCH (70%), with no signals from DDT metabolites. The HCH isomers and the phosphate pesticides explain the interrelation and the local or regional source of addition. Factor 2 is composed of HCH and dicofol, with the DDD compounds (38%), indicating past deposition of dicofol and long-term transportation. The biotransformation of DDT to DDD affects the historical usage. Factor 3, composed without DDD, indicated that all compounds originated from the same source, primarily a higher proportion towards the monsoonal inputs from the surrounding area. The PMF modelling suggests anthropogenic input of pesticides in the Kol wetland. The HCH, DDT, and Phosphate composites are accumulated together within the inner core with pore water.

4. Conclusion

Wetland mitigation requires regulations to support wetland sustainability. The success rate of these projects could improve if sites were assessed using a systematic, ordered approach. Systematic restoration with multifunctional activities could be explored in the new era of these unique terrains. The debatable development also highlights unintended and undesirable consequences for the overall environmental niche. However, the mechanisms of the serious action plan for this amalgam remain inadequately understood, especially in wetland sediments. The preservation of existing wetlands, the creation of new wetlands, and the restoration of previously converted cropland into a newly mechanized one were included in wetland mitigation strategies. In this context, sustainable management of these remaining wetland agroecosystems becomes imperative from ecological, economic, and socio-cultural perspectives. The total concentration in all surface sediment sampling sites decreased in the order of α -HCH > γ -HCH > β -HCH > δ -HCH. The presence of migratory birds, phytoplankton, and freshwater fishes directly affects the consequences of the OC components due to their widespread distribution. Two prominent entries to the environmental matrices are the dumping of waste and industrial effluent discharges. Besides, diffuse sources of deposition and atmospheric pathways also contribute to the contamination of the wetland ecosystem. The δ -HCH is only present at the Pullu site (dry season), indicating that mostly HCH was used previously in this particular region. The most abundant HCH isomer was α -HCH in the wet and dry seasonal sediments. The α -HCH/ γ -HCH ratio in both dry and wet seasons was under 3, which reveals freshly added lindane from local usage. It is also supported by the PMF modelling factor detection. A higher $\sum$ DDT was detected in the dry season, rather than in the wet season sediments. The total concentration of each isomer decreases in the order of DDE > DDD > DDT, in both the wet and dry seasons. The evidence of the ratio DDE /DDD supports the aerobic process and the past use of DDT in the same Kol surface sediment samples. Elevated levels of Butachlor were detected during the dry seasonal agrarian time in the Kol wetland system. The high risk imposes a potential ecological pressure on the benthos and related environments. The presence of β -HCH in the bottom portions indicates the movement towards the pore space of the Kol sediment system. The high variance of pesticide concentration in wet season depth sediments describes the agrarian inputs of these moieties in the Kol ecosystem. The sediment quality guidelines indicate moderate potential risk to organisms in wet surface sediment samples and a moderate risk to biological organisms in the dry surface sediment. Depth sediment samples, only on the top sub-surface samples of Muriyad, show a moderate ecological risk value. The $\sum$ DDE concentration was

higher than the ISQG, and the TEL level indicates the risk of DDE components in the surface sediment. Studies on the residual level of pesticide accumulation in wetland sediments are limited, especially in agrarian field sediments. Generally, the vaporisation mechanism is faster in wet sediments than in dry seasonal sediments due to the adsorption rates, capillary movement, and sediment distributional phase on the bed surface. The moderate risk in this ecosystem suggests conservation and management practices in the Kol wetlands.

Credi authorship contribution statement

Nisari A R: Writing – original draft, Formal analysis, Validation, Investigation, Data curation.

Sujatha C H: Writing – review & editing.

Declaration of competing interests

We wish to confirm that there are no conflicts of interest associated with this manuscript.

Data availability

Data will be made available on request.

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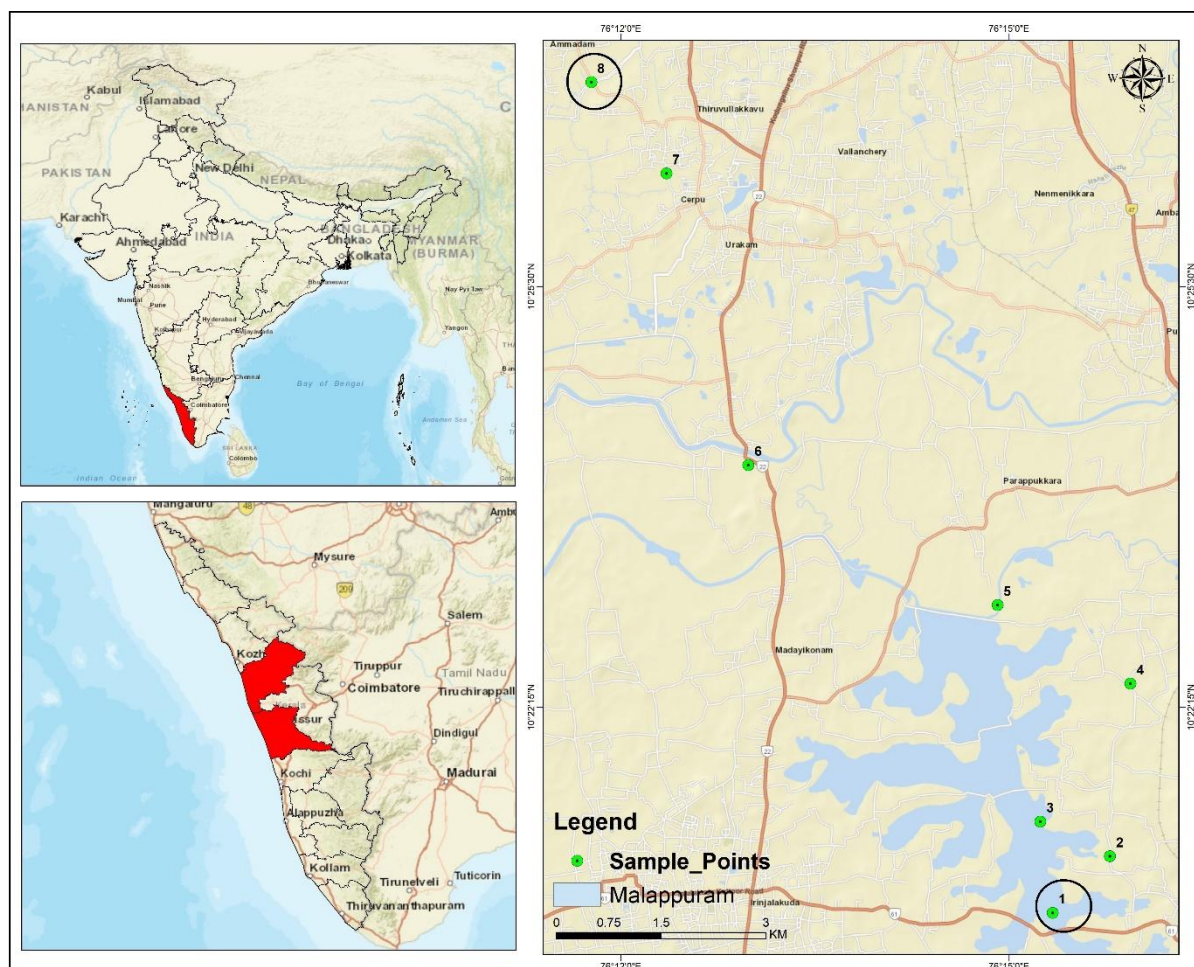
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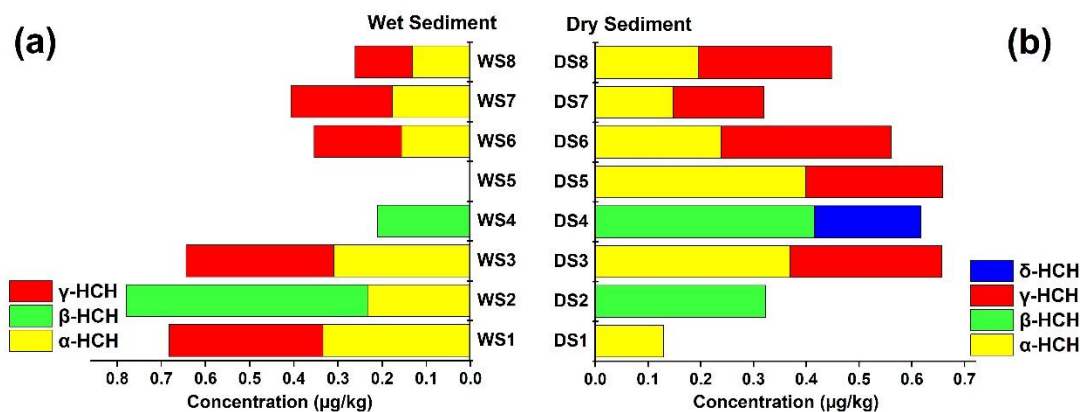
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793 **Figure 1** Study area map of Kerala Kol wetlands

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Figure 2 HCH isomer composition in the (a) wet and (b) dry seasonal surface sediment.

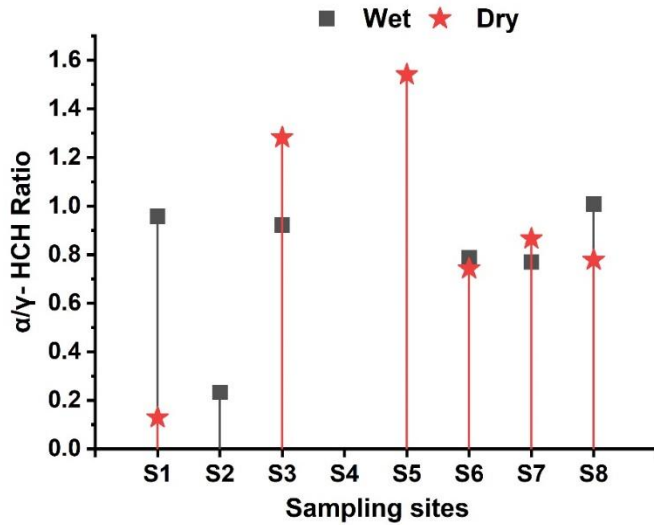


Figure 3 α -HCH/ γ -HCH ratio of Kol sediment.

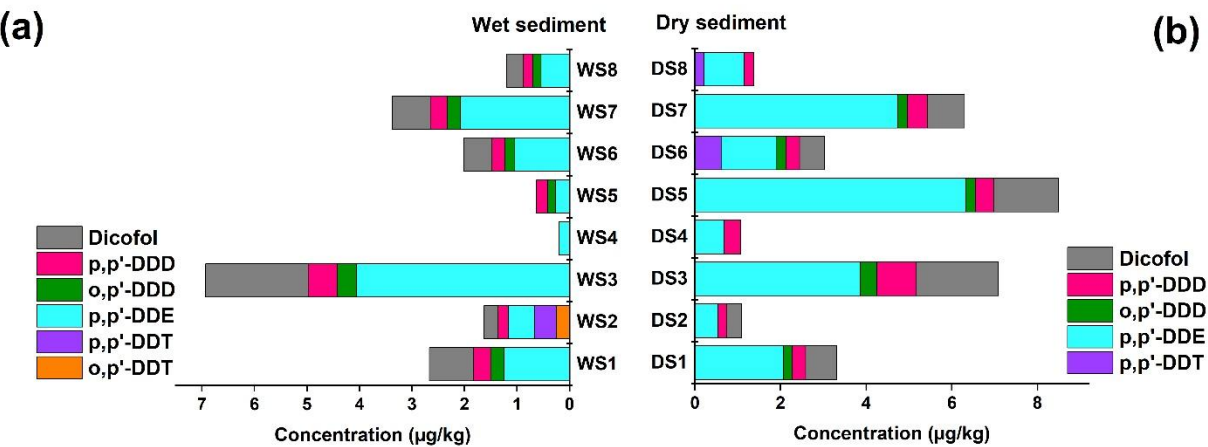


Figure 3 Distribution of DDT in the (a) wet and (b) dry surface sediment.

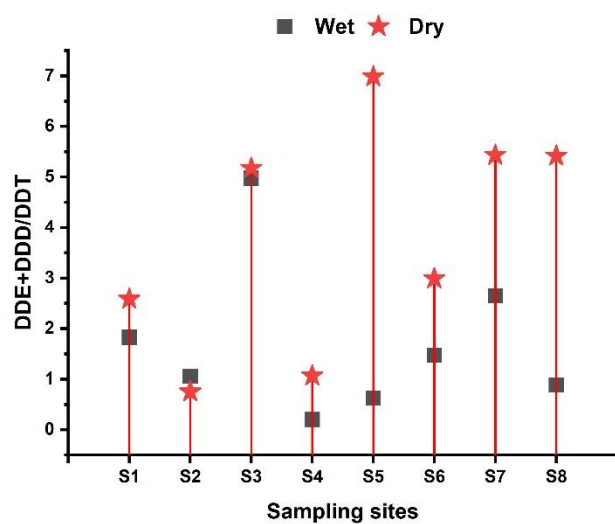
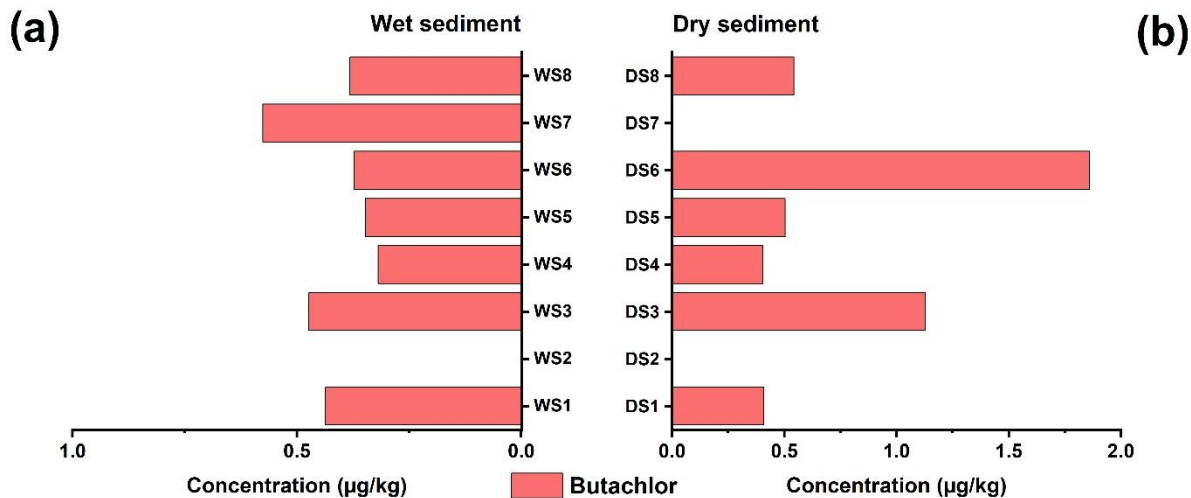


Figure 5 DDE+DDD/DDT ratios of surface sediment.

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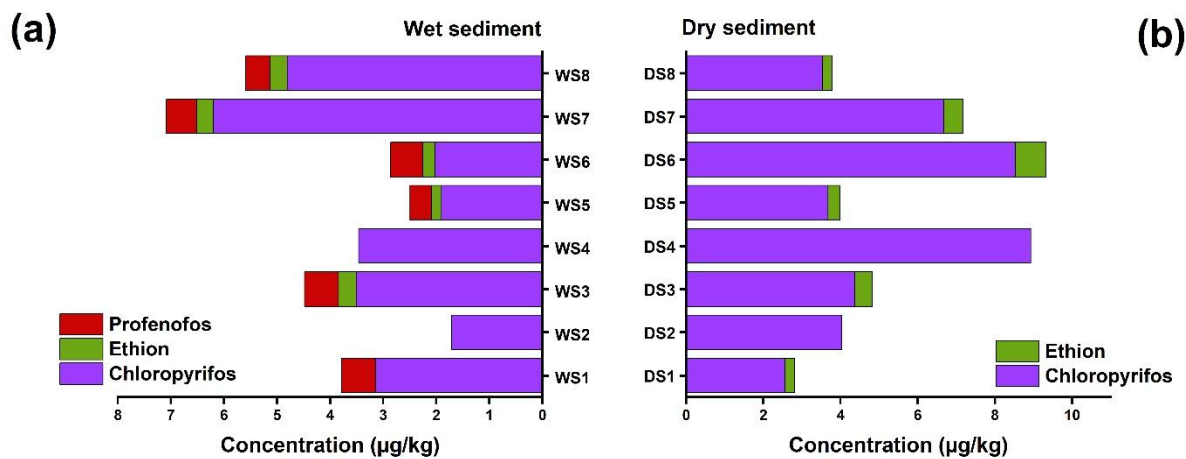


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819 **Figure 4** Butachlor in the Kol surface sediment in (a) wet and (b) dry seasons.

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822 **Figure 5** OP in the surface sediments of Kol wetlands in the (a) wet and (b) dry seasons.

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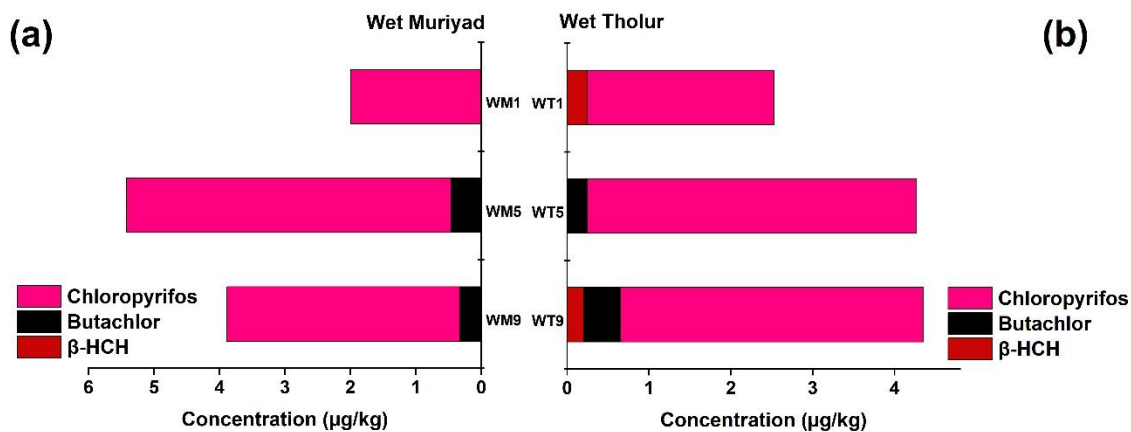


Figure 6 Pesticide residues in the wet Kol bottom sediment of (a) Wet Muriyad and (b) Wet Tholur.

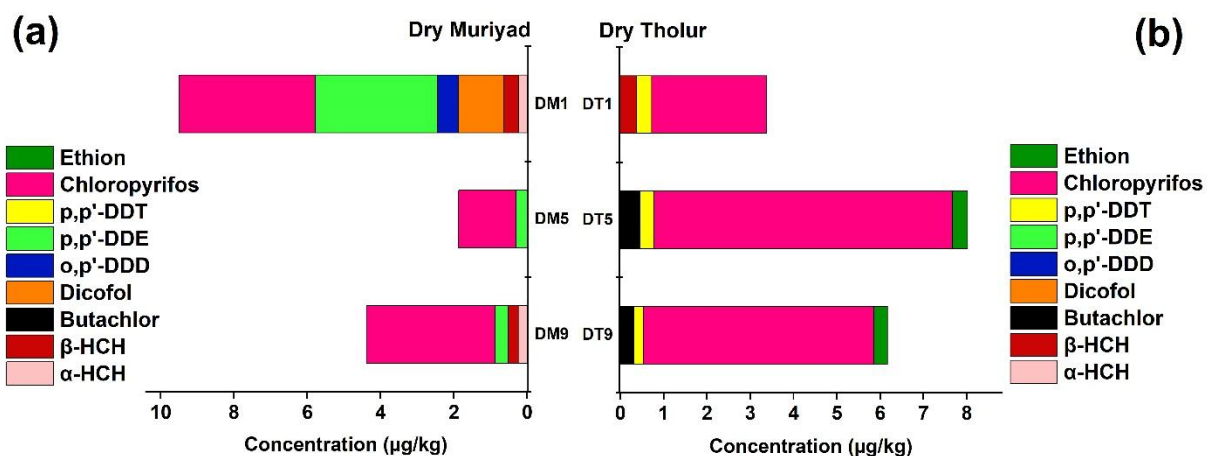
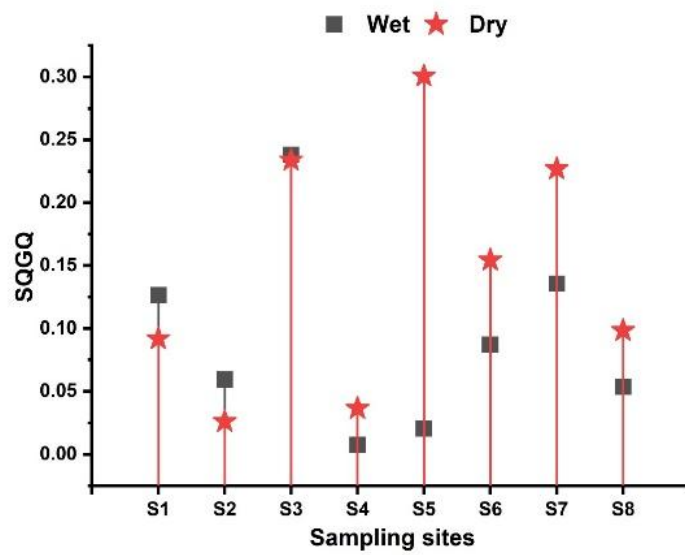


Figure 7 Pesticide residue in the dry Kol bottom sediment of (a) Dry Muriyad and (b) Dry Tholur.

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843 **Figure 10** Sediment Quality Guideline Quotient of surface sediment.

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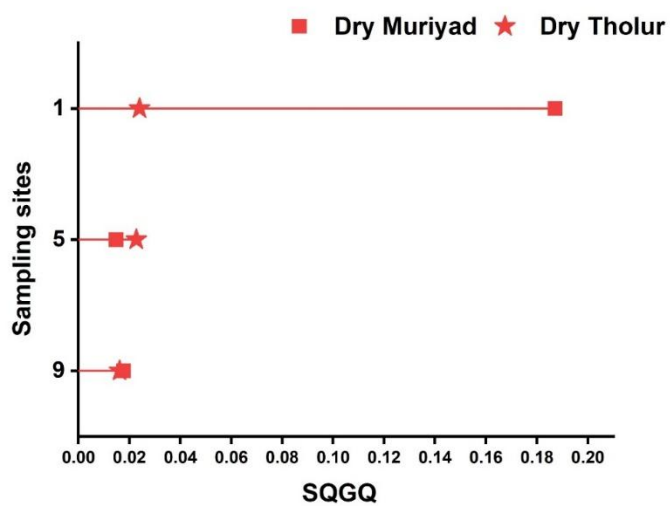


Figure 11 Sediment Quality Guideline Quotient of bottom sediment.

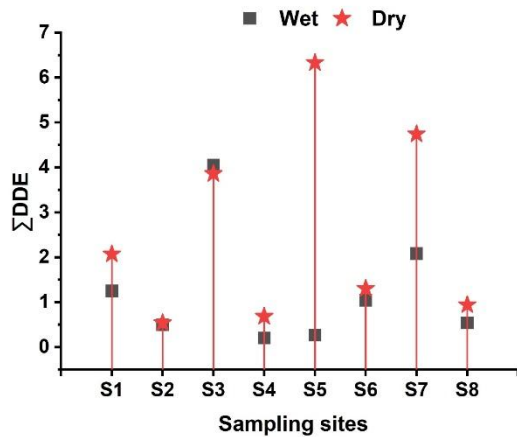
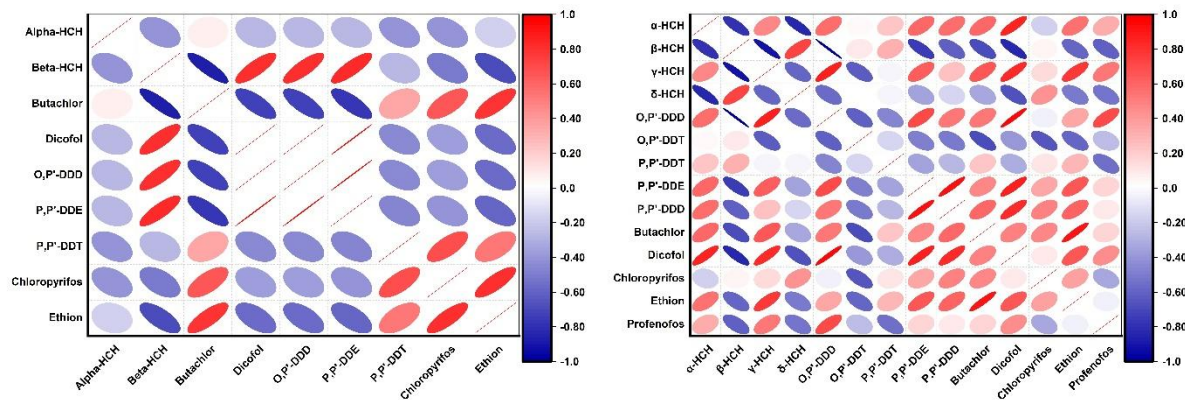


Figure 12 Σ DDE concentration of surface sediments in wet and dry seasons.



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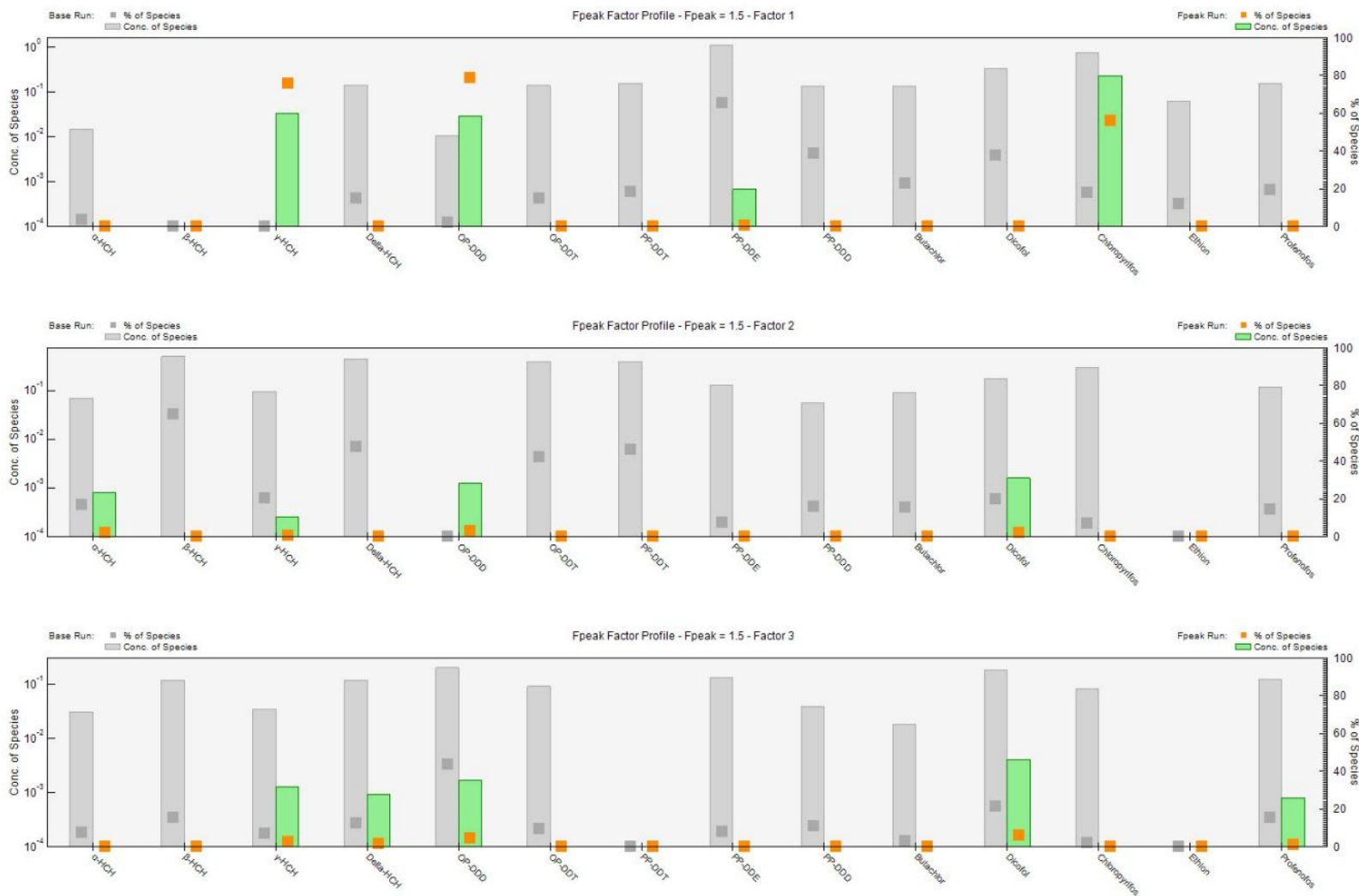
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Figure 13 Correlation plot of the top and bottom portions of the Kol sediments.



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Figure 14 Compositions and distributions of pesticides in the 3 factors from PMF running with Kol sediment.

Table 1 Coordinates of selected surface sampling study points in Kol wetlands.

Basins	Stations	Sites	Coordinates		Description
South	Muriyad	1	10° 21' 06.0" N	076° 15' 46.9" E	Agriculture area
	Parappukara	2	10° 23' 02.4" N	076° 14' 54.8" E	The presence of freshwater ponds
	Mullurkayal	3	10° 26' 22.4" N	076° 12' 21.2" E	Near to residential activities
	Pullu	4	10° 27' 04.7" N	076° 11' 46.4" E	Rice cultivated field
North	Vazhakkal	5	10° 27' 14.0" N	076° 10' 37.2" E	Residential area
	Manakody	6	10° 29' 22.3" N	076° 07' 53.0" E	Presence of brick manufacturing unit
	Manaloor	7	10° 30' 00.7" N	076° 06' 37.5" E	Combination of rice and fish culture
	Tholur	8	10° 33' 22.9" N	076° 06' 02.9" E	Commercial area

Table 2 Comparison of OC pesticide concentrations ($\mu\text{g/kg}$) in sediments from other worldwide

Area	Year	Σ DDTs	Σ HCHs	References
Hugli Estuary, India	2003	0.18–1.93	0.11–0.40	Guzzella et al., 2005
Vietnam Estuary	2003–2004	0.31–274	ND–1.00	Hong et al. (2008)
Maryut Lake, Egypt	2005	0.07–105.6	ND–2.20	Barakat et al., 2002
Baiyangdian Lake, China	2007–2008	1.3–51.3	4.7–679	Hu et al., 2010
Cochin Estuary	2009–2011	229–418	423–23.7	Akhil & Sujatha, 2014
Kol wetlands	2017–2018	0.25–20.45	0.75–1.45	Present study

locations.

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906 **Table 3** Comparison of OC pesticide concentrations in Kol with the International Toxicity

907 Guidelines.

OCPs (µg/kg)	Canada		USEP		Surface		Depth	
	ISQG	PEL	TEL	PEL	Wet	Dry	Wet	Dry
γ-HCH	0.94	1.38	2.37	4.99	BDL–0.35	BDL–0.32	BDL	BDL
ΣDDT	1.19	4.77	4.16	62.9	BDL–0.67	BDL–0.61	BDL	BDL–0.34
ΣDDE	1.42	6.75	3.16	31.3	0.2–4.05	0.53–6.33	BDL	BDL–3.34
ΣDDD	3.54	8.51	4.88	28	BDL–0.93	0.21–1.31	BDL	BDL–0.57

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