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Hidden risk of terrestrial food chain contamination from organochlorine insecticides in a vegetable cultivation area of Northwest Bangladesh

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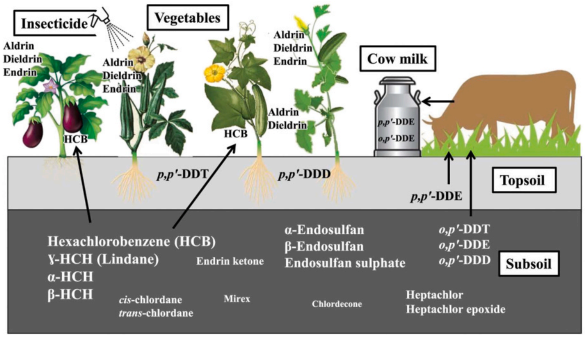
HIGHLIGHTS

- Organochlorine insecticide residues are alarming for terrestrial food chain.
- Diversified insecticides residues were detected in the subsoil than topsoil.
- Aldrines and hexachlorobenzene were present in vegetables and DDT in milk.
- Both historical and recent insecticides applications behind the contamination
- Combined concentration of multiple insecticide residues poses a greater risk.

GRAPHICAL ABSTRACT



- Multiple organochlorine insecticide residues detected in soil, vegetables, and milk within acceptable single residue levels.
- Greater diversity of organochlorine insecticide residues in the subsoil than topsoil might have resulted from historical applications.
- Aldrines and hexachlorobenzene in vegetables might have resulted from both historical and recent applications and DDT in milk from grazing on contaminated land.
- Combined concentration of acceptable levels of single residue could pose greater risks when multiple residues are present.
- Strong embargoes on fresh applications of organochlorine insecticides, restricted pasture on contaminated land, and regular monitoring are needed.

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ABSTRACT

Organochlorine insecticide (OCI) exposures in terrestrial food chains from historical or current applications were studied in a vegetable production area in northwest Bangladesh. A total of 57 subsoil, 57 topsoil, and 57 vegetable samples, as well as 30 cow's milk samples, were collected from 57 farms. Multiple OCI residues were detected using GC–MS/MS with modified QuEChERS in 20 % of subsoils, 21 % of topsoils, 23 % of vegetables, and 7 % of cow's milk samples. Diversified OCI residues were detected in subsoils (17 residues with a concentration of 179.15 ± 148.61 μg kg^{-1}) rather than in topsoils (3 DDT residues with a concentration of 25.76 ± 20.19 μg kg^{-1}). Isomeric ratios indicate intensive historical applications of OCIs. According to Dutch and Chinese standards, the lower concentrations of individual OCI residues in the soil indicate negligible to slight soil pollution, assuming local farmers follow local pesticide use regulations. However, a maximum of 78.24 μg kg^{-1} ΣAldrines and 35.57 μg kg^{-1} ΣHCHs were detected (1–4 residues) in 60 % of brinjal, 28 % of cucumber, 29 % of sponge gourd, and 20 % of lady's finger samples, which could be a result of either historical or current OCI applications, or both. A strong positive correlation between aldrines in subsoils and cucurbit vegetables indicates greater bioaccumulation. Cow milk samples contained up to 6.96 μg kg^{-1} ΣDDTs, which resulted either from rationing contaminated vegetables or grazing on contaminated land. Individual OCI in both vegetables and cow's

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milk was below the respective maximum residue limits of US and FAO/WHO CODEX and poses little or no risk to human health. However, combined exposure to multiple pesticides could increase human health risks. A cumulative health risk assessment of multiple pesticide residues is suggested to assess the suitability of those soils for cultivation and grazing, as well as the safety of vegetables and cow's milk for human consumption.

1. Introduction

Organochlorine insecticides (OCIs) are chemically stable xenobiotic compounds (Bergkvist et al., 2012; Oehme, 1991). OCIs first became widely used in the 1950s in agriculture and health sectors because of their effectiveness, lower price, and wider-range of insect-controlling efficiency (Oliveira et al., 2016; Zehra et al., 2015; Zhi et al., 2015). Regardless of their benefits to eradicate unwanted insects and ensure food security, these OCIs compounds are currently grouped as persistent organic pollutants (POPs) because of their intensive widespread use which has polluted soils as well as the environment (Silva et al., 2019).

Soil is a repository of agricultural OCIs since soil absorbs most of the OCIs and their degradation products which ends up depositing higher concentrations of compounds in subsoils than in top soils (Bhandari et al., 2020; Zhang et al., 2006). Crops can uptake OCIs from soils which could in turn make the crops potentially toxic for human and livestock consumption (Clostre et al., 2015). Although the fate, behaviour, and distribution of OCIs is greatly influenced by soil properties, the persistence, lipophilic properties and chronic toxicity of OCIs enable their bioaccumulations and biomagnifications in the environment and food chains, posing a threat to humans as well as animals (Bettinetti et al., 2016; Miglioranza et al., 2013). Thus, these synthetic chemicals have become an alarming global issue causing many countries to have begun restricting the use of OCIs starting in the 1970s and 1980s (Oliveira et al., 2016; Xu et al., 2013; Zhi et al., 2015).

Until the early 1980's, the supply of pesticides was subsidized in Bangladesh which encouraged farmers to intensify their use of some OCIs like DDT, aldrin, dieldrin, chlordane, heptachlor, HCH and HCB. Bangladeshi farmers used OCIs for over three decades to increase agricultural production. The agricultural use of DDT had been prohibited in Bangladesh since the early 1980s but the official manufacturing was sustained until 1991, mainly for controlling malaria vectors. However, dieldrin, heptachlor and chlordane were used from 1986 to 1997 (Bergkvist et al., 2012; DoE, 2007). Later, the Stockholm Convention Treaty initiated by the United Nations Environment Programme (UNEP) in 2001 to forbid or restrict twelve identified POPs, namely polychlorinated biphenyls (PCBs) polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and nine OCIs (DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, hexachlorobenzene, mirex, and toxaphene). Afterwards hexachlorocyclohexane, pentachlorobenzene, pentachlorophenol chlordecone, endosulfan and lindane were included in the list of restricted compounds (UNEP, 2015). The Stockholm Convention Treaty was ratified by Bangladesh in 2007 (Bergkvist et al., 2012). Although restricted in many countries, OCIs could have been used or could be currently used illegally in crop production and in controlling insect vectors in some developing countries (Bhandari et al., 2020; Bigus et al., 2014; Oyekunle et al., 2011; Yuan et al., 2015). The limited enforcement of existing regulations (Bangladesh Pesticide Ordinance, 1971; Pesticide Rules, 1985; Bangladesh Environmental Conservation Act, 1995; Bangladesh Environment Conservation Rules,1997) (Uddin et al., 2016) and farmers' lack of knowledge and awareness of the risks of applying OCIs (Akter et al., 2018) might explain the recent illegal use of banned OCIs in crop cultivation in Bangladesh.

Both the historical residues and the current indiscriminate application of banned OCIs have drawn global attention due to the potential risks that these compounds pose to human health and the environment (Bettinetti et al., 2016; Jiang et al., 2009; Zehra et al., 2015). Public concern was raised after reports on the sporadic detection of different levels of OCI contamination in soil (Uddin et al., 2016), water (Islam et al., 2007), breast milk (Bergkvist et al., 2012; Haque et al., 2017), beef and dairy milk (Haque et al., 2017) and fresh and dried fish samples (Haque et al., 2017; Hussain et al., 2018) from different areas of Bangladesh, although most of the OCIs detected in these studies have been restricted or banned for import and use since 1997 (DoE, 2007). Commercial vegetable production in North-Western (NW) Bangladesh has exposed the farm ecosystems to extensive OCI use for >20 years in the past. However, information about the occurrence and sources of soil OCI residues and their distribution in the terrestrial food chains, especially in the intensive vegetable production areas in Bangladesh, is very limited. The assessment of OCI residue occurrence, frequency and concentration levels in the terrestrial ecosystem is necessary to reveal or predict the sources and entry points of these banned or restricted pollutants in the terrestrial food chain.

The current study was aimed to investigate the occurrence and concentrations of some frequent OCI residues from previously used OCIs in soils, their bioaccumulation in vegetables and cow's milk obtained from an intensive horticultural production area in the NW regions of Bangladesh. Hence, the study investigated the soil pollution status based on the presence of 23 frequent OCI residues of DDTs, HCHs, Aldrines, Endosulfans, Heptachlors, Chlordanes, Chlordecone and Mirex in collected soils of two depths of the selected vegetable fields from the study area. We also aimed to assess the safety of vegetables grown on the soils as well as the safety of cow's milk from cows allowed to graze on the polluted soils in the study area based on maximum acceptable residue limits.

2. Methods

2.1. Study area and sampling scheme

The research was conducted in the Islampur Upazila region of the Jamalpur district, located in the north-western part of Bangladesh (25.0833°N, 89.7917°E) (Fig. 1). It is one of the major intensively managed vegetable growing areas in North-western Bangladesh. The climate of this area is tropical, with characteristic dry (November to February with winter and less precipitation) and wet (May to September with heavy monsoon rainfall and flooding) seasons having 2041 mm mean rainfall and 25.4 °C mean temperature. The study area is located in the Old Brahmaputra Floodplain (Agro Ecological Zone-9), which has amassed considerable amounts of old Brahmaputra river sediments, resulting in silt loams to silty clay loams soils with low to moderate organic matter content and moderately acidic (pH 5.1–5.6) topsoils and neutral subsoils (BBS, 2011b).

Two major vegetable growing communities, namely the Palbandha union (A) and the Char Goalini union (B) (Fig. 1) were selected for the study after consultations with the local Agricultural Extension Office. The Palbandha union encompasses 1534 ha of land and a population of 13,389 in 3570 households. The Char Goalini union comprises 1778 ha of land and a population of 18,282 in 4197 households (BBS, 2011a). Most of the vegetable farmers have small split farm holdings with 200 m^2 to 10,000 m^2 of cultivated land. In each area, vegetable farms were carefully chosen for this study, and a total of 57 fields were selected. The selection criteria were a previous survey (Akter et al., 2018) and the history of vegetable farming (farming for at least 20 years with a history of OCI application). A variety of vegetables were grown in the selected sampling fields with different crop rotations every year (Akter et al., 2018). Eight of the most commonly cultivated vegetables were selected for the study, namely: bitter gourd, brinjal, chilli, cucumber, lady's finger, ridge gourd, sponge gourd, and yard-long bean. In the study area, a few farm families were found to rear dairy cattle, which were generally grazed on fallow vegetable fields and fed either on grass or the vegetation left in fields after harvesting. Soil and vegetable samples were collected from the 57 small vegetable farm holdings (Fig. 2) between December 2014 and June 2015. Milk samples from the cows on the farms were also collected.

2.2. *Sampling strategies*

Since most vegetable fields were irregular in shape and size, with irregular square or rectangular portions, three to five subsamples of topsoil and subsoil weighing one kg each were randomly gathered with a soil auger from a depth of 0–15 cm and 15–50 cm depth, respectively, combined to make one composite topsoil and one subsoil sample for each sample site weighing one kg, and transported to the laboratory. Foreign bodies were removed from the collected soil samples and crushed after air-drying at ambient temperature. The soil samples were then stored at -18 °C after being sieved with a 100-mesh sieve until analysis could be carried out. The soil physical characteristics for each site were also analysed. Organic matter (OM) was measured by dry ashing at 550 °C (Salehi et al., 2011). Soil pH was analysed using a standard method (Silva et al., 2019). Soil particle size analysis was done following the Bouyoucos' hydrometer method (Bouyoucos, 1962).

From each vegetable field, a total of >1 kg of vegetable sample (three to five vegetable units were harvested from the area around the sites where soil samples were taken) was randomly collected. One mixed sample from each vegetable farm was placed in a labelled plastic container, carried to and stored in the laboratory at -18 °C until analysis could be carried out following the European Commission Vegetable Sample Collection Guidelines set for each type of vegetable (European Commission, 2012).

A total of 30 fresh cow's milk samples, 15 from each of the two selected unions, were collected in 50 mL Greiner tubes. The tubes were then labelled with the individual cow and stored in a freezer at -18 °C until analysis.

2.3. *Selection of organochlorine residues for analysis*

The initial list of organochlorine residues was compiled by considering the compounds with higher soil persistence that had been most frequently used in the past, including those compounds banned by the Stockholm Convention. The main metabolites from the active compounds were selected for analysis. However, due to logistical, financial, and analytical limitations, a few compounds listed initially were excluded. Compounds were prioritized for the ability to be analysed by a multi-residue analysis method. The final list consisted of 23 OCI residues, hereafter called analytes (Supplementary Table 1), which were analysed for each of the 57 topsoil, 57 subsoil, 57 vegetable, and 30 cow's milk samples.

2.4. *Chemicals and reagents used*

The reference standard solutions (2000 μg/mL) of OCIs, including DDTs (*p,p*′-DDT, *p,p*′-DDE, *p,p*′-DDD, *o,p*′-DDT, *o,p*′-DDE and *o,p*′-DDD), aldrins (aldrin, dieldrin, endrin and endrin-ketone), HCHs (alpha, beta, and gamma-HCH or lindane), endosulfans (alpha- and beta-endosulfan, endosulfan-sulfate), hexachlorobenzene (HCB), chlordanes (cis- and trans-chlordane), chlordecone, heptachlor and heptachlor epoxide (cis), and mirex were prepared using reference compounds obtained from Dr. Ehrenstofer and Riedel-de-Haen (Germany). All stock-solutions, with the exception of Alpha HCH, were prepared in acetonitrile. Alpha HCH was dissolved in acetone. All solvents were of analytical reagent grade. Individual compound stock-solutions were combined into one mixture and diluted with acetonitrile to obtain the desired concentrations. Acetic acid (CH_3COOH; ≥99.8 %) and Acetonitrile (C_2H_3N; 99.95 % LC grade) were purchased from Biosolve BV (The Netherlands) and Actu-All Chemicals (The Netherlands), respectively. Sodium Acetate from Merck (Darmstadt, Germany) and Sodium Acetate from VWR International (Leuven, Belgium) were used. Primary secondary amine sorbent (PSA) and C_{18} sorbent from Agilent Technologies Netherlands B.V. (The Netherlands) were purchased and used.

2.5. *Sample extraction and clean-up*

Thawing of the soil, vegetables, and cow's milk samples was done on

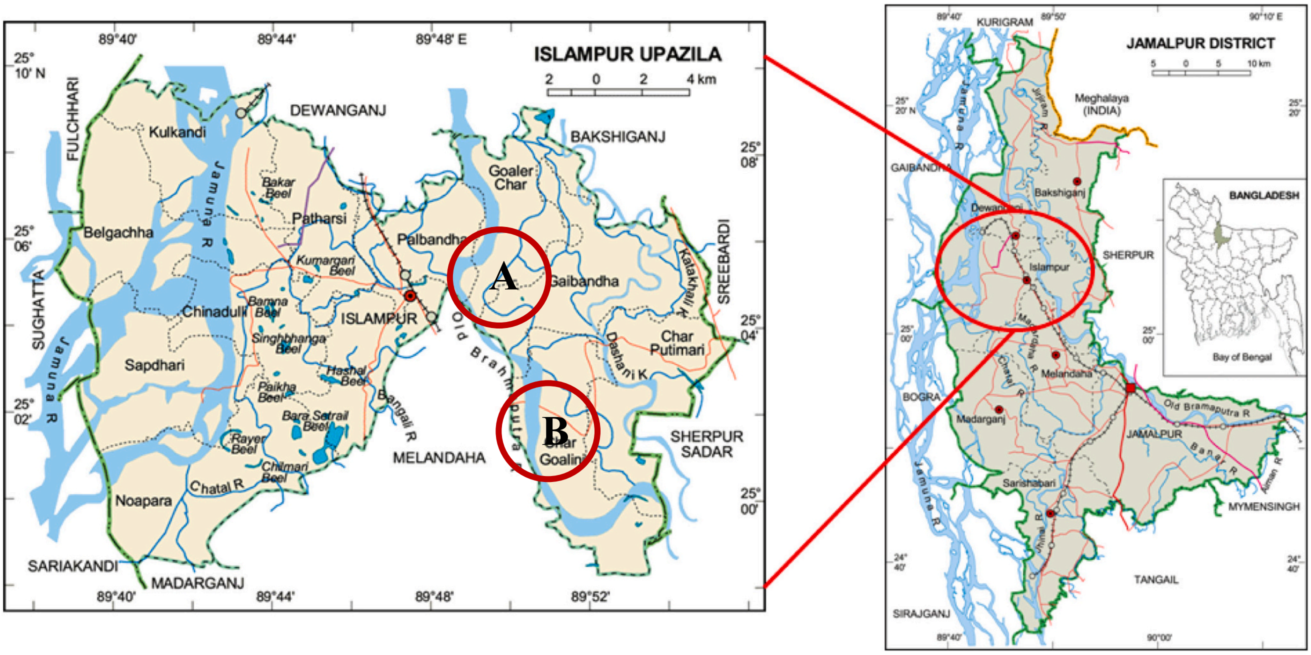

Fig. 1. Geographical map indicating the study locations in Islampur upazila of Jamalpur district) (A) Palbandha union and (B) Char Goalini union.

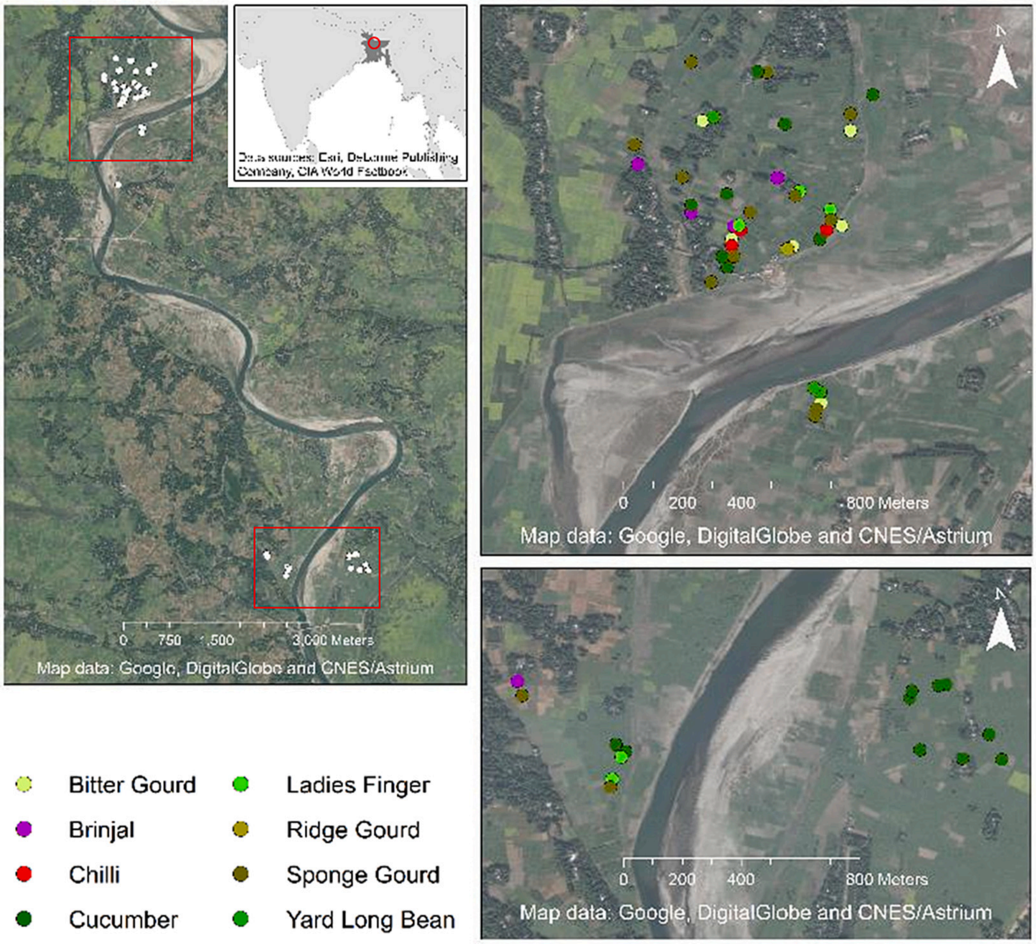

Fig. 2. Study locations showing specific vegetable fields selected for sampling in the Palbandha union (top) and the Char Goalini union (bottom).

the previous day of the pesticide residues extraction. Once thawed, visually homogenous samples were obtained by stirring the samples with a spoon. The modified QuEChERS approach was adapted to extract the organochlorine insecticides from the soil, vegetable, and cow's milk samples, following the methodology identical to the one developed and reported by previous researchers from Wageningen Food Safety Research (Anastassiades et al., 2003; Anastassiades et al., 2007; Lehotay et al., 2010; Lehotay et al., 2005; Mol et al., 2008). For soil samples, the process involved mixing 5 g (air-dried weight) of a homogenized soil sample together with 5 mL of Millipore water. For vegetables, the process involved mixing 2.5 g (fresh weight) of a homogenized vegetable sample together with 7.5 mL of Millipore water. Homogenized cow's milk sample of 2.5 mL was mixed together with 7.5 mL of Millipore water in a polypropylene (PP) tube of 50 mL capacity. The PP tube was then shaken by hand after addition of 10 mL of the extraction solvent (CH_3CN + 1 % HAc) to the tube. Then the mixture in the PP tube was agitated for 30 min in an end-over-end shaker, after which phase separation was induced by adding 1 g of sodium acetate and 4 g of magnesium sulphate in to the tube. The tube was then vortexed, followed by centrifugation at 3500 rpm for 5 min and collection of the resulting supernatant.

For the dispersive SPE clean-up step for GC–MS/MS analysis, 250 μL of the supernatant and 250 μL of the extraction solvent were transferred into an Eppendorf tube containing 38 mg of C_{18}, 50 mg of primary secondary amine (PSA), and 150 mg of magnesium sulphate. Later, 38 μL of an injection standard in the GC–MS/MS analysis, PCB-198 (1 μg/mL), was added to the Eppendorf tube. After thorough mixing, centrifugation of the Eppendorf tube was done at 13,000 rpm for 15 min, and 150 μL of the resultant clean supernatant was taken for analysis in a vial made of amber glass.

2.6. GC–MS/MS analysis

Injection of 5 μL cleaned extract was done into a Bruker 300 GC-triple quadrupole MS (GC–MS/MS) system from Bruker (Bremen, Germany). The Cl-Pesticide column used was 30 mm × 0.25 mm size and 0.25 μm film-thickness and purchased from Restek (Bellefonte, PA, USA). The injector of the GC–MS/MS system was used in PTV mode. The oven program of the GC was initiated at 60 °C for 2 min. Then, the oven temperature was raised to 150 °C with increments of 20 °C per minutes. The temperature was further increased to 280 °C with increments of 10 °C per minutes and finally to 320 °C with increments of 25 °C per minutes. This final temperature was maintained for 2 min.

The guidance document on analytical quality control and method validation procedures for pesticide residue analysis in food and feed (European Commission, 2015) was followed during the chemical determinations and the quality control of the analytical results. Briefly, a set of multipesticides, matrix matched and calibration standards were prepared. A calibration curve of calibration standards (0, 2.5, 10, 25, 50 and 100 ng mL^{-1}) was injected at the beginning of each batch of analysis. Satisfactory linearity of response versus concentration was presented by the calibration curves, with correlation coefficients above 0.99 and residuals of response lower than ±20 %. Fortified blank soils (3 to 6), as well as samples of vegetables and cow's milk obtained from a previous study and analysed during the method development phase of the current study and deficient in any of the tested residues were also included in each sample sequence. These soils, vegetable and milk samples were spiked with the mixture solutions of the reference standards and analysed.

The method that was applied to our samples used the default spiking levels of 0.01 and 0.05 mg kg^{-1} (Silva et al., 2019). Based on the signals for the fortified samples at the 0.01 mg kg^{-1} level, for each compound, an LOQ was established based on the s/n ratio of the most intense transition. The established LOQs ranged between 0.0025 and 0.01 mg kg^{-1}. An overview of all the LODs and LOQs for the compounds analysed using the GC–MS/MS based multi-method is listed in Supplementary Table 1. Each of the analytes was recognized based on retention time, shape of the peak for particular reference standard, and the ion ratio within ±30 % of the mean ion ratio for the calibration standards. The GC–MS/MS analyte response was normalized based on the PCB-198 response. The analyte concentration was determined according to bracketing calibration, with a matrix-matched calibration standard (10 ng mL^{-1}) tested every 10–15 injections/samples following modified GC–MS/MS based multi-method (Silva et al., 2019).

2.7. Statistical analysis

Data analysis was done using STATISTICA version12 and GraphPad Prism 6 software. As each compound was analysed in duplicate, the average concentration of both aliquots was regarded as the concentration in the sample. The concentration in each of the two aliquots was within ±35 % of the average concentration of both aliquots. Sporadically, where the compound concentration was ≥LOQ in single aliquots, this value ≥LOQ was regarded as the concentration of the sample, as

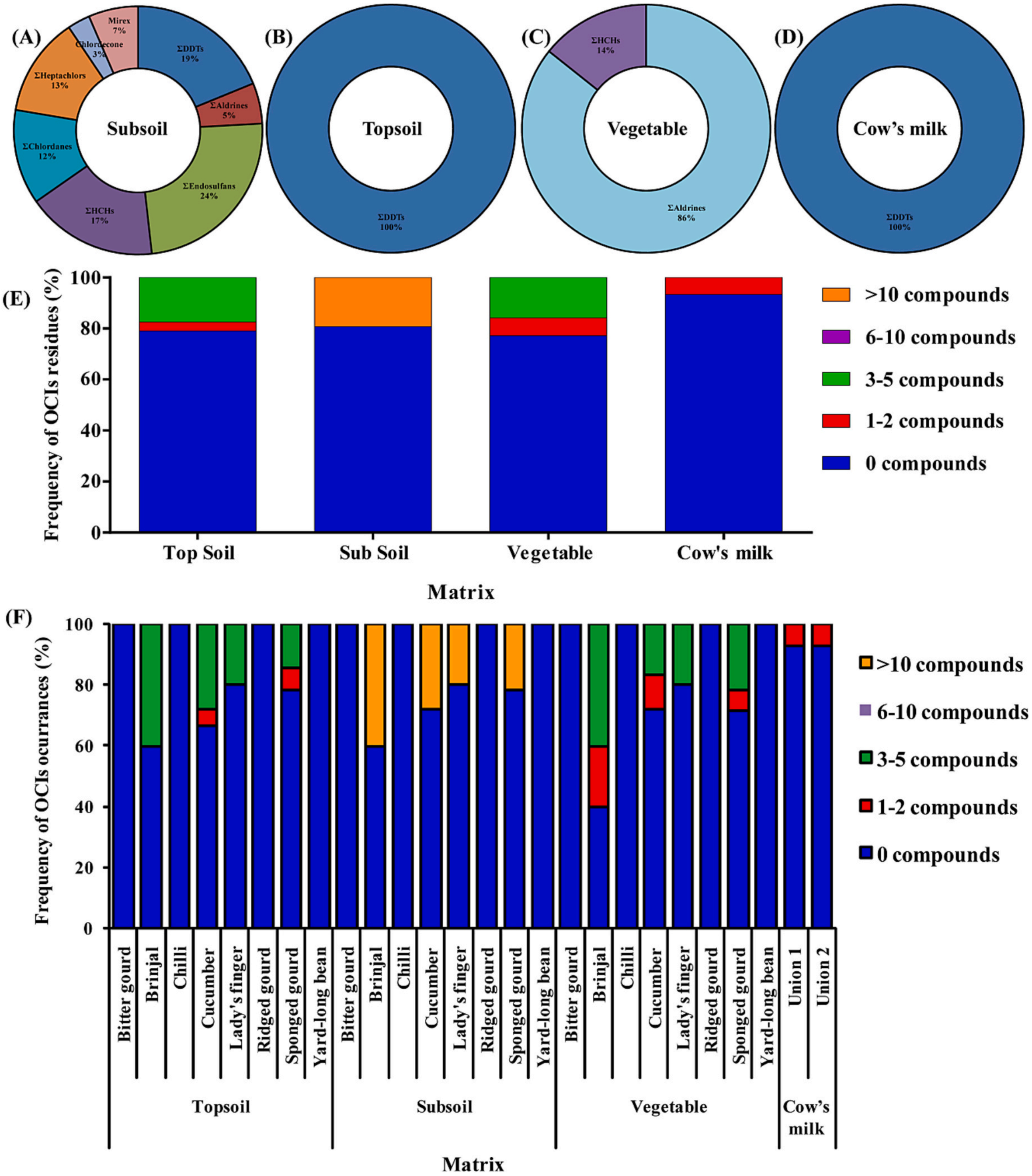

Fig. 3. Occurrence of different OCI residues in subsoils (A), topsoils (B), vegetables (C), and cow's milk matrixes (D); Frequency of occurrence of OCI residues in different matrixes (E) and in soils from different vegetable fields, vegetables from different fields and cow's milk from two different locations (F).

both the values less than or equal to or above LOQ were marginal to the LOQ value. To avoid underestimating OCI concentrations in different matrixes, only pesticide residue concentration ≥ LOQ was taken in the analysis of data (Sun et al., 2016). Levene's test was performed to check the normality of data. Normally distributed data were analysed using one-way ANOVA followed by Tukey's Honestly Significant Difference (HSD) test to compare the numbers and concentrations of pesticides in different matrixes. Mann Whitney-*U* test using the STATISTICA version12 software was performed for data not normally distributed. When significant variation was seen at the 95 % confidence level ($p < 0.05$), the Bonferroni posthoc test was performed. In the figures, the total pesticide content in topsoil, subsoil, and vegetables were aggregated by concentration (μg kg^{-1}). The OCI hotspot maps considering these categories were generated using ArcGIS 10.4 software. Probable relationships between the occurrences and concentrations of OCIs in soils with soil physicochemical properties and the OCI concentrations in vegetables with the soil OCI levels were explored by Principal component analysis (PCA) and correlation analysis (Spearman's coefficients) using XLSTAT 2020.3.1.18 trial version.

The composition quotients or isomeric ratios are a good indicator of pollution status in the environment to differentiate the application status of OCIs used in the cultivated soils of the research area (Atuanya and Aborisade, 2017; Joseph et al., 2020; Kumar et al., 2018; Wang et al., 2016; Wang et al., 2010; Yu et al., 2013). The historical and current applications of banned OCIs were distinguished according to the threshold values used earlier (Atuanya and Aborisade, 2017; Wang et al., 2016; Wang et al., 2010). Therefore, the residue composition quotients of different OCIs were calculated.

3. Results

3.1. Occurrences of OCI residues in soils, vegetables, and cow's milk

Among the 23 analytes tested, 17 types of OCI residues were detected in subsoils, 3 in topsoils, 4 in vegetables, and 2 in cow's milk (Figs. 3E, F, and 6E; Supplementary Table 2). At least one OCI residue was detected in 19 % of subsoils, 21 % of topsoils, 23 % of vegetables, and 7 % of cow's milk samples analysed (Fig. 3E and F). The number of OCI residues varied significantly in different matrixes ($p < 0.001$; Fig. 4). OCI residues were found more frequently in the subsoils (15–50 cm depth) than in the topsoils (0–15 cm depth) (Fig. 3A, B, and E). All eight OCI groups were detected in subsoils, whereas only ΣDDT was detected in topsoils (Fig. 3A and B; Supplementary Table 3). A large number of OCI residues (>10 residues) were detected in 19 % of the tested subsoils (Fig. 3E). Subsoil samples from fields of brinjal (40 %), cucumber (33 %), lady's finger (20 %) and sponge gourd (21 %) contained detectable OCI residues (Fig. 3F).

The number of OCI residues detected in soils from brinjal, cucumber, lady's finger and sponge gourd fields did not vary significantly ($p > 0.05$; Fig. 4). A maximum of 3 to 5 compounds were found in 16 % of the tested vegetables (Fig. 3E). The most frequently detected residues, aldrin, dieldrin, endrin, and HCB, were found in almost all positive vegetables tested (60 % of brinjal, 28 % of cucumber, 20 % of lady's finger, and 29 % of sponge gourd samples) (Fig. 3F). The number of OCI residues detected in these vegetables did not vary significantly ($p > 0.05$; Fig. 4). A maximum of 1 to 2 compounds were found in 7 % of the tested cow's milks (Fig. 3E). DDT metabolites *p,p'*-DDE and *o,p'*-DDE were exclusively found in the tested cow's milk (Figs. 3D and 6E).

The categorization of the OCI residues and their concentrations detected in different matrixes revealed that ΣDDTs (*o,p'*-DDT, *o,p'*-DDD, and *o,p'*-DDE), ΣAldrines (Endrin ketone), ΣEndosulfans, ΣHCHs, ΣChlordanes, ΣHeptachlors, chlordecone and mirex were 15 %, 5 %, 16 %, 31 %, 11 %, 13 %, 4 % and 5 % of total ΣOCIs detected in the subsoil matrix, respectively (Figs.6A and 7C). However, only ΣDDTs (*p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE) were found in topsoils (Figs.6B, E, and 7B). ΣAldrines (aldrin, dieldrin, and endrin) and ΣHCHs (HCB) were 87 % and 13 %, respectively, of total ΣOCIs detected in vegetables (Figs.6C, E, and 7A), and only ΣDDTs (*o,p'*-DDE and *p,p'*-DDE) were found in tested cow's milks (Figs.6D and E).

3.2. Concentration and distribution of the residues of organochlorine insecticide in soils, vegetables, and cow's milk matrixes

ΣOCIs concentration detected in different matrixes varied significantly ($p < 0.001$, Fig. 5). The highest concentration of ΣOCI was detected in subsoils, and the lowest was in cow's milk (Fig. 5 and

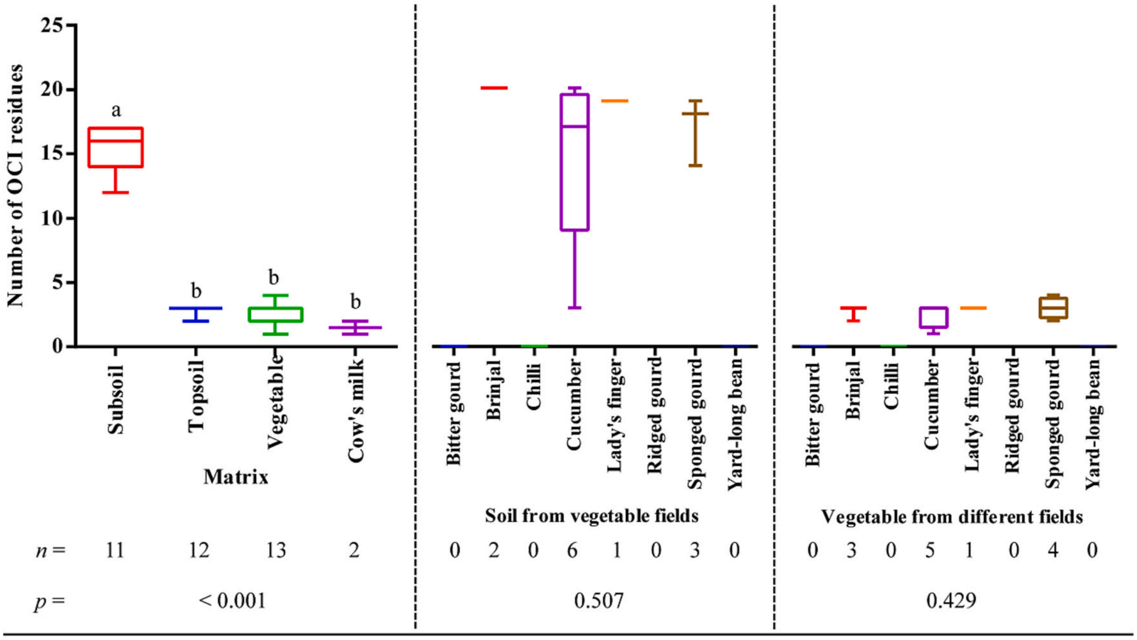

Fig. 4. Box plots for comparisons of average OCI residues number in different matrixes, in soils from different fields of vegetable and vegetables from different fields with *p* values. Different letters indicate significant differences among different matrixes. Median values are indicated by concrete lines within the box while box borders demonstrate the 5–95 percentiles. The highest and lowest data values are indicated by Box whiskers.

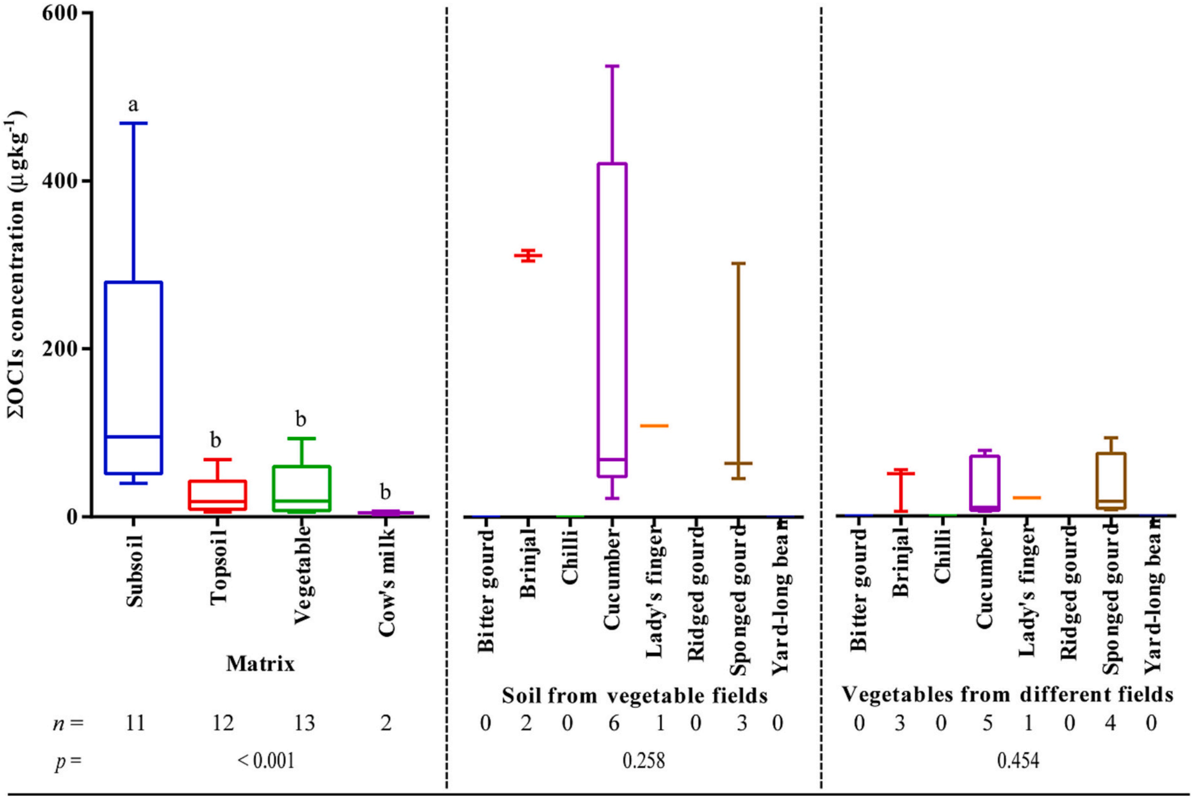

Fig. 5. Box plots for comparisons of average ΣOCI residues concentration in different matrixes, in soils from different fields of vegetable and in different groups of vegetables with *p* values. Different letters indicate significant differences among different matrixes. Median values are indicated by concrete lines within the box while box borders demonstrate the 5–95 percentiles. The highest and lowest data values are indicated by Box whiskers.

Supplementary Table 3).

The concentrations of ΣOCIs in subsoils and topsoils matrixes ranged from 39.81 to 468.94 μg kg^{-1} and from 5.96 to 68.16 μg kg^{-1}, respectively (Supplementary Table 3). However, no significant variation was observed in ΣOCI concentrations detected in soils from different groups of vegetable fields ($p = 0.258$, Fig. 5). The concentration of ΣDDTs detected in subsoils and topsoils matrixes ranged from 6.12 to 68.13 and from 5.96 to 68.15 μg kg^{-1}, respectively (Fig. 6E; Supplementary Table 3). Among the different DDT metabolites present in soils, *o,p'*-DDT (8.45 ± 6.36 μg kg^{-1}) was found in 91 % of tested positive subsoils, and both *o,p'*-DDD (9.50 ± 7.30 μg kg^{-1}) and *o,p'*-DDE (9.64 ± 7.42 μg kg^{-1}) were found in 100 % of the positive subsoil samples (Supplementary Table 2). The topsoils showed different metabolites of DDT than the subsoils. Among the ΣDDTs in topsoils, *p,p'*-DDT (8.96 ± 6.17 μg kg^{-1}) was found in 83.33 % of the positive samples, and both *p,p'*-DDD (9 ± 7.25 μg kg^{-1}) and *p,p'*-DDE (9.29 ± 7.33 μg kg^{-1}) were in 100 % of the positive samples (Supplementary Table 2). In general, topsoils (0–15 cm) contained higher concentrations and numbers of DDTs and their degradation product residues than subsoils (15–50 cm).

Among the ΣAldrines, only endrin ketone (the degradation product of endrin) was detected in subsoils with concentrations ranging from 2.95 to 25.44 μg kg^{-1} (Fig. 6E and Supplementary Table 3). ΣAldrines were absent in the topsoils of the research area. Subsoils ΣHCHs concentrations ranged from 11.35 to 150.41 μg kg^{-1} (Fig. 6A and Supplementary Table 3). Among the ΣHCHs in subsoils, gamma-hexachlorocyclohexane (ɣ-HCH) or lindane (13.04 ± 10.36 μg kg^{-1}), α-HCH (15.38 ± 12.40 μg kg^{-1}), and β-HCH (9.82 ± 7.82 μg kg^{-1}) were present in 100 % of tested positive subsoils, and HCB was present (23.64 ± 18.55 μg kg^{-1}) in 73 % of tested positive subsoils (Supplementary Table 2).

The concentrations of ΣEndosulfans, ΣChlordanes, ΣHeptachlors, Chlordecone, and Mirex detected only in subsoils matrix ranged from 3.38 to 77.81, 4.18 to 49.99, 7.27 to 54.88, 11.17 to 20.51, and 2.52 to 21.78 μg kg^{-1}, respectively (Fig. 6A and Supplementary Table 3). Different isomeric forms of endosulfans with their metabolite (endosulfan sulphate) were present in the subsoils of the study area. α-endosulfan (11.07 ± 8.41 μg kg^{-1}) was present in 100 % of the positive samples (Fig. 6E and Supplementary Table 2). Whereas β-endosulfan (12.19 ± 8.13 μg kg^{-1}) and endosulfan sulfate (10.36 ± 7.34 μg kg^{-1}) were both present in 82 % of the positive subsoil samples (Fig. 6E and Supplementary Table 2). Among the ΣChlordanes, *cis*-chlordane (10.57 ± 7.75 μg kg^{-1}) was found in 91 % of the positive subsoil samples and *trans*-chlordane (10.35 ± 7.76 μg kg^{-1}) in 100 % of the positive subsoil samples (Fig. 6E and Supplementary Table 2). Among the ΣHeptachlors, Heptachlor (12.83 ± 9.92 μg kg^{-1}) and its metabolite Heptachlor epoxide (10.72 ± 8.24 μg kg^{-1}) were present in 100 % of the positive subsoil samples (Fig. 6E and Supplementary Table 2).

The concentrations of ΣOCIs in vegetable matrixes ranged from 5.42 to 93.22 μg kg^{-1} (Supplementary Table 3). However, no significant variation was observed in ΣOCI concentrations detected in different vegetables ($p = 0.454$; Fig. 5). ΣDDTs, ΣEndosulfans, ΣChlordanes, ΣHeptachlors, Chlordecone, and Mirex residues were absent in vegetable matrixes (Fig. 6E; Supplementary Table 3). ΣAldrines concentrations detected in vegetable matrixes varied from 2.86 to 78.24 μg kg^{-1} (Fig. 6E and Supplementary Table 3). Aldrin (13.93 ± 11.60 μg kg^{-1}), dieldrin (11.60 ± 6.97 μg kg^{-1}), and endrin (12.21 ± 6.49 μg kg^{-1}) were present in the collected vegetable samples, but endrin ketone was absent. 60 % of collected brinjal (36.28 ± 29.04 μg kg^{-1}), 28 % of cucumber (33.30 ± 35.01 μg kg^{-1}), 29 % of sponge gourd (20.92 ± 24.66 μg kg^{-1}), and 20 % of lady's finger (21.88 μg kg^{-1}) were the vegetables that contained ΣAldrines (Supplementary Table 3). ΣHCHs concentrations detected in vegetables varied from 2.56 to 35.57 μg kg^{-1} (Fig. 6C and Supplementary Table 3). Among the ΣHCHs, only HCB was present in the vegetable matrix, where brinjal (20 %, 2.56 μg kg^{-1}) and sponge

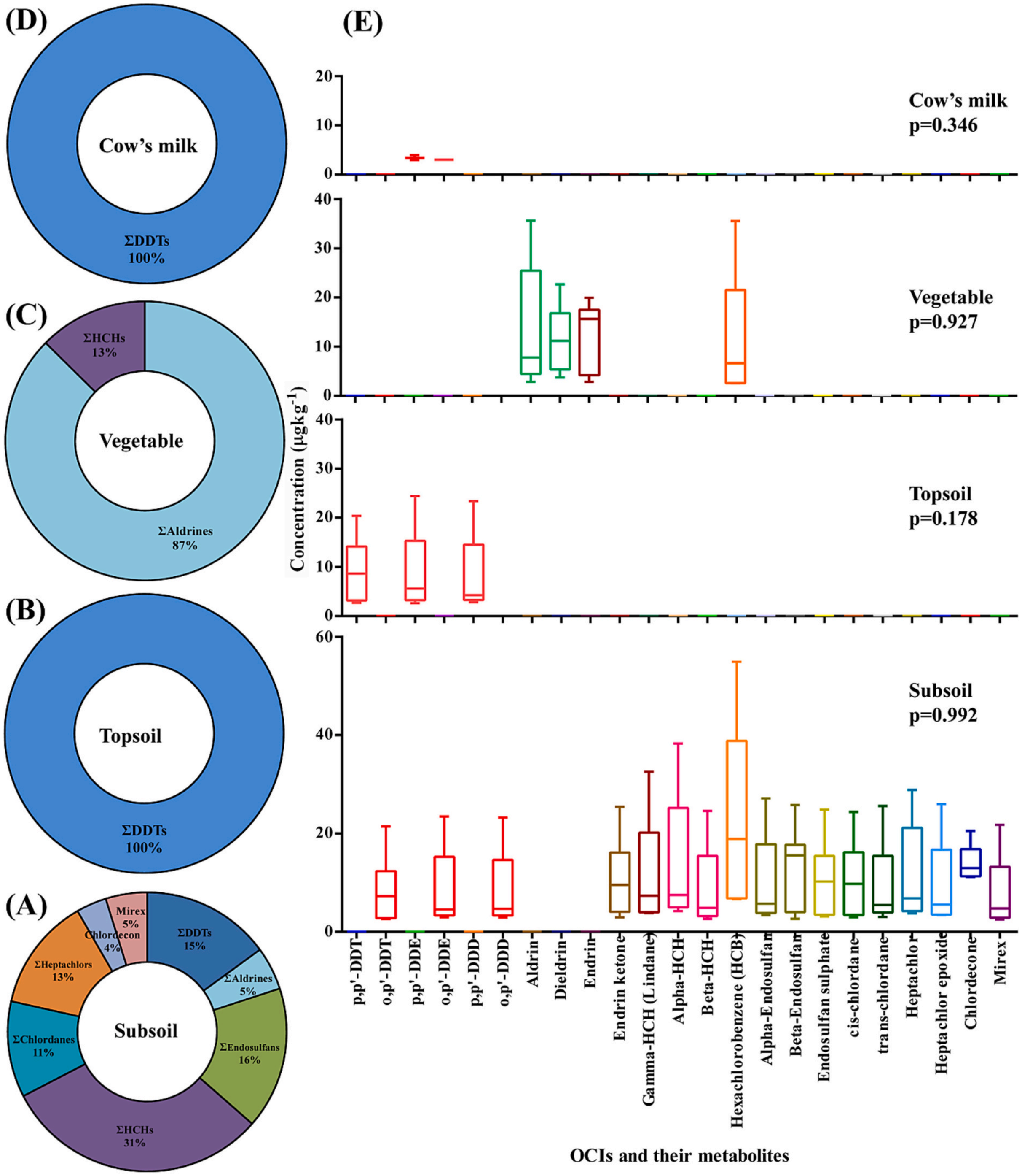

Fig. 6. Distribution of different ΣOCI concentrations in subsoil (15–50 cm) (A), topsoil (0–15 cm) (B), vegetable (C) and cow's milk (D) matrixes; and box plots for concentrations of different OCIs and their metabolites in different matrixes (E). Median values are indicated by concrete lines within the box while box borders demonstrate the 5–95 percentiles. The highest and lowest data values are indicated by Box whiskers.

gourd (29 %, 13.09 ± 15.13 µg kg^{-1}) were the major vegetables contaminated with ΣHCHs (Supplementary Table 2).

Among the ΣOCIs, ΣDDTs were detected in the cow's milk matrix in concentrations ranging from 2.92 to 6.96 µg kg^{-1} (Fig. 6E; Supplementary Table 3). DDT metabolites *p,p'*-DDE (3.44 µg kg^{-1}) and *o,p'*-DDE (3.00 µg kg^{-1}) were also present in cow's milk (Supplementary Table 2).

3.3. Correlations between soil physicochemical properties with OCI residues detected in soils and vegetables

The analyses of physicochemical properties of subsoils and topsoils revealed that topsoils (pH ranging from 4.55 to 6.94 with a mean value of 5.74 ± 0.53) were significantly more acidic ($p < 0.01$) than subsoils (pH ranging from 5.18 to 6.87 with a mean value of 6.33 ± 0.41) (Supplementary Table 4 and 5). Moreover, the topsoils contained significantly more ($p < 0.01$) organic carbon and organic matter (ranging from 0.85 to 1.85 % with a mean value of 1.34 ± 0.25 % and 1.46 %–3.19 % with a mean value of 2.31 ± 0.44 %, respectively) than

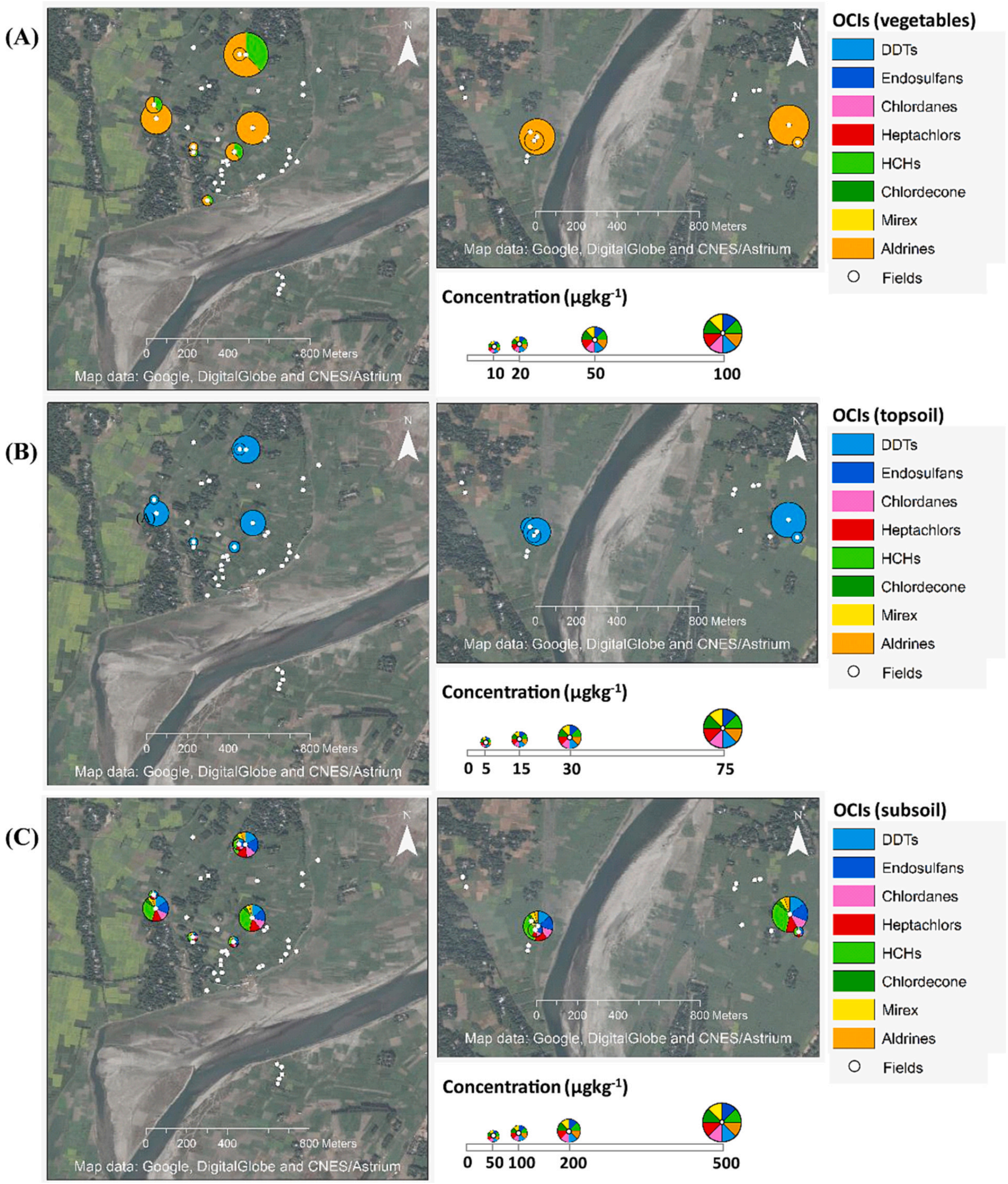

Fig. 7. OCI hotspots in vegetable (A), topsoil (0–15 cm) (B) and subsoil (15–50 cm) matrixes (C) of Palbandha union (left) and the Char Goalini union (right). The pie-charts represent the fraction of OCIs with pesticide concentration in each sample. The OCI concentration thresholds of 0, 10, 20, 50 and 100 μg kg^{-1} were used for the vegetable matrix depicted in (A); OCI concentration thresholds of 0, 5, 15, 30 and 75 μg kg^{-1} were used for the topsoil matrix in (B); OCI concentration thresholds of 0, 50, 100, 200 and 500 μg kg^{-1} were used for the subsoil matrix in (C). The size of the pie-charts symbolizes the total OCI content, with larger circles equivalent to a greater concentration of OCIs in respective samples.

corresponding subsoils (ranging from 0.58 to 1.65 % with a mean value of 1.14 ± 0.25 % and 0.99–2.84 % with a mean value of 1.96 ± 0.42 %, respectively) (Supplementary Table 4 and 5). The soil texture of both topsoils and subsoils were mainly silty loam but significant site differences in percentages of sand were observed in subsoils.

The Spearman correlation analysis was performed to understand the relationship between physicochemical properties of soil and detected OCI residues in subsoils, topsoils, and vegetables (Supplementary Table 6). The frequency and concentrations of ΣOCIs in soils were weakly correlated with soil properties, while the correlation between subsoil pH and subsoil ΣOCI frequency and concentrations were negative but statistically significant ($p < 0.05$) for ΣEndosulfans, ΣHCHs and Mirex concentrations. Negative correlation between ΣOCI frequency with % organic matter, % clay, and % silt of topsoils were statistically

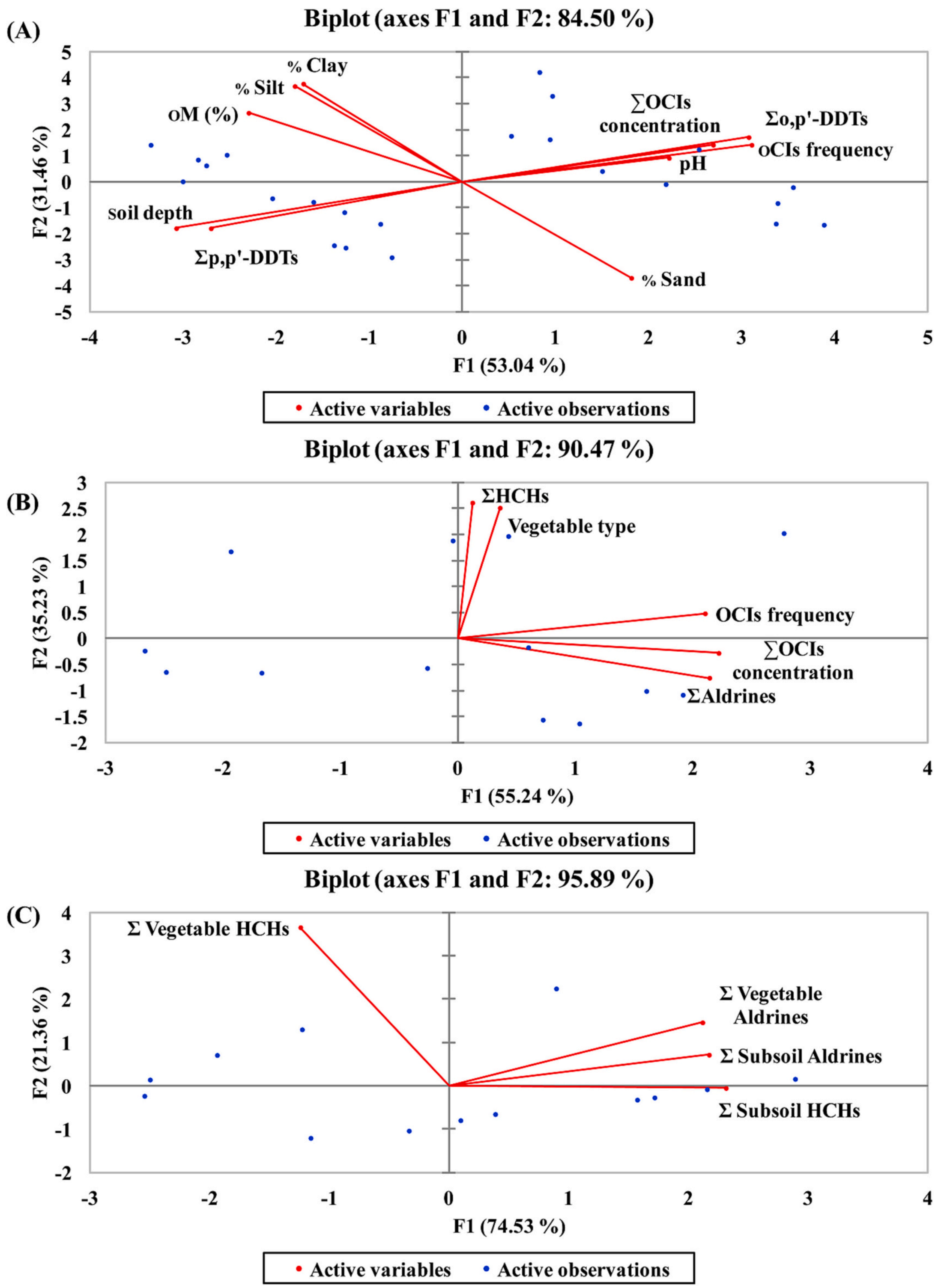

Fig. 8. Loading plots of PCA showed loadings of the frequency and average concentrations of detected OCIs and their metabolites in soil with soil physicochemical properties at two soil depths (A), in vegetables (B) and the relationship of detected OCI concentrations in subsoil and vegetables (C).

significant ($p < 0.01$). Moreover, the ΣOCI frequency in vegetables was negatively correlated with % organic matter, % clay and % silt of subsoils and % organic matter, % clay, % silt and % sand of topsoils. The correlations were statistically significant.

ΣOCI frequency and ΣOCI concentrations in subsoils had statistically significant strong positive correlation ($p < 0.01$), while the correlation between ΣOCI frequency and ΣOCI concentrations in topsoils was also statistically positive ($p < 0.05$). Statistically significant strong positive correlation was observed between ΣDDT concentrations in subsoils and topsoils ($p < 0.01$). Positive correlation found between ΣOCI frequency in subsoils and ΣOCI concentrations in vegetables was statistically significant ($p < 0.05$), while the ΣOCI concentration in subsoils and ΣOCI concentrations in vegetables were also strongly positively correlated and the correlation was statistically significant ($p < 0.01$). In the relationship between detected pesticide residues in topsoil and subsoil, only ΣDDTs showed statistically significant positive correlations. The rest of the OCI residues were detected only in subsoils. Hence, no correlation was observed between other OCIs detected in topsoils and subsoils. Moreover, no correlation was observed between ΣDDT residues in soil and vegetables. Statistically significant apparent positive relationship were found between ΣAldrines in subsoils and vegetables ($p < 0.01$). However, strong positive correlations were absent between ΣHCHs in subsoils and vegetables ($p > 0.05$).

Principal component analysis (PCA) revealed that the three principal components (PC) explained 84.50 %, 90.47 % and 95.89 % of the total variance remains in the data set. F1 accounted for the larger fraction of the data variance (53.04 %), (55.24 %) and (70.30 %) while F2 explained (31.46 %), (35.23 %) and (21.36 %), respectively, having fewer data variations. For the PCA in Fig. 8(A), Σ*o,p'*-DDT concentration, soil ΣOCI concentration, soil OCI frequency and soil pH were strongly correlated with each other but negatively correlated with Σ*p,p'*-DDT concentrations in soil and soil depth. For the PCA in Fig. 8(B), concentrations of ΣOCIs and ΣAldrines in vegetables were strongly correlated with each other while ΣHCHs in vegetables and vegetable types were strongly correlated with each other. For the PCA in Fig. 8(C), Σsubsoil Aldrines and Σvegetable Aldrines were also strongly positively correlated with each other while Σsubsoil HCHs and Σvegetable HCHs were weakly correlated.

4. Discussion

4.1. OCI pollution status in soils, vegetables, and cow's milk matrixes

Earlier studies have detected the highly persistent OCIs in soils (Aiyesanmi and Idowu, 2012; Fosu-Mensah et al., 2016; Jiang et al., 2009; Mishra et al., 2012; Oyekunle et al., 2011). A greater diversity and higher concentrations of most of the detected OCIs were found in subsoils as compared to topsoils in a study area in China (Bai et al., 2015; Gereslassie et al., 2019). Varieties of OCI metabolites from different sampling sites might be influenced by different OCI usage patterns of the individual farmers or landowners (Bai et al., 2015). In Bangladesh, there were no set standard limits, environmental standards, or ecological risk values for minimum amounts of OCI residue in the contaminated soils during a particular period. The concentrations of DDTs in topsoils and DDTs, Aldrines, Endosulfans, HCHs, Chlordanes, and Heptachlors in most subsoil samples from the study area were above the Dutch target value for unpolluted soil, but below the Dutch intervention values (Supplementary Table 7) (The Netherlands Ministry of Housing, 2000). However, the levels of ΣDDT detected in agricultural soils in the study area were consistent with a few reported cases in other Asian countries (Bhandari et al., 2020; Jiang et al., 2009; Zhang et al., 2006). Moreover, based on Chinese soil environmental quality standards (Ma et al., 2016; Shi et al., 2005), we found negligible DDT contamination (<50 μg kg^{-1}) in around 90 % of the total positive subsoil and topsoil samples. We found lower HCH contamination (50–500 μg kg^{-1}) in around 45 % of the samples and negligible HCH contamination (<50 μg kg^{-1}) in around 45 % of the total positive soil samples. Therefore, the soils in the study area were only barely contaminated by OCIs and were thus suitable for growing several crops.

The lower concentration levels of OCIs detected in this area suggest that the declining levels of soil OCI concentrations could be a result of vegetable farmers in the study area complying with local regulations concerning the use of banned pesticides in agriculture. Reports on recent detection of DDT and other OCI residues in locally produced vegetables in Bangladesh are currently not available (Hossain et al., 2015). However, DDT isomers along with metabolites were the major OCIs found in Bangladeshi (Haque et al., 2017) and Indian cow's milk samples (John et al., 2001; Kaushik et al., 2014; Nag and Raikwar, 2008; Pandit and Sahu, 2002; Régo et al., 2019). Among the OCIs detected, aldrin, and dieldrin levels in brinjal, cucumber, and sponge gourd; HCHs particularly HCB in brinjal and sponge gourd; and DDT metabolites in the cow's milks obtained from the study region were lower than Maximum Residue Levels (MRL) for United States Markets (BCGLOBAL, 2020) and the FAO/WHO CODEX (Supplementary Table 8).

The detection of OCIs in vegetables from the study area was not completely unexpected. Dieldrin, endrin, different HCH isomers, and HCB metabolites were also found in vegetables and fruits in Turkey and were below the MRLs (Dursun and Köysüren, 2014). Levels of dieldrin, aldrin, endrin, and its metabolites present in commonly grown horticultural crops in Nigeria were higher than the EU/UK regulatory limits (Adeleye et al., 2019) and recent use of these groups of OCIs by farmers was suspected. The presence of DDT metabolites in the milk samples was not surprising since DDTs bio-accumulate and are biomagnified in animal fat tissues (Bergkvist et al., 2012; Kuba et al., 2015; Wong et al., 2005). Some researchers have detected *p,p'*-DDE in cow's milk samples from several areas of Bangladesh (Haque et al., 2017). DDT isomers along with metabolites, especially DDE, were also present in cow's milk from Brazil (Heck et al., 2007), Jordan (Salem et al., 2009), Uganda (Kampire et al., 2011), Spain (Luzardo et al., 2012), Ethiopia (Waktola et al., 2014), and Greece (Tsakiris et al., 2015).

We analysed 1 soil and vegetable sample in each field but our sample is composite sample which were combined with different sampling sites. Meanwhile, due to the restriction of sampling and transportation, we have to compromise our analysis. The presence of multiple OCI residues in soils from the various fields, vegetables, and cow's milk samples in the present study area was within or close to the individual regulatory limits, or MRLs. However, the bioaccumulation prospective of multiple OCIs raises severe health concerns for agricultural workers along with consumers who might be exposed through farming activities and contaminated food chains. Moreover, some vegetables and other crops have the potential to uptake the OCI residues through their root systems and translocate them into the food chain. There should be continuous inspection of OCI residues in soils, and agricultural food commodities, including vegetables and cow's milk. Modified cropping patterns using substitute crops that have poorly developed root systems and short vegetation cycles or non-edible crops could be planted in places where OCI residues remain in the subsoils.

4.2. Possible sources and fate of OCI residues in soil matrixes

The most important source of OCI pollution in agricultural soil is the direct uses of OCIs in agricultural crop production (Qu et al., 2016) or the discharge of OCIs from manufacturing industries, storage facilities, or transport (Tao et al., 2008). The absence of pesticide manufacturing or storage facilities in the study area that would produce or store OCIs over the last few decades indicates that, the occurrence of OCIs in the agricultural soils may be primarily connected with historical or recent illegal applications, since most OCIs are currently banned for use in agriculture (DoE, 2007). OCIs stemming from historical applications have leached from the topsoil and accumulated in subsoils where there is limited exposure to environmental factors that would facilitate biodegradation. Any suspected recent illegal application of OCIs could be related to the fact that these compounds are cheaper and more effective in controlling a broad spectrum of insect pests (Adeleye et al., 2019).

The isomeric ratios or composition quotients of detected OCI metabolites and parent compounds (Li et al., 2006; Qiu et al., 2004; Qiu et al., 2005) indicate that the ΣDDTs in the subsoils of the study area might be from historical applications (DDE + DDD)/DDT ratios were $>$ 1in 100 % of samples), and in topsoils the ΣDDTs could be from both historical and recent illegal applications (DDE + DDD)/DDT ratios were >1 in 90 % of samples) (Supplementary Table 9). The DDTs detected in topsoils might stem from technical DDT (as the ratios of *o,p'*-DDT/ *p,p'*-DDT were zero), and those in subsoils could be from dicofol (as higher ratios of *o,p'*-DDT/*p,p'*-DDT were found) (Supplementary Table 9). Moreover, 0.14 mg kg^{-1} dicofol was detected in cucumber samples in Bangladesh (Alamgir Zaman Chowdhury et al., 2013). The degradation of DDT in subsoils (DDD/DDE ratios were >1 in 54.54 % of positive samples) and topsoils (DDD/DDE ratios were < 1 in 58.33 % of positive samples) in the study area was mainly under anaerobic and aerobic conditions, respectively, which was consistent with the ploughing methods used locally (Ma et al., 2016). This strongly supported the possibility that the DDT residues detected in this research came from historical DDT applications in the study area. Although the applications of DDT have been prohibited in Bangladesh since the 1980s, it might still be in use in some regions. Current applications of DDT in the terrestrial ecosystem have been revealed in several Asian countries like India, Pakistan, and Nepal (Alamdar et al., 2013; Bhandari et al., 2020; Syed et al., 2013). Further research is essential to explore whether there are as yet unidentified DDT inputs, in addition to dicofol, still being used in Bangladesh.

The presence of endrin ketone, a metabolite of endrin (Buah-Kwofie and Humphries, 2017), in the subsoil samples of the vegetable fields in this study reflects the historical applications of endrin in vegetable cultivation. There could be more recent applications of technical endosulfan (α-endosulfan/β-endosulfan ratios were > 1 in around 20 % of the positive samples) (Supplementary Table 10), along with its historical usage in the study area (Atuanya and Aborisade, 2017; Ouyang et al., 2012). Again, endosulfan sulphate, which was also present in subsoils, indicated the historical applications of this compound as an OCI in the study area since α-endosulfan and β-endosulfan can be easily metabolised into more persistent endosulfan sulphate (Joseph et al., 2020). The HCH source of the subsoils of current study area might be the historical applications of a technical product and/or the current uses of γ-HCH or lindane (the ratios of α-HCH/γ-HCH varied from 1.02 to 1.25, much less than technical HCH) (Supplementary Table 10) (Yang et al., 2010). The ratios of $\beta-/(\alpha+\gamma)$-HCH for all subsoil samples were below 0.5, indicating historical use of HCHs (Liu et al., 2012). Moreover, the prevalence of HCB as an abundant isomer of HCH in current study indicates the metabolite of ɣ-HCH (lindane) (Arias et al., 2011; Manz et al., 2001). Lindane has been forbidden for use in crop production by the Bangladesh government since 1997 (DoE, 2007). The samples with HCHs residues suggest that the subsoils contamination with HCHs was due to the past applications of technical HCHs or the degradation product of ɣ-HCH from current illegal applications, either intentionally or as impurities in other pesticide formulations (Qiu et al., 2004; Thakur and Pathania, 2020). The α-chlordane/γ-chlordane ratios from about 80 % of the positive subsoils in this study were < 1 but >0.77, and the remaining 20 % of subsoils had a ratio > 1 (Supplementary Table 10), indicating the possibility that the chlordane residues detected were derived from both recent illegal applications as well as historical ones (Zhang et al., 2006; Zhao et al., 2013), since Chlordane 40WP has been banned for use in Bangladesh since 1997 (DoE, 2007). Similar concentrations of more toxic metabolite heptachlor epoxide and the main compound heptachlor in subsoils of the study area indicate the wide historical application of heptachlor and the active degradation of heptachlor in the subsoils, as heptachlor has been banned in Bangladesh since 1997 (DoE, 2007). The distribution of Chlordecone and mirex in the subsoils of the study area might be derived from historical or recent illegal applications, either intentionally as direct applications or unintentionally as adulterants of other pesticides, since these compounds had never been imported or used in the area, thus they were never registered in Bangladesh (DoE, 2007). The present study also revealed a very weak correlation between the frequency and concentrations of ΣOCIs in soils and the soil physicochemical properties.

4.3. Transfer of OCI residues from the soil to the food chain

For OCI residues detected in vegetables, both ΣAldrines and ΣHCHs showed a positive correlation with corresponding subsoil residues. Moreover, the statistically significant strong positive correlation between ΣAldrines in subsoils and vegetables, particularly in cucurbit samples, indicates either the recent use of these compounds in vegetable cultivation in the study area or the uptake and bioaccumulation of these compounds by crop plants grown in contaminated soils. The Bio Accumulation Factors (BAF) of ΣAldrines from subsoils to vegetables were > 1 (3.67 ± 1.40, ranging from 1.38 to 5.77, Supplementary Table 11), indicating the bioaccumulation of ΣAldrines in vegetables from the subsoils of the study area. Crop plants from the Cucurbitaceae family, like zucchini, cucumber, squash, pumpkin, and melon, are able to uptake and bioaccumulate dieldrin and endrin residues from contaminated soils (Donnarumma et al., 2009; Jorgenson, 2001; Otani et al., 2007). Along with the cucurbits, jute (Tiliaceae) also showed higher concentration (approximately 250 $\mu g\ kg^{-1}$) of dieldrin, and a small uptake and bioaccumulation of endrin (Otani et al., 2007). The Cucurbitaceae crops have much higher bioaccumulation factors for dieldrin than non-Cucurbitaceae crops except for potatoes (*Solanum tuberosum* L.), carrots (*Dancus carota* L.), Japanese radishes (*Raphanus sativus* L.), and komatsunas (*Brassica campestris* var. perviridis) and are inappropriate for growing in dieldrin-polluted fields (Saito et al., 2012). Tomato, cabbage, celery, lettuce, kidney bean, and other non-cucurbit crops were suggested as alternative crops (Donnarumma et al., 2009; Otani et al., 2007; Yamamoto, 1973) that can be grown in dieldrin-contaminated fields similar to the fields in this study area. Substitute crops could be grown in organochlorine-polluted soils to reduce further health risks. In addition, cultivation of hyper-accumulating crops such as jute could be suggested for bioremediation of dieldrin-contaminated fields.

The BAF of ΣHCHs from subsoils to vegetables was 0.16 ± 0.27, which ranged from 0.00 to 0.62 (Supplementary Table 11), indicating the bioaccumulation of ΣHCHs from recent applications in vegetable cultivation in the study area. Crops have been shown to bioaccumulate HCB in their roots and in lower stems with larger residues linked to the higher lipid concentration of plants (Scheunert et al., 1983; Smelt and Leistra, 1974). However, it is also assumed that direct diffusion of gaseous HCB in soil into plant roots might happen or that plant foliage can take up the evaporated HCB (Ecker and Horak, 1994). Some studies with different arguments suggest non-significant HCB translocation from either roots or shoots, and the residues in roots and shoots were associated only with root uptake from the soil and foliar uptake, respectively (Schroll et al., 1994). However, Ecker and Horak (1994) reported that oil pumpkin roots can uptake HCB and translocate to the shoots.

Grazing dairy cattle on perennial grass or weeds grown on OCI contaminated agricultural soil might be a potential source of OCI found in cow's milk (Haque et al., 2017). When cattle were allowed to graze on land previously used as orchards, residues of DDE were detectable in milk fat (Willett et al., 1993). Cows feeding on the rejected parts or by-products of organochlorine-contaminated vegetables could also explain the residues found in milk, to some extent (Bushra et al., 2014). Agricultural soils with a history of intensive OCI application are thus not suitable for forage production or cattle grazing without first eliminating residues through remedial action.

4.4. Potential risks of multiple OCI residues in the terrestrial food chain for human health

Concern over the potential effects of pesticide residues in the terrestrial food chain on human health has grown due to the risks associated with cumulative exposure to multiple pesticides. Although trace amounts of highly persistent OCIs in contaminated soils in our study may pose a lower occupational health risk to humans, the presence of multiple residues, as well as their uptake and bioaccumulation in crop plants, continues to threaten overall food safety, both nationally and internationally. It is concerning that multiple OCI residues were found in the vegetables and cow milk in our study, which are below the individual substance-by-substance MRLs but highly hazardous to mammals and have been linked to negative human health effects. When highly persistent pesticide residues, such as OCIs, are ingested through contaminated foods, they can cause acute poisoning, but these cases are uncommon (Mendes et al., 2005). For over a century, the cumulative effects of repeated low-level exposures to pesticide residues in food have generated concern and sparked political and scientific debate, but they have largely gone unnoticed. Chronic health impacts, including damage to the brain and neurological system, cancer and other tumors, birth abnormalities, infertility and other reproductive problems, liver, kidney, lung, and other organ damage, can result from long-term exposure to pesticide residues (Melanda and Galiciolli, 2022).

Although it is very difficult to predict the effects of long-term low-level exposures to multiple OCI residues, there may be a correlation between the rising number of cancer patients in Bangladesh (NICRH, 2022) and lifetime low-level exposures to multiple pesticide residues from eating contaminated food and engaging in agricultural practices on contaminated lands. In Bangladesh, men from intensive cropping areas who worked primarily in agriculture made up the majority of newly registered cancer patients between 2018 and 2020 (NICRH, 2022).

We require integrated risk assessments that take into account the combined effects of these various pesticide residue mixtures in the real world in order to better understand the risks to human health. The development and harmonization of methodologies to assess the cumulative adverse effects of pesticide mixtures in a scientific manner should serve as the foundation for risk management. Since the 1980s, methods have been developed to estimate the risks associated with dietary exposure to multiple pesticides. These methods rely on the dose-addition of substances within a mixture that have similar biological activity but differ in potency. The primary difficulty lies in defining a cumulative assessment group (CAG), which is largely dependent upon a reliable and excellent toxicological database. Because of the process's intricacy, regulatory agencies have not yet harmonized, and the procedure is not used to determine maximum residue levels (Caldas, 2023). The majority of studies carried out globally have only indicated possible health risks from cumulative exposure when extremely conservative assessment assumptions were made. Duan et al. (2021) proposed a cumulative exposure assessment approach where data on pesticide residues are sufficient, but the individual dietary consumption is inadequate (Duan et al., 2021). Some authors also suggested considering an additional assessment factor to account for the additive, but also potential synergistic simultaneous pesticide mixture risk during pesticide risk assessment (Weisner et al., 2021).

5. Conclusions

This study quantified OCI residues in soils, vegetables, and cow's milk from an intensive vegetable producing area of NW Bangladesh. Negligible to low contamination levels of currently banned highly persistent OCI residues like ΣDDTs, ΣAldrines, ΣEndosulfans, ΣHCHs, and ΣHeptachlors were detected in soils, indicating extensive application of these OCIs for vegetable production in the study area. The presence of OCI residues stems from both historical use of the compounds and from current applications, especially ΣEndosulfans, as indicated by source analysis. The highly persistent OCI compounds take years to decompose, and some of them degrade into more toxic compounds in soil. Their bioaccumulation capacity makes these OCIs serious potential health threats to farmers exposed to them during farming activities as well as consumers consuming contaminated food. Non-edible hyperaccumulating crops like jute could be cultivated for the bioremediation of polluted fields. Non-cucurbitaceous, shallow rooted and quick growing vegetables could be suggested as substitute crops for the study area. Organochlorine-contaminated agricultural soils are not suitable for forage production or cattle grazing without taking remedial action to eliminate residues. The levels of the OCIs like Aldrines and HCHs detected in vegetables and DDT metabolites (*p,p'*- and *o,p'*-DDE) in cow's milk were lower than the MRLs for these compounds. However, the detected residues in vegetables and milk could pose the threat of both carcinogenic and non-carcinogenic chronic toxicity and health risks to consumers, as multiple insecticide residues may exceed the MRLs for single residue concentrations. It is apparent that the multiple OCI compounds raise serious health concerns regarding both vegetables and cow's milk, which are regularly consumed by young children and pregnant women. Human risk assessments and MRLs for multiple residues are grossly lacking and should be more closely examined. Therefore, more emphasis should be given to routine analysis of insecticide residues in soil as well as residues in commonly consumed food commodities, including vegetables and cow's milk in Bangladesh. There is also a strong need for legal enforcement of insecticide regulations and maximum residue limits for pesticide mixtures. In addition, farmers and other stakeholders should be trained with the aim of discouraging the illegal use of banned insecticides and encouraging farmers to follow the compulsory pre-harvest intervals for vegetable production.

CRediT authorship contribution statement

Mousumi Akter: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Md. Shohidul Alam:** Data curation, Software, Writing – review & editing. **Xiaomei Yang:** Data curation, Writing – review & editing. **João Pedro Nunes:** Data curation, Visualization. **Paul Zomer:** Data curation, Methodology, Validation. **Md. Mokhlesur Rahman:** Writing – review & editing. **Hans Mol:** Data curation, Methodology, Supervision, Validation. **Coen J. Ritsema:** Conceptualization. **Violette Geissen:** Conceptualization, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

Adeleye, A.O., Sosan, M.B., Oyekunle, J.A.O., 2019. Dietary exposure assessment of organochlorine pesticides in two commonly grown leafy vegetables in South-Western Nigeria. Heliyon 5, e01895.

Aiyesanmi, A., Idowu, G., 2012. Organochlorine pesticides residues in soil of cocoa farms in Ondo state Central District, Nigeria. Environ. Nat. Resour. Res. 2.

Akter, M., Fan, L., Rahman, M.M., Geissen, V., Ritsema, C.J., 2018. Vegetable farmers' behaviour and knowledge related to pesticide use and related health problems: a case study from Bangladesh. J. Clean. Prod. 200, 122–133.

Alamdar, A., Syed, J.H., Malik, R., Katsoyiannis, A., Liu, J., Li, J., et al., 2013. Organochlorine pesticides in surface soils from obsolete pesticide dumping ground in Hyderabad City, Pakistan: contamination levels and their potential for air-soil exchange. Sci. Total Environ. 470-471C, 733–741.

Alamgir Zaman Chowdhury, M., Fakhruddin, A.N.M., Nazrul Islam, M., Moniruzzaman, M., Gan, S.H., Khorshed, Alam M., 2013. Detection of the residues of nineteen pesticides in fresh vegetable samples using gas chromatography–mass spectrometry. Food Control 34, 457–465.

Anastassiades, M., Lehotay, S.J., Štajnbaher, D., Schenck, F.J., 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. J. AOAC Int. 86, 412–431.

Anastassiades, M., Scherbaum, E., Taşdelen, B., štajnbaher, D., 2007. Recent Developments in QuEChERS Methodology for Pesticide Multiresidue Analysis, pp. 439–458.

Arias, A.H., Pereyra, M.T., Marcovecchio, J.E., 2011. Multi-year monitoring of estuarine sediments as ultimate sink for DDT, HCH, and other organochlorinated pesticides in Argentina. Environ. Monit. Assess. 172, 17–32.

Atuanya, E., Aborisade, W., 2017. Pesticide pollution status in cocoa plantation soil. Glob. J. Environ. Sci. Manag. 3, 287–298.

Bai, J., Lu, Q., Zhao, Q., Wang, J., Gao, Z., Zhang, G., 2015. Organochlorine pesticides (OCPs) in wetland soils under different land uses along a 100-year chronosequence of reclamation in a Chinese estuary. Sci. Rep. 5, 17624.

BBS, 2011a. Population and Housing Census-2011. 2. Statistics and Information Division, Ministry of Planning.

BBS, 2011b. Yearbook of Agricultural Statistics of Bangladesh, 2011. Bangladesh Bureau of Statistics (BBS), Statistics and Informatics Division, Ministry of Planning, Government of the People's Republic of Bangladesh Dhaka, p. 320.

BCGLOBAL, 2020. Pesticide MRLs. https://bcglobal.bryantchristie.com/db#pesticides/query.2020.

Bergkvist, C., Aune, M., Nilsson, I., Sandanger, T.M., Hamadani, J.D., Tofail, F., et al., 2012. Occurrence and levels of organochlorine compounds in human breast milk in Bangladesh. Chemosphere 88, 784–790.

Bettinetti, R., Quadroni, S., Boggio, E., Galassi, S., 2016. Recent DDT and PCB contamination in the sediment and biota of the Como Bay (Lake Como, Italy). Sci. Total Environ. 542, 404–410.

Bhandari, G., Atreya, K., Scheepers, P., Geissen, V., 2020. Concentration and distribution of pesticide residues in soil: non-dietary human health risk assessment. Chemosphere 253, 126594.

Bigus, P., Tobiszewski, M., Namieśnik, J., 2014. Historical records of organic pollutants in sediment cores. Mar. Pollut. Bull. 78, 26–42.

Bouyoucos, G.J., 1962. Hydrometer method improved for making particle size analyses of soils1. Agron. J. 54, 464–465.

Buah-Kwofie, A., Humphries, M.S., 2017. The distribution of organochlorine pesticides in sediments from iSimangaliso Wetland Park: ecological risks and implications for conservation in a biodiversity hotspot. Environ. Pollut. 229, 715–723.

Bushra, I., Samina, S., Shafiqur, R., 2014. Assessment of the dietary transfer of pesticides to dairy milk and its effect on human health. Afr. J. Biotechnol. 13, 476–485.

Caldas, E.D., 2023. Approaches for cumulative dietary risk assessment of pesticides. Curr. Opin. Food Sci. 53, 101079.

Clostre, F., Letourmy, P., Magalie, L.-J., 2015. Organochlorine (chlordecone) uptake by root vegetables. Chemosphere 118C, 96–102.

DoE, 2007. Bangladesh National Implementation Plan (NIP) For Management of Persistent Organic Pollutants (POPs) Prepared under UNDP Project BGD/02/G31/1G/99 Bangladesh: Preparation of the POPs National Implementation Plan under the Stockholm Convention. Department of Environment (DoE), Ministry of Environment and Forests, Government of the People's Republic of Bangladesh, Dhaka, p. 216.

Donnarumma, L., Pompi, V., Faraci, A., Conte, E., 2009. Dieldrin uptake by vegetable crops grown in contaminated soils. J. Environ. Sci. Health B 44, 449–454.

Duan, Y., Ramilan, T., Luo, J., French, N., Guan, N., 2021. Risk assessment approaches for evaluating cumulative exposures to multiple pesticide residues in agro-products using seasonal vegetable monitoring data from Hainan, China: a case study. Environ. Monit. Assess. 193.

Dursun, S., Köysüren, H., 2014. Determination of pesticide residues in fruits and vegetables in Konya city. J. Food Agric. Environ. 12, 998–1000.

Ecker, S., Horak, O., 1994. Pathways of HCB-contamination oil pumpkin seeds. Chemosphere 29, 2135–2145.

European Commission, 2012. Sampling: Vegetables and fruits, non-frozen. In: https://ec.europa.eu/taxation_customs/dds2/SAMANCTA/EN/SamplingProcedure/VegetablesFruitNon-frozen_EN.htm.

European Commission, 2015. Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticides Residues Analysis in Food and Feed.

Fosu-Mensah, B.Y., Okoffo, E.D., Darko, G., Gordon, C., 2016. Assessment of organochlorine pesticide residues in soils and drinking water sources from cocoa farms in Ghana. Springerplus 5, 869.

Gereslassie, T., Workineh, A., Atieno, O., Wang, J., 2019. Determination of occurrences, distribution, health impacts of organochlorine pesticides in soils of Central China. Int. J. Environ. Res. Public Health 16, 146.

Haque, R., Inaoka, T., Fujimura, M., Ahmad, S.A., Ueno, D., 2017. Intake of DDT and its metabolites through food items among reproductive age women in Bangladesh. Chemosphere 189, 744–751.

Heck, M.C., Sifuentes dos Santos, J., Bogusz Junior, S., Costabeber, I., Emanuelli, T., 2007. Estimation of children exposure to organochlorine compounds through milk in Rio Grande do Sul, Brazil. Food Chem. 102, 288–294.

Hossain, M., Fakhruddin, A.N.M., Chowdhury, M., Rahman, M., Alam, M., 2015. Health risk assessment of selected pesticide residues in locally produced vegetables of Bangladesh. Int. Food Res. J. 22, 110–115.

Hussain, M.A., Kabir, M.L., Sayeed, M.A., Mahbub-E-Elahi, A.T.M., Ahmed, M.S., Islam, M.J., 2018. Organochlorine pesticide residues and microbiological quality assessment of dried barb, Puntius sophore, from the northeastern part of Bangladesh. Fishes 3, 44.

Islam, M., Hoque S, M., Chowdhury, M., Rahman, M., Fardous, Z., 2007. Monitoring of organochlorine pesticide residues in surface water samples of the agricultural field of Bangladesh. J. Subtrop. Agric. Res. Dev. 5, 357–360.

Jiang, Y.-F., Wang, X.-T., Jia, Y., Wang, F., Wu, M.-H., Sheng, G.-Y., et al., 2009. Occurrence, distribution and possible sources of organochlorine pesticides in agricultural soil of Shanghai, China. J. Hazard. Mater. 170, 989–997.

John, P.J., Bakore, N., Bhatnagar, P., 2001. Assessment of organochlorine pesticide residue levels in dairy milk and buffalo milk from Jaipur City, Rajasthan, India. Environ. Int. 26, 231–236.

Jorgenson, J.L., 2001. Aldrin and dieldrin: a review of research on their production, environmental deposition and fate, bioaccumulation, toxicology, and epidemiology in the United States. Environ. Health Perspect. 109 (Suppl. 1), 113–139.

Joseph, L., Paulose, S.V., Cyril, N., Santhosh, S.K., Varghese, A., Nelson, A.B., et al., 2020. Organochlorine pesticides in the soils of Cardamom Hill reserve (CHR), Kerala, India: geo spatial distribution, ecological and human health risk assessment. Environ. Chem. Ecotoxicol. 2, 1–11.

Kampire, E., Kiremire, B.T., Nyanzi, S.A., Kishimba, M., 2011. Organochlorine pesticide in fresh and pasteurized cow's milk from Kampala markets. Chemosphere 84, 923–927.

Kaushik, C.P., Kaushik, A., Sharma, H.R., 2014. Seasonal trends in organochlorine pesticide residues in raw bovine milk from rural areas of Haryana, India. Bull. Environ. Contam. Toxicol. 92, 15–22.

Kuba, J., Tomza-Marciniak, A., Pilarczyk, B., Tarasewicz, N., Pilarczyk, R., Ligocki, M., 2015. Comparison of DDT and its metabolites concentrations in cow milk from agricultural and industrial areas. J. Environ. Sci. Health B 50, 1–7.

Kumar, B., Mishra, M., Verma, V.K., Rai, P., Kumar, S., 2018. Organochlorines in urban soils from Central India: probabilistic health hazard and risk implications to human population. Environ. Geochem. Health 40, 2465–2480.

Lehotay, S.J., de Kok, A., Hiemstra, M., Van Bodegraven, P., 2005. Validation of a fast and easy method for the determination of residues from 229 pesticides in fruits and vegetables using gas and liquid chromatography and mass spectrometric detection. J. AOAC Int. 88, 595–614.

Lehotay, S., Son, K., Kwon, H.-Y., Koesukwiwat, U., Fu, W., Mastovska, K., et al., 2010. Comparison of QuECHERS sample preparation methods for the analysis of pesticide residues in fruit and vegetables. J. Chromatogr. A 1217, 2548–2560.

Li, J., Zhang, G., Qi, S., Li, X., Peng, X., 2006. Concentrations, enantiomeric compositions, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China. Sci. Total Environ. 372, 215–224.

Liu, W.-X., He, W., Qin, N., Kong, X.-Z., He, Q.-S., Ouyang, H.-L., et al., 2012. Residues, distributions, sources, and ecological risks of OCPs in the water from Lake Chaohu, China. Sci. World J. 2012, 897697.

Luzardo, O.P., Almeida-González, M., Henríquez-Hernández, L.A., Zumbado, M., Álvarez-León, E.E., Boada, L.D., 2012. Polychlorobiphenyls and organochlorine pesticides in conventional and organic brands of milk: occurrence and dietary intake in the population of the Canary Islands (Spain). Chemosphere 88, 307–315.

Ma, J., Pan, L.-b., Yang, X.-y., Liu, X.-l., Tao, S.-y., Zhao, L., et al., 2016. DDT, DDD, and DDE in soil of Xiangfen County, China: residues, sources, spatial distribution, and health risks. Chemosphere 163, 578–583.

Manz, M., Wenzel, K.D., Dietze, U., Schüürmann, G., 2001. Persistent organic pollutants in agricultural soils of Central Germany. Sci. Total Environ. 277, 187–198.

Melanda, V.S., Galiciolli, M.E.A., 2022. Impact of Pesticides on Cancer and Congenital Malformation: A Systematic Review, p. 10.

Mendes, C.A., Mendes, G.E., Cipullo, J.P., Burdmann, E.A., 2005. Acute intoxication due to ingestion of vegetables contaminated with aldicarb. Clin. Toxicol. (Phila.) 43, 117–118.

Miglioranza, K.S., Gonzalez, M., Ondarza, P.M., Shimabukuro, V.M., Isla, F.I., Fillmann, G., et al., 2013. Assessment of Argentinean Patagonia pollution: PBDEs, OCPs and PCBs in different matrices from the Río Negro basin. Sci. Total Environ. 452, 275–285.

Mishra, K., Sharma, R.C., Kumar, S., 2012. Contamination levels and spatial distribution of organochlorine pesticides in soils from India. Ecotoxicol. Environ. Saf. 76, 215–225.

Mol, H.G., Plaza-Bolaños, P., Zomer, P., de Rijk, T.C., Stolker, A.A., Mulder, P.P., 2008. Toward a generic extraction method for simultaneous determination of pesticides, mycotoxins, plant toxins, and veterinary drugs in feed and food matrixes. Anal. Chem. 80, 9450–9459.

Nag, S., Raikwar, M., 2008. Organochlorine pesticide residues in bovine milk. Bull. Environ. Contam. Toxicol. 80, 5–9.

NICRH, 2022. Hospital cancer registry report 2018-2020. Department of Cancer Epidemiology, National Institute of cancer Research & Hospital (NICRH), Dhaka, Bangladesh.

Oehme, M., 1991. Dispersion and transport paths of toxic persistent organochlorines to the Arctic—levels and consequences. Sci. Total Environ. 106, 43–53.

Oliveira, A.H., Cavalcante, R.M., Duaví, W.C., Fernandes, G.M., Nascimento, R.F., Queiroz, M.E., et al., 2016. The legacy of organochlorine pesticide usage in a tropical semi-arid region (Jaguaribe River, Ceará, Brazil): implications of the influence of sediment parameters on occurrence, distribution and fate. Sci. Total Environ. 542, 254–263.

Otani, T., Seike, N., Sakata, Y., 2007. Differential uptake of dieldrin and endrin from soil by several plant families and Cucurbita genera. Soil Sci. Plant Nutr. 53, 86–94.

Ouyang, H.-L., He, W., Qin, N., Kong, X.-Z., Liu, W.-X., He, Q.-S., et al., 2012. Levels, temporal-spatial variations, and sources of organochlorine pesticides in ambient air of Lake Chaohu, China. Sci. World J. 2012, 504576.

Oyekunle, J.A.O., Ogunfowokan, A.O., Torto, N., Akanni, M.S., 2011. Determination of organochlorine pesticides in the agricultural soil of Oke-Osun farm settlement, Osogbo, Nigeria. Environ. Monit. Assess. 177, 51–61.

Pandit, G., Sahu, S., 2002. Assessment of risk to public health posed by persistent organochlorine pesticide residues in milk and milk products in Mumbai, India. J. Environ. Monit. 4, 182–185.

Qiu, X., Zhu, T., Li, J., Pan, H., Li, Q., Miao, G., et al., 2004. Organochlorine pesticides in the air around the Taihu Lake, China. Environ. Sci. Technol. 38, 1368–1374.

Qiu, X., Zhu, T., Yao, B., Hu, J., Hu, S., 2005. Contribution of Dicofol to the current DDT pollution in China. Environ. Sci. Technol. 39, 4385–4390.

Qu, C., Albanese, S., Chen, W., Lima, A., Doherty, A.L., Piccolo, A., et al., 2016. The status of organochlorine pesticide contamination in the soils of the Campanian plain, southern Italy, and correlations with soil properties and cancer risk. Environ. Pollut. 216, 500–511.

Régo, I.C.V., Santos, GnVd, Santos, GnVd, Ribeiro, J.S., Lopes, R.B., Santos, Sbd, et al., 2019. Organochlorine pesticides residues in commercial milk: a systematic review. Acta Agronómica 68, 99–107.

Saito, T., Otani, T., Seike, N., Okazaki, M., 2012. A comparison of dieldrin residues in various vegetable crops cultivated in a contaminated field. Soil Sci. Plant Nutr. 58, 373–383.

Salehi, M., Beni, O., Harchegani, H., Esfandiarpour, I., Motaghian, H., 2011. Refining soil organic matter determination by loss-on-ignition. Pedosphere 21, 473–482.

Salem, N., Ahmad, R., Estaitieh, H., 2009. Organochlorine pesticide residues in dairy products in Jordan. Chemosphere 77, 673–678.

Scheunert, I., Marra, C., Viswanathan, R., Klein, W., Korte, F., 1983. Fate of hexachlorobenzene-14C in wheat plants and soil under outdoor conditions. Chemosphere 12, 843–858.

Schroll, R., Bierling, B., Cao, G., Dörfler, U., Lahaniati, M., Langenbach, T., et al., 1994. Uptake pathways of organic chemicals from soil by agricultural plants. Chemosphere 28, 297–303.

Shi, Y., Meng, F., Guo, F., Lu, Y., Wang, T., Zhang, H., 2005. Residues of organic chlorinated pesticides in agricultural soils of Beijing, China. Arch. Environ. Contam. Toxicol. 49, 37–44.

Silva, V., Mol, H.G.J., Zomer, P., Tienstra, M., Ritsema, C.J., Geissen, V., 2019. Pesticide residues in European agricultural soils – a hidden reality unfolded. Sci. Total Environ. 653, 1532–1545.

Smelt, J.H., Leistra, M., 1974. Hexachlorobenzene in soils and crops after soil treatment with pentachloronitobenzene. Agric. Environ. 1, 65–71.

Sun, H., Qi, Y., Zhang, D., Li, Q.X., Wang, J., 2016. Concentrations, distribution, sources and risk assessment of organohalogenated contaminants in soils from Kenya, Eastern Africa. Environ. Pollut. 209, 177–185.

Syed, J.H., Malik, R., Li, J., Chaemfa, C., Zhang, G., Jones, K., 2013. Status, distribution and ecological risk of organochlorines (OCs) in the surface sediments from the Ravi River, Pakistan. Sci. Total Environ. 472.

Tao, S., Liu, W., Li, Y., Yang, Y., Zuo, Q., Li, B., et al., 2008. Organochlorine pesticides contaminated surface soil as reemission source in the Haihe Plain, China. Environ. Sci. Technol. 42, 8395–8400.

Thakur, M., Pathania, D., 2020. Chapter 12 - environmental fate of organic pollutants and effect on human health. In: Singh, P., Kumar, A., Borthakur, A. (Eds.), Abatement of Environmental Pollutants. Elsevier, pp. 245–262.

The Netherlands Ministry of Housing, 2000. Annex A: Target Values, Soil Remediation Intervention Values and Indicative Levels for Serious Contamination. Dutch Target and Intervention Values, 2000 (the New Dutch List) Version, februari 4th, 2000, p. 51.

Tsakiris, I.N., Goumenou, M., Tzatzarakis, M.N., Alegakis, A.K., Tsitsimpikou, C., Ozcagli, E., et al., 2015. Risk assessment for children exposed to DDT residues in various milk types from the Greek market. Food Chem. Toxicol. 75, 156–165.

Uddin, M., Chowdhury, M., Fardous, Z., Md. Hasanuzzaman D., 2016. Quantification of pesticide residues in some soils of Narshingdi area. Bangladesh J. Sci. Res. 29, 85.

UNEP, 2015. Stockholm Convention. http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPS/tabid/2509/Default.aspx. Accessed from 28/06/2016.

Waktola, H., Hymete, A., Bekhit, A., Mohamed, A.-M., Bekhit, A., 2014. Persistent organochlorine pesticides residues in cow and goat milks collected from different regions of Ethiopia. Chemosphere 106.

Wang, G.-l., Ma, L.-m., Sun, J.-h., Zhang, G., 2010. Occurrence and distribution of organochlorine pesticides (DDT and HCH) in sediments from the middle and lower reaches of the Yellow River, China. Environ. Monit. Assess. 168, 511–521.

Wang, B., Wu, C., Liu, W., Teng, Y., Luo, Y., Christie, P., et al., 2016. Levels and patterns of organochlorine pesticides in agricultural soils in an area of extensive historical cotton cultivation in Henan province, China. Environ. Sci. Pollut. Res. Int. 23.

Weisner, O., Frische, T., Liebmann, L., Reemtsma, T., Roß-Nickoll, M., Schäfer, R.B., et al., 2021. Risk from pesticide mixtures – the gap between risk assessment and reality. Sci. Total Environ. 796, 149017.

Willett, L.B., O'Donnell, A.F., Durst, H.I., Kurz, M.M., 1993. Mechanisms of movement of organochlorine pesticides from soils to cows via forages. J. Dairy Sci. 76, 1635–1644.

Wong, M.H., Leung, A.O., Chan, J.K., Choi, M.P., 2005. A review on the usage of POP pesticides in China, with emphasis on DDT loadings in human milk. Chemosphere 60, 740–752.

Xu, W., Wang, X., Cai, Z., 2013. Analytical chemistry of the persistent organic pollutants identified in the Stockholm convention: a review. Anal. Chim. Acta 790, 1–13.

Yamamoto, M., 1973. Residues of organochlorinated insecticides in various vegetable crops. Bull. Kochi Inst. Agric. Forest Sci. 5, 1–8.

Yang, H., Xue, B., Yu, P., Zhou, S., Liu, W., 2010. Residues and enantiomeric profiling of organochlorine pesticides in sediments from Yueqing Bay and Sanmen Bay, East China Sea. Chemosphere 80, 652–659.

Yu, H.Y., Li, F.B., Yu, W.M., Li, Y.T., Yang, G.Y., Zhou, S.G., et al., 2013. Assessment of organochlorine pesticide contamination in relation to soil properties in the Pearl River Delta, China. Sci. Total Environ. 447, 160–168.

Yuan, X., Yang, X., Na, G., Zhang, A., Mao, Y., Liu, G., et al., 2015. Polychlorinated biphenyls and organochlorine pesticides in surface sediments from the sand flats of Shuangtaizi estuary, China: levels, distribution, and possible sources. Environ. Sci. Pollut. Res. 22, 14337–14348.

Zehra, A., Eqani, S.A.M.A.S., Katsoyiannis, A., Schuster, J.K., Moeckel, C., Jones, K.C., et al., 2015. Environmental monitoring of organo-halogenated contaminants (OHCs) in surface soils from Pakistan. Sci. Total Environ. 506–507, 344–352.

Zhang, H.B., Luo, Y.M., Zhao, Q.G., Wong, M.H., Zhang, G.L., 2006. Residues of organochlorine pesticides in Hong Kong soils. Chemosphere 63, 633–641.

Zhao, Z., Zeng, H., Wu, J., Zhang, L., 2013. Organochlorine pesticide (OCP) residues in mountain soils from Tajikistan. Environ. Sci. Process Impacts 15, 608–616.

Zhi, H., Zhao, Z., Zhang, L., 2015. The fate of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in water from Poyang Lake, the largest freshwater lake in China. Chemosphere 119, 1134–1140.