Perennial Existence of Organochlorine Pesticides in the Soils of Amghara, Kuwait

Hassan Alshemmari

Abstract
A comprehensive study from the surface soil samples of 14 locations from Amghara, Kuwait were assessed for the investigation of organochlorine pesticides (OCPs). There is limited information regarding the distribution pattern of OCPs in the soil samples of Kuwait. The total concentration of OCPs was in the range of 209.39 pg/g - 7449.18 pg/g with an average value of 1313.04 pg/g. DDT had higher concentrations in soil samples (969.52 pg/g) than the other pesticides, according to the findings. The distribution pattern of OCPs in the Amghara soils revealed their origin as both historical and recent applications of pesticides. The study extended, how residual quantities could be used to determine health risks of both children and adults. Children and adults in all the locations were subject to negligible cancer risk, according to the health risk evaluation.

Keywords Organochlorine pesticides · Soil samples · Pesticide residue · Health risk assessment

Introduction
Organochlorine pesticides (OCPs), which are semi-volatile and stable synthetic chemicals, enter the environment by numerous matrices and bioaccumulate in food chains as they pass through different biological trophic layers (Wang et al. 2015). Last few decades the widespread use of OCPs were observed. Furthermore, these chemicals were extensively used to deter vector-borne epidemic diseases in tropical countries. Due to the high level of environmental toxicity and health impacts, the large-scale production and use of OCPs (benzene hexachlorides (BHC) and dichlorodiphenyltrichloroethylene (DDTs) is currently prohibited. However, the environmental, human and wildlife health impacts of their residues have been detected and reported in many countries (Alshemmari, 2021a). BHCs and DDTs are often used as representative compounds in assessing the environmental status of OCPs due to their wide variety of historical uses, human health, and environmental impacts. POPs are particularly obstinate to chemical and biological degradation and thus live for long periods in the environment (Alshemmari, 2021b). To treat the persistent organic pollutants (POPs) in an excellent way the Stockholm Convention has listed variety classes of POPs based on their toxicity. Soil was a repository for all kinds of contaminants, including OCP inputs. Many OCPs have a strong preference for dirt, which could be absorbed by crops and grazing animals and thereby enter humans. They may also have been washed into watercourses through run-off from the soil and discharged into the atmosphere by volatilization, resulting in water and atmospheric pollution.

Pesticide intake and human health data over the last two decades have shown that some pesticides cause neurological disorders and degenerative diseases, that some affect fetal development and cause congenital defects, and that some are carcinogenic to humans (Asghar et al. 2016; Alshemmari et al. 2022). Pesticides have been linked to a variety of negative health effects, which vary in severity and length of exposure. Pesticides have a wide variety of health effects, from minor asthma, rashes, respiratory problems, neurotoxicity, and reproductive disorders to lethal chronic diseases such as cancer. The evaluation and control of OCPs
in vegetable crops provides a foundation for assessing the risk of these toxins to human health (Qu et al. 2015). Gevao et al., 2018 reported on previous studies of organochlorine pesticides in Kuwait, with the emphasis on air samples from urban, rural, and industrial areas. Along the urban, remote, and industrial areas, the concentrations were 33-1352 pg/m3, 4.5–556 pg/m3, and 8.8–533 pg/m3, respectively. The recent study reported in the agricultural region of Sulaibiya shows the average concentration of OCPs was 3062 pg/g (Alshemmari et al. 2021). The present study discussed the distribution pattern of 22 congeners of OCPs (Pentachlorobenzene; Hexachlorobenzene; BHC-alpha, beta, gamma, & delta; Heptachlor; Aldrin; Heptachlor exo-epoxide (isomer B); Chlordane-oxy, trans, & cis; DDE-o,p' & p,p'; DDD-o,p' & p,p'; DDT-o,p' & p,p'; Endosulfan; and Nonachlor cis & trans) along the Amghara locations situated in Kuwait. The study has also discussed the health risk assessment due to the use of OCPs along the observed locations.

Materials and Methods

Sampling

The location of the sampling at the Amghara is shown in the Fig. 1. The region is about 20 km north of Kuwait City and 1.5 km from the Gulf coast. The sites are close to commercial centers. It houses a historic scrap metal plant that can accept and handle all forms of metal scrap, including end-of-life cars (Alshemmari, 2021b). Using a pre-cleaned stainless steel scoop, four subsamples were gathered inside a 50 m x 50 m plot at each position and thoroughly combined to create a homogeneous composite sample. All samples were wrapped in aluminum foil, covered in polythene containers, and stored at -4 °C until ready to be analyzed.
Extraction and Analysis

The US-EPA suggested 8080 A method was used for OCP study of soil samples (Yang et al. 2013). Prior to Soxhlet-dichloromethane (DCM) extraction, portions of 10 g air-dried soils were spiked with 20 ng mixed recovery surrogates containing 2, 4, 5, 6-tetrachloro-m-xylene (TCmX) and decachlorobiphenyl (PCB209) for 24 h. The OCP extracts were first dissolved in hexane and the final amount was reduced to 2–3 mL by rotary evaporation. To purify the concentrate, the OCPs were eluted with 30 mL DCM/hexane (2/3, v/v) on an alumina/silica (v/v = 1:2) gel column (48 h DCM extraction, then 180 and 240 °C 12 h muffle drying, all 3% H2O deactivated). The eluent was condensed to 0.2 mL using a gentle nitrogen current. The samples were then moved to 100-L glass inserts and spiked with 20 ng isodrin before being analyzed using an Agilent 7890B gas chromatograph for organochlorine pesticides (OCPs) coupled to a triple quadruple mass spectrometer in electron ionization mode.

Quality Assurance/ Quality Control

Stringent quality-assurance and quality-control protocols were implemented to monitor the analytical process. Identification and quantification were done using 5 calibration levels of known concentrations. A peak was positively established if it was within 0.05 min of the calibration standard’s retention period, and only quantified if the S/N was 3 and the ratio of the ion to its qualifier ion was within 20% of the standard value. There was no discernible difference between laboratory and field blanks, implying negligible contamination during transport, storage, and examination. When analytes were found in a batch of samples in a blank, the values were subtracted from those found in the sample extracts. The method detection limits (MDLs) were calculated using the mean of the field blank +3×SD. In situations where the target analytes were not found in the field blanks, the given MDL value was calculated as three times the signal-to-noise ratio of the lowest calibration. Surrogate recovery was found to be 85±12% for the majority of pesticides studied.

Carcinogenic Risk Assessment

Cancer hazards from ingestion, dermal route, and inhalation of soil particles were calculated using the following Eqs. (1), (2), and (3), which were modified from two US Environmental Protection Agency reports (U.S. EPA) (USEPA, 1997, 2009) (Qu et al. 2017).

\[
C_{\text{ingest}} = \frac{C_{\text{soil}} \times \text{IngR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF} \times SF_{\text{soil}}
\]

\[
C_{\text{inhale}} = \frac{C_{\text{soil}} \times \text{SA} \times \text{InhR} \times \text{AF}_{\text{inh}} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{AT}} \times \text{IUR}
\]

where Csoil is the contaminant content of soil (mg kg⁻¹), IngR is the ingestion rate of soil (mg d⁻¹), EF is the exposure level (days year⁻¹), ED is the exposure period (a), BW is the average body weight (kg), AT is the averaging time (d), and CF is the conversion factor (1 x 10⁻⁶ kg mg⁻¹), and SForal is the oral slope factor (2.0E+00 (mg kg⁻¹ d⁻¹⁻¹)).

SA is the surface region of the skin that touches the soil (cm²), AF soil is the soil adherence factor (mg cm⁻²), and ABS is the dermal absorption factor (chemical specific). The percentage of contaminants ingested in the gastrointestinal tract is known as GIABS.

Results and Discussions

Distribution Pattern of OCPs

The present study discusses the level of OCPs and health risk assessment of these OCPs along the 14 locations of the Amghara. There are few studies have done about the OCPs in the soil samples of Kuwait. In this paper, 17 congeners out of 22 congeners were significantly contributing and those congeners were included in the discussion. The level of DDT is dominating compared to the level of other OCPs studied.

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was 19.42 pg/g. The range of Σ22OCP along the Amghara locations were ND to 7449.19 pg/g. The distribution pattern of BHC is shown in the Fig. 2. The level of BHC were observed at only 5 locations (A, B, C, E, and F). The rest all the observed locations were in the below detection range of BHC. The least observed form of BHC was delta among the all 4 forms of BHC. Apart from that delta form of BHC was observed only at one location (A) and the correspondent concentration was 10.93 pg/g. Each form of OCP had a different distribution pattern in Amghara, implying that different groups of OCPs were not used at the same time in this region. In comparison to the amount of DDTs in this sample, all types of BHC have moderately low concentrations.

The α/γ -ratio is used to differentiate fresh BHC inputs based on the composition of BHCs (Alshemmari et al. 2021). A high ratio of α/γ -BHC thus represents historical evidence of BHCs, while a low ratio of α/γ -BHC indicates recent use of BHC (Tao et al. 2005). The present study showed the α/γ-BHC ratios of 0.79–0.89 indicates the recent use of these BHC. However, the use of these pesticides are legally stopped in Kuwait, it might be originated from the obsolete stocks. The ratio of - βHCH/ΣHCH is less than 0.5, indicating recent HCH inputs (Aamir et al. 2018). According to the current research, the ratio was in the range of 0.34 to 0.42. It alludes to BHC’s recent activities. In all the stations relatively higher proportion of β-BHC was observed. Both α and γ -BHCs are commonly transformed to β -BHC in the soil matrix, which may be one of the reasons for the high prevalence of β -BHC in Amghara soils. The results also suggest that β -BHC’s (relatively persistent form) predominance may be attributable to its recent use. β - BHC has a higher tolerance for soil organic matter and a lower rate of evaporation. Furthermore, as opposed to other types of BHCs, the organization of chlorine atoms in the molecular structure of β -BHC prevents microbial degradation. The proliferation of β-HCH is due to its lower degradation, water solubility, and good affinity for soil adsorption (Onogbosele et al., 2014), as well as microorganisms and photoisomerization conversion of γ-HCH isomer to β-HCH (Zhang et al. 2003).

Hexachlorobenzene was ubiquitous along the observed locations and the concentration was in the range of ND-1297.64 pg/g. Chlordane-oxy was observed only at two locations with an average value of 40.56 pg/g. Chlordane-cis and trans were in the range of ND-36.56 pg/g and ND-50 pg/g respectively (Fig. 3). Heptachlor was in the range of ND-40.56 pg/g. The level of nonachlor-cis and trans were shown in the Fig. 4 and it was in the range of ND-11.33 and ND-23.22 respectively. Aldrin and dieldrin were detected with an average value of 52.43 pg/g and 38.67 pg/g respectively. The higher average value of Aldrin is due to the elevated level of Aldrin at the location B. The rest all the stations the level of Aldrin is quite low. Aldrin has the affinity for the swift conversion in to Dieldrin (Akhil and Sujatha 2014). The present data of Aldrin and dieldrin follows the quick conversion rate of Aldrin to dieldrin. The level of endosulfan was comparatively lower with respect to the previously reported values from the soil of Kuwait (Alshemmari et al. 2021). The present study showed, endosulfan has an average value of 58.67 pg/g. While comparing the values of endosulfan reported in the other part of the world like India, the concentration was very low. Endosulfan residues in various (isomeric) types have been found in agricultural soils in southern India (Sunitha et al. 2011). According to GFEA-U (2007), the half-lives of α, β, and total endosulfan in soil under aerobic conditions will range from 12 to 39, 108–264, and 288–2241 days, respectively. Endosulfan and its residue can cause a variety of deformities in humans, including brain injury, autism, cerebral palsy, cancer, and more. β -endosulfan is less soluble in soil than β-endosulfan, and it has more harmful effects on organisms than α-endosulfan (Lu et al. 2000).

![Fig. 2 The distribution pattern of BHC along the observed Amghara locations (BDL represents Below Detection Limit and it is 5 ppb)](image-url)
or present soil contamination to this isomer. If the ratio is less than 1, the old practice of DDT can be concluded. If this ratio is greater than 1, it indicates that the environment has recently been affected by DDT. The present study shows the degradation degree in the range of 0.17–0.99. This data reveals that, observed level of DDT was due to the old practice. 

The longer half-life period of DDT might be a reason for the prevalence dominance of DDT compared to the other OCPs observed in the current study. The metabolic ratio studies in the present work is agreeing with the

The most predominant OCPs observed in the present study was DDTs. The distribution pattern of DDTs along the observed locations is shown in the Fig. 5. All the locations, except the location D, the significant level of DDTs were observed. The level of DDE-o, p’ and DDE-p, p’ were in the range of ND-68.15 pg/g and ND-5094.71 pg/g respectively. The reported level of DDD-o, p’ and DDD-p, p’ were in the range of ND-99.8 pg/g and ND-203.33 pg/g. The concentration of DDT-o, p’ and DDT-p, p’ were in the range of ND-181.03 pg/g and ND-1444.39 pg/g respectively. The ‘p, p’-DDT/ (p, p’-DDE + p, p’-DDD)’ ratio can also serve as a signal of the degradation degree of p, p’-DDT in the soil

or present soil contamination to this isomer. If the ratio is less than 1, the old practice of DDT can be concluded. If this ratio is greater than 1, it indicates that the environment has recently been affected by DDT. The present study shows the degradation degree in the range of 0.17–0.99. This data reveals that, observed level of DDT was due to the old practice. 

DDD and DDE may have formed as a result of DDT dehydrochlorination caused by biotic or abiotic decomposition reactions. The longer half-life period of DDT might be a reason for the prevalence dominance of DDT compared to the other OCPs observed in the current study. The metabolic ratio studies in the present work is agreeing with the
The study’s cancer risk appraisal scores is below the mark, indicating that cancer is not a significant danger to people who are exposed to polluted soil. Our findings are consistent with those of other research (Ge et al. 2013; Qu et al. 2017), which found no evidence of cancer risk from various routes of exposure due to low levels of pesticides in soil. Throughout the present report, the average incidence of cancer in children was higher than in adults in every station. Many of the imbalances can be attributed to the ingestion and dermal routes, since children are more likely to be exposed to soil as a result of their play (Qu et al. 2017). Inhalation > dermal > ingestion was the pattern of rising risk. Inhalation of OCPs containing soil particles has a carcinogenic effect that is 10^4-10^5 times smaller than ingestion and dermal interaction with soil-containing OCPs, so inhalation of OCP particles is insignificant for all three exposure pathways. Despite the fact that the current research found no evidence of a cancer risk associated with soil, extra precautions must be taken to avoid possible exposure to several toxins in different routes.

**Conclusions**

The current study assessed the major groups of OCPs. The prevalence of β -BHC in Amghara soils might be due to the transformation of α and γ -HBCs med to β -BHC in the soil matrix. Moreover, the proliferation of β-HCH was observed due to its lower degradation, water solubility, and good affinity for soil adsorption. The longer half-life period of DDT might be a reason for the prevalence dominance of DDT compared to the other OCPs observed in the current study. The cancer risk assessment levels in this sample are below average, meaning that cancer is not a significant threat to people exposed to contaminated soil. Extra measures must be taken to avoid possible exposure to several toxins in different routes.
be taken to prevent potential exposure to several contaminants via various routes. Individuals may be exposed to these possible OCPs in the soil, posing a health risk.

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**References**

Aamir M, Khan S, Li G (2018) Dietary exposure to HCH and DDT congeners and their associated cancer risk based on pakistani food consumption. Environ Sci Pollut Res 25(9):8465–8474

Akhil PS, Sujatha CH (2014) Spatial budgetary evaluation of organochlorine contaminants in the sediments of Cochin Estuary, India. Mar Pollut Bull 78(1–2):246–251

Alshemmari H (2021a) An overview of persistent organic pollutants along the coastal environment of Kuwait. Open Chem 19(1):149–156

Alshemmari H (2021b) Inventories and assessment of POPs in the state of Kuwait as a basis for Stockholm Convention implementation, vol 7. Emerging Contaminants, pp 88–98

Alshemmari H, Al-Shareedah AE, Rajagopalan S, Talebi LA, Hajeyah M (2021) Pesticides driven pollution in Kuwait: the first evidence of environmental exposure to pesticides in soils and human health risk assessment. Chemosphere 273:129688

Alshemmari H, Kavil YN, Sheredah A, Rajagopalan S, (2022) Inevitable human exposure of flame retardants on the potential health risk and assessment of PBDEs in soils collected from Sulaibiya, Kuwait. Arab J Geosci 15(24):1784.

Asghar U, Malik MF, Javed A (2016) Pesticide exposure and human health: a review. J Ecosys Ecograph S, 5, p.2

Ge J, Woodward LA, Li QX, Wang J (2013) Composition, distribution and risk assessment of organochlorine pesticides in soils from the Midway Atoll, North Pacific Ocean. Sci Total Environ 452:421–426

GFEA-U E (2007) Draft dossier prepared in support of a proposal of endosulfan to be considered as a candidate for inclusion in the CLRTAP protocol on persistent organic pollutants. German Federal Environment Agency–Umweltbundesamt, Berlin
Gopalan NK, Chenicherry S (2018) Fate and distribution of organochlorine insecticides (OCIs) in Palakkad soil, India. Sustainable Environ Res 28(4):179–185
Kafaei R, Arfaeinia H, Savari A, Mahmoodi M, Rezaei M, Rayani M, Sorial GA, Fattahi N, Ramavandi B (2020) Organochlorine pesticides contamination in agricultural soils of southern Iran. Chemosphere, 240, p.124983
Lu Y, Morimoto K, Takeshita T, Takeuchi T, Saito T (2000) Genotoxic effects of alpha-endosulfan and beta-endosulfan on human HepG2 cells. Environ Health Perspect 108(6):559–561
Onogbosele CO, Scrimshaw MD (2014) Hexabromocyclododecane and hexachlorocyclohexane: how lessons learnt have led to improved regulation. Crit Rev Environ Sci Technol 44(13):1423–1442
Qu C, Qi S, Yang D, Huang H, Zhang J, Chen W, Yohannes HK, Sandy EH, Yang J, Xing X (2015) Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill region: a case study from Ningde, southeast China. J Geochem Explor 149:43–51
Qu C, Albanese S, Lima A, Li J, Doherty AL, Qi S, De Vivo B (2017) Residues of hexachlorobenzene and chlorinated cyclodiene pesticides in the soils of the Campanian Plain, southern Italy, vol 231. Environmental Pollution, pp 1497–1506
Sunitha S, Krishnamurthy V, Mahmood R (2011) Analysis of endosulfan residues in cultivated soils in Southern India. In Proceedings of International Conference on Biotechnology and Environment Management, IACSIT Press, Singapore (p. 18)
Tao S, Xu FL, Wang XJ, Liu WX, Gong ZM, Fang JY, Zhu LZ, Luo YM (2005) Organochlorine pesticides in agricultural soil and vegetables from Tianjin, China, vol 39. Environmental science & technology, pp 2494–2499. 8
Yang D, Qi S, Zhang J, Wu C, Xing X (2013) Organochlorine pesticides in soil, water and sediment along the Jinjiang River mainstream to Quanzhou Bay, southeast China. Ecotoxicol Environ Saf 89:59–65
Zhang ZL, Hong HS, Zhou JL, Huang J, Yu G (2003) Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. Chemosphere, 240, p.124983

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