

ORGANOCHLORINE PESTICIDES RESIDUES IN SOIL OF SOROCA DISTRICT, REPUBLIC OF MOLDOVA

Elena Culighin

*Institute of Chemistry, 3, Academiei str., Chisinau MD-2028, Republic of Moldova
e-mail: culighin.elena@gmail.com; phone: (+373 22) 73 71 44*

Abstract. The level, composition, and distribution of hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) residues were determined by GC-ECD technique in soil samples from the Soroca district, Republic of Moldova. The concentrations of DDTs and HCHs were up to 1100 and 640 mg/kg, respectively. The obtained results indicated that in 77% of analysed soil samples the (DDE+DDD)/DDT ratios showed aged sources of DDT pollution, suggesting that in the studied area, the DDT residues have been transformed significantly into their degradation products. The α -HCH/ γ -HCH ratios were generally high (in the range of 1-28) suggesting that technical HCH is the main source of contamination. The high concentration and the degradation rates of pesticides in soil suggest that the contaminated sites are acting as continuous sources of pollution for the environment.

Keywords: pesticide, hexachlorocyclohexane, dichlorodiphenyltrichloroethane, soil, Republic of Moldova.

Received: 02 April 2020/ Revised final: 02 June 2020/ Accepted: 06 June 2020

Introduction

Pesticides are mostly used to prevent pests and to combat various biological vectors of human and animal diseases [1]. The main fields of pesticides use are health and agriculture sectors [2]. The distribution and fate of pesticides in the environment depends on many factors, including the dispersion method, their distribution in the environment, their physico-chemical properties (partition coefficients, degradation, and deposition rates) and the characteristics of the environment itself [3]. The most lasting pesticides are termed "persistent organic pollutants" (POPs). As it comes from their name, POPs are compounds that are resistant to chemical, biological and physical degradation and tend to accumulate in tissues of living organisms and along the food chain, causing a wide range of health problems to animals, fishes, and humans [4]. These are considered endocrine disruptors; exposure to POPs could lead to reproductive and immune dysfunctions, brain and nervous system disorders, developmental disorders, and cancer [5]. The most harmful pesticides such as organochlorine pesticides (OCPs) including HCHs (isomers of hexachlorocyclohexane), DDTs (dichlorodiphenyl trichloroethane, its isomers and degradation products isomers), polycyclic aromatic hydrocarbons, and triazines are listed in the Stockholm Convention, also named by the United Nations Environmental Program as "the Dirty

Dozen" [6]. Because of their persistence, OCPs are found in the environment even after 20-30 years of application to the soil and crops. To control soil pesticides pollution, regulatory guidance values are applied worldwide.

In the Republic of Moldova, the high level of the organochlorine pesticides in the soil is due to the historical intensive use in agriculture, a situation that is still maintained through the use of new generation preparations, components less stable in the environment. The application of OCPs on the territory of the Republic of Moldova has been suspended since 1970, but several decades of their use in the Moldovan agriculture has left hundreds of contaminated sites, persisting until now [7-9]. According to regulatory guidance of the Republic of Moldova for values of several organic compounds in soil, the maximum allowable concentration for DDTs, for lindane (γ -HCH) and for HCH (hexachloran) is 0.1 mg/kg [10,11].

Inventory of old pesticide warehouses performed by the Ministry of Environment of the Republic of Moldova during 2008-2010 has demonstrated that there is a great number of sites polluted with POPs [12,13]. Previous studies have shown that there are 252 POPs polluted sites in the Republic of Moldova, with the concentration higher than 50 mg/kg and the pollution spectra of the analysed sites is comprised mainly of five compound groups: DDT, HCH, chlordane,

heptachlors and toxaphene [12,14]. Studies have shown the presence of DDTs and HCHs compounds in soil, water, and biota of the Republic of Moldova [9,15-18]. According to the Dniester hydrographic district management plan, there are 12 warehouses that contain about 1045.4 tons of pesticides [19]. One of the districts with contaminated sites is Soroca with 34.4 tons of pesticides that are stored in known locations, but their fate and impact on the environmental ecosystems was not assessed.

The goal of this study was to investigate the residue level and composition of OCPs, and to identify their possible sources in soil of Soroca district, Republic of Moldova, as well as their correlation to the total OCPs pollution of soil.

Experimental

Materials

Acetone, *n*-hexane, dichloromethane, anhydrous sodium sulphate and OCPs standard solution (a mix of 14 different OCPs: α -HCH, β -HCH, γ -HCH, heptachlor, heptachlor epoxide, aldrine, endrine, chlordane, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT) of residue analysis grade were purchased from Supelco® and Sigma Aldrich.

Standard solutions of OCPs with initial concentrations varying from 24.0 to 248.0 $\mu\text{g}/\text{mL}$ were prepared by diluting the stock standard solution (Sigma Aldrich standard mix of 14 different OCPs) in methanol. The stock standard solution was diluted at 5 different

concentrations: 1:1000 (1 mL of standard mix and 1000 mL solvent), 1:500 (1 mL of standard mix and 500 mL solvent), 1:200 (1 mL of standard mix and 200 mL solvent), 1:100 (1 mL of standard mix and 100 mL solvent), 1:50 (1 mL of standard mix and 50 mL solvent).

The internal standard method using decachlorobiphenyl was used for the quality control.

Soil sampling

Soil samples were collected in spring-summer of 2012, from the proximity of 56 former storage sites in 30 settlements of the Soroca district, Republic of Moldova (Figure 1).

Sampling was performed according to the method described in ISO 18400-101 [20]. One composite soil sample (2.5 kg of soil) comprising 25 samples (0.1 kg each), was collected per contaminated site. Sampling depth was 10-15 cm from the ground line; the soil samples were combined in a rigid plastic bag in the field, labelled and transported to the laboratory facility.

Pesticide residue determination

Before pesticide residue extraction and determination, the collected soil samples were air dried at room temperature (18-20°C), ground, thoroughly mixed and sieved at 250 μm particle size. The extraction procedure was made according to the United States Environmental Protection Agency method 3500B [21]. The extraction of the analytes of interest (DDTs and HCHs) was performed by the microwave assisted extraction procedure.

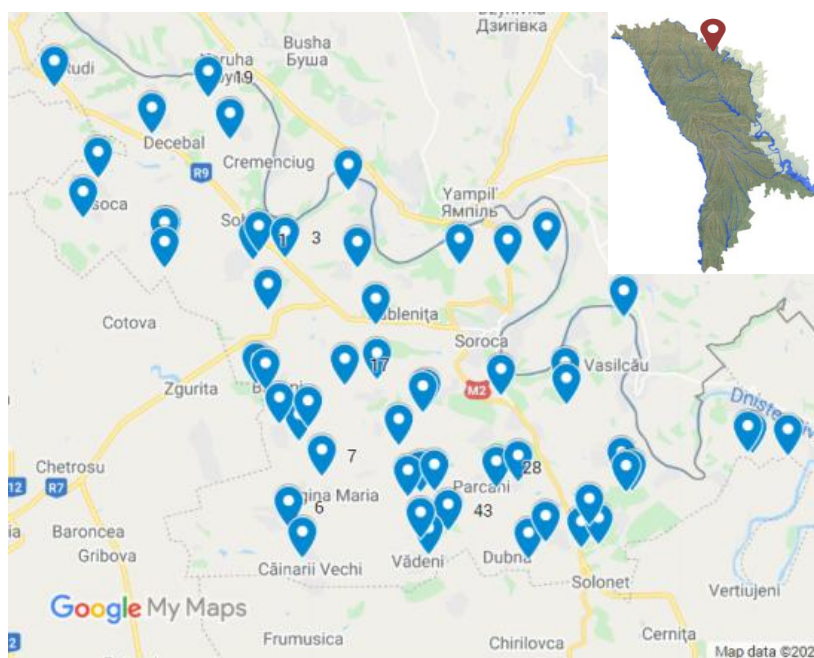


Figure 1. The map of sampling sites of the Soroca district (Republic of Moldova).

For this purpose, a portion of 10 g of sample was placed in the extraction vessel to which a volume of 20 mL of appropriate solvent (*n*-hexane/acetone, 1:2, v/v) was added. For a better extraction yield, for each sample the extraction was done twice at maximal power of microwave extraction system (140 W) for 15 min. After cooling down, the extracts were collected in the glass condenser and concentrated in *n*-hexane to a 1 mL volume. Extracts were purified on adsorption chromatography columns filled up with 1 g of silica gel previously activated for 16 h at 135°C. The column was conditioned with 5 mL of hexane. The analytes of interest were eluted from column with 5 mL of *n*-hexane, followed by 5 mL of *n*-hexane/dichloromethane mixture (1:1, v/v). The final elutes were concentrated to 1 mL under argon flow. One blank sample was prepared for each set of soil samples. The blank value was subtracted from the sample chromatogram for further calculations.

An internal standard (spike) was added to samples prior to extraction. The spiking was done by adding 1 mL of decachlorobiphenyl to each sample, to achieve a concentration of 0.05 µg/mL in the final sample.

The method used for the OCPs determination was validated within laboratory conditions and the limit of detection (LOD), limit of quantification (LOQ), precision (RSD_R), recovery and working range were calculated (Table 1). LOD and LOQ were calculated based on the standard deviation of the response and the slope by using Eq.(1) and Eq.(2), respectively:

$$\text{LOD}(\mu\text{g}/\text{kg}) = 3.3 \times \sigma/S \quad (1)$$

$$\text{LOQ}(\mu\text{g}/\text{kg}) = 10 \times \sigma/S \quad (2)$$

where σ - the standard deviation of the response, µg/kg;

S- the slope of the calibration curve [22].

The precision and recovery of the analytical procedure were tested with a reference material (CRM847, clay loam, Sigma-Aldrich, USA). The recovery was calculated as the ratio between the found concentration of analyte and the concentration stated to be present in the sample. The precision of the analytical procedure was calculated as the standard deviation of a series of measurements.

Instrumentation

Determination of OCPs was done according to the operational procedure based on SM SR ISO 10382:2008 on a gas chromatograph 6890 system of Agilent [23]. System parameters were: injector type: split/splitless; 300°C temperature; 2 µL injected volume; split 5:1; carrier gas: He, 1.4 mL/min, or average velocity 30 cm/sec, constant flow; column type: HP-5MS with length of 30 m, internal diameter 320 µm, and 0.25 µm film thickness; detector: µECD, 3200°C temperature; oven program: initial: 100°C for 1 min, 1st rate 20°C/min, isothermal: 200°C for 3 min, 2nd rate 10°C/min, isothermal: 280°C for 6 min, ChemStation, ChemStation Integrator.

Statistical Analysis

The statistical analysis of the experimental data was performed using the Analyse-It Add-in of Microsoft Excel 2016 software. The link between the OCPs concentrations was described by the Pearson correlation test, at the $p \leq 0.05$ degree of confidence [24,25]. The principal component analysis tool was used for predicting the sources of pollution by grouping the data into different interrelated modules based on their component loading [26,27].

Results and discussion

To fulfil the aim of this study, concentrations of organochlorinated pesticides such as DDTs and HCHs were assessed in soils of the Sorooca district, Republic of Moldova in the proximity to the former pesticides' storages.

Table 1

Validation parameters of the SM SR ISO 10382:2008 method.

Compound	LOD, µg/kg	LOQ, µg/kg	Concentration range, µg/kg	RSD _R , %	Recovery, %
α-HCH	0.003	0.008	0.005-0.05	9.45	94
β-HCH	0.014	0.041	0.015-0.2	7.03	107
γ-HCH	0.004	0.012	0.005-0.05	7.36	93
<i>o,p'</i> -DDE	0.014	0.041	0.028-0.45	8.24	91
<i>p,p'</i> -DDE	0.013	0.041	0.015-0.2	8.36	92
<i>o,p'</i> -DDD	0.043	0.130	0.045-0.4	10.89	89
<i>p,p'</i> -DDD	0.025	0.077	0.025-0.38	12.89	113
<i>o,p'</i> -DDT	0.014	0.041	0.028-0.45	5.59	100
<i>p,p'</i> -DDT	0.021	0.065	0.025-0.52	16	113

Results of this study will offer a better understanding on the fate of these contaminants in the environment and the risks associated with agricultural and industrial pollution.

The chromatogram of one of the samples with composite soil extract for the study area is shown in Figure 2. The statistical results of OCPs in the soils from Soroca district, Republic of Moldova, are presented in Table 2. According to the obtained results, the overall concentration

of OCPs (Σ OCPs) in surface soils of Soroca district, Republic of Moldova, ranged between 0.072 and 1953.6 mg/kg with mean concentration of 84 mg/kg. The order of overall OCPs concentration in different sites was: γ -HCH > p,p' -DDT > α -HCH > o,p' -DDT > p,p' -DDE > β -HCH > o,p' -DDD > p,p' -DDD > o,p' -DDE. The degree of contamination is in concordance with the study performed previously by Bogdevich, O. *et al.* [28].

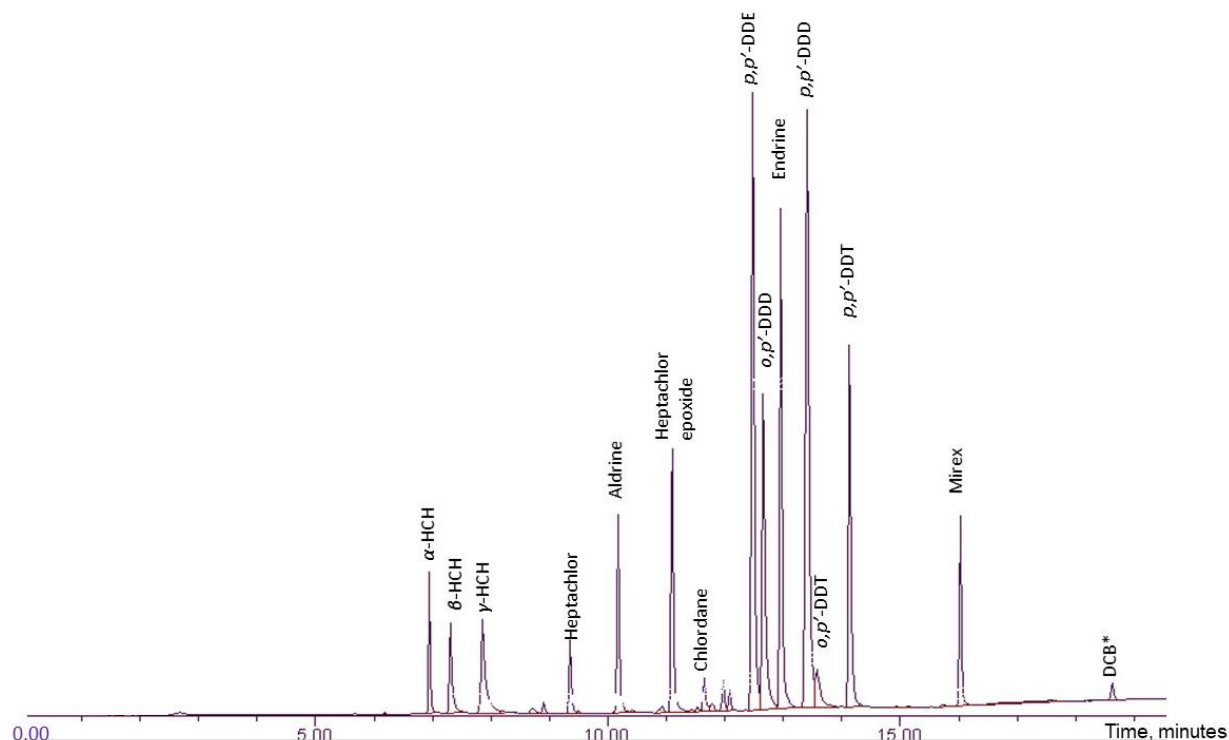


Figure 2. Chromatogram of the soil extract (DCB*-indicates the internal standard).

Table 2

Organochlorine pesticides concentration (mg/kg) in analysed soil.

Compound	Mean	SD	Median	Minimum	Maximum
α -HCH	11.2	51.9	0.26	ND	369
β -HCH	4.23	13.6	0.29	ND	87.7
γ -HCH	18.8	131	0.07	ND	978
Σ HCHs	34.3	160	0.77	ND	1096
o,p' -DDE	1.54	7.32	0.06	ND	53.8
p,p' -DDE	6.57	36.0	0.43	ND	270
o,p' -DDD	2.90	14	0.09	ND	101
p,p' -DDD	2.34	10.1	0.10	ND	69.8
o,p' -DDT	8.76	34.7	0.26	ND	212
p,p' -DDT	12.5	71.4	0.23	ND	531
Σ DDTs	34.6	141	1.38	ND	841
Σ OCPs	83.99	286.56	4.1	0.072	1953.6

Note: Mean, standard deviation (SD), maximum and minimum were calculated assuming that non-detected (ND) measurements were equal to zero.

Total DDT concentrations (Σ DDTs), comprised of two DDT isomers and four DDT degradation products (*o,p'*-DDT, *p,p'*-DDT and *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE), were up to 841 mg/kg dry weight. The average concentration of total DDT observed in sampling locations was 34.6 mg/kg.

The total content of HCHs (Σ HCHs) that is the sum of concentrations of α , β and γ isomers, was up to 1096 mg/kg dry weight and the overall concentration of the total HCHs was 34.3 mg/kg.

Σ DDTs concentration in most of the soil samples (57.17%) is relatively higher than the Σ HCHs concentrations (42.9%), however the mean concentrations are equal, indicating that the concentrations of DDTs and HCHs are evenly distributed among samples (Figures 3 and 4).

There are two possible reasons that might explain the high concentrations of DDTs in soil samples of Soroca district compared to HCHs concentration. The first possibility is that HCHs have less lipophilic properties, higher volatility and water solubility than DDTs [29], thus could be more easily transferred from the source point to surrounding farmland *via* surface runoff. On the other hand, it may be due to their different use and stored amount over the soviet period (during 1960-1980). There was a correlation between Σ HCHs concentration and Σ DDTs concentration ($R^2 > 0.42$) as shown in Figure 5, suggesting that they may have similar sources and fate in this area [29].

Dichlorodiphenyltrichloroethane and its degradation products

Technical DDT generally consists of *p,p'*-DDT isomer (approx. 85%), with lesser amounts of *o,p'*-DDT and *o,o'*-DDT isomers [30]. Residues of DDTs in the environment include *p,p'*-DDT, its isomer *o,p'*-DDT and their degradation products (*o,p'*- and *p,p'*-dichlorodiphenyldichloroethylene (*o,p'*- and *p,p'*-DDE) and *o,p'*- and *p,p'*-dichlorodiphenyldichloroethane (*o,p'*- and *p,p'*-DDD)). In environmental ecosystems, *p,p'*-DDT degrades mainly to *p,p'*-DDE and *p,p'*-DDD as a consequence of different environmental factors [30].

The *p,p'* isomers of DDT, DDD and DDE were present in higher concentration than the associated *o,p'* compounds (Table 2). The *p,p'*-DDT residues were detected in levels ≤ 531.0 mg/kg dry weight in 96% of the total soil samples. The *p,p'*-DDE isomer was detected in 98%, with levels ≤ 69.8 mg/kg and *p,p'*-DDD in 77% with levels ≤ 270 mg/kg.

The mean concentrations of individual compounds in soil samples were as follows: *o,p'*-DDE < *p,p'*-DDD < *o,p'*-DDD < *p,p'*-DDE < *o,p'*-DDT < *p,p'*-DDT (Table 2). Such an order could be explained by the transformation of DDT to its degradation products, DDE and DDD.

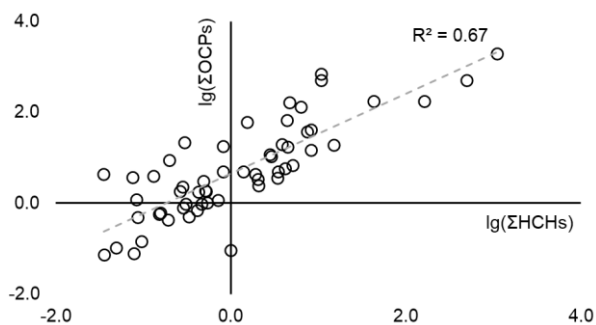


Figure 3. Σ HCHs distribution in studied soil samples.

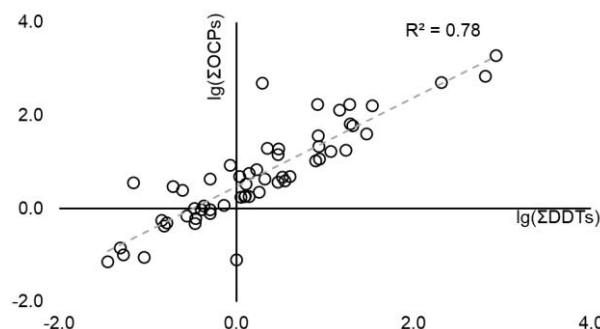


Figure 4. Σ DDTs distribution in studied soil samples.

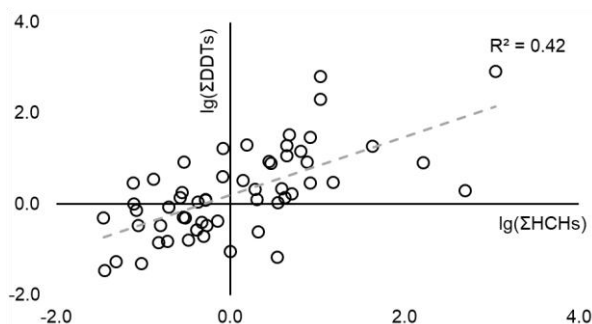


Figure 5. Correlation of Σ DDTs and Σ HCHs.

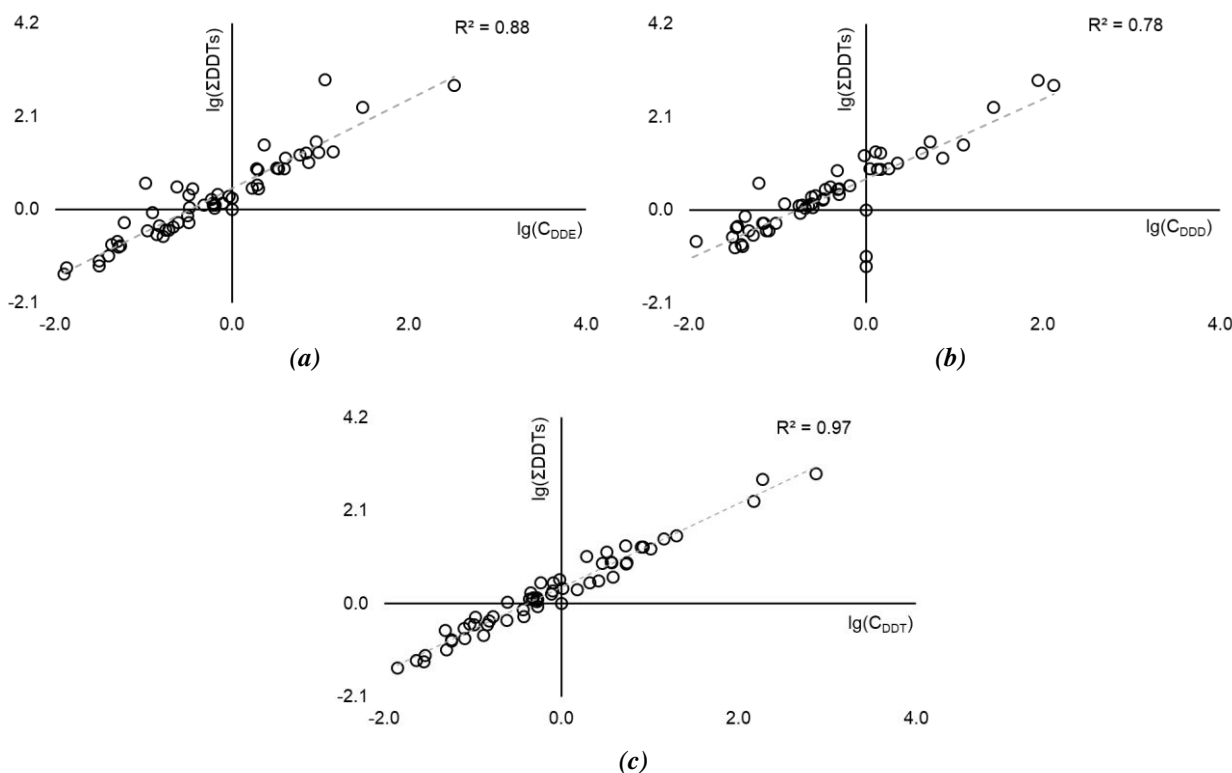


Figure 6. Distribution of DDT isomers concentration: correlation for the concentrations of DDE isomers (a), DDD isomers (b), DDT isomers (c) to the total DDT isomers concentrations (Σ DDTs).

After DDT usage, a considerable amount of DDT may be converted to *p,p'*-DDE [31]. In Figure 6, the distribution of total concentration of DDT isomers, and their degradation products (DDE and DDD) is shown, suggesting that DDT isomers are more abundant in the soils of the studied area. Thereby, sources of DDTs could be identified according to the ratios of (*p,p'*-DDE+*p,p'*-DDD)/*p,p'*-DDT or *p,p'*-DDE/*p,p'*-DDT. A ratio value >1 suggest a past input of DDT, and a ratio <1, respectively, suggest a recent input of the pollution [29,32].

The degradation status of DDT was evaluated using (DDE+DDD)/DDT ratios, which varied from 0.005 to 49.3 [33]. In 77% of analysed soil samples these ratios showed aged sources of pollution with DDT, indicating that DDT residues have significantly been transformed into their degradation products in these areas. There are strong positive correlations in the concentrations of the DTT isomers and their degradation products ($R^2= 0.78-0.97$, $p < 0.01$), indicating common sources of pollution (Figure 6).

Hexachlorocyclohexanes

The α -HCH residues were detected in levels up to 369.0 mg/kg dry weight in 96% of the total soil samples. The β -HCH isomer was

detected in 98% of analysed samples, with levels up to 87.7 and γ -HCH isomer in 80% with levels ≤ 978 mg/kg (Table 2).

The percentage distribution of HCH isomers in total HCHs varied among soil samples (Figure 7). This may be related to the isomerization of HCH during the transformation process in soil as well as the differences in physico-chemical properties and degradation rates [34]. The β -HCH was the most dominant isomer in soil samples that is due to the differences in the degradation rates of the HCH isomers, β -HCH being the most stable and persistent in soil [34,35]. The persistence of β -HCH in soil is mainly due to a higher partition coefficient (K_{ow}) and a lower vapour pressure than of other HCH isomers, which enhances its adsorption into soil and hinders its evaporation. The α -HCH/ γ -HCH ratios varied from 0 to 28 and both low and high ratios were found in samples, indicating both lindane and technical HCH as the sources of HCH contamination. Very high ratios may be related to old inputs and transformation of γ -HCH into α -HCH [36]. There are strong positive correlations in the concentrations of most HCH isomers ($R^2= 0.48-0.90$, $p < 0.01$) (Figure 7), indicating common pollution sources.

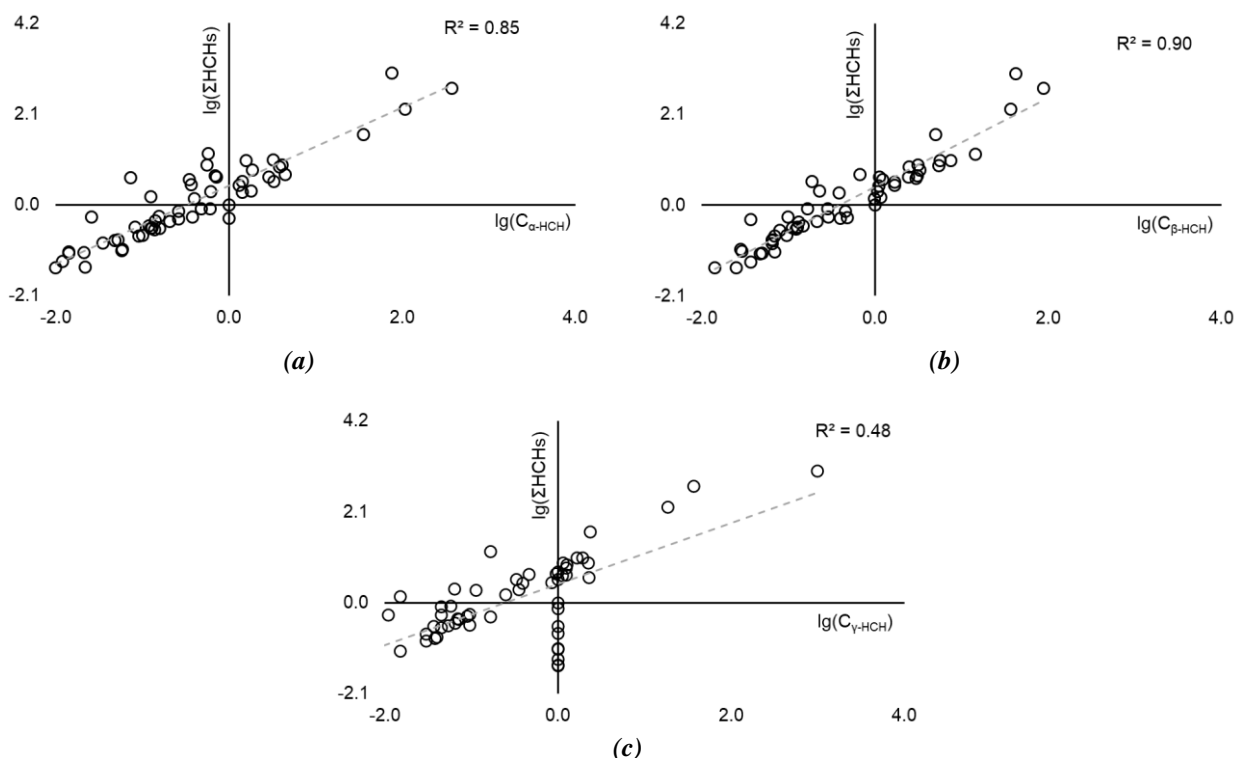


Figure 7. Distribution of HCH isomers concentration: correlation for the α -HCH isomer (a), β -HCH isomer (b), and γ -HCH isomer (c) to the total HCH isomers concentration (Σ HCHs).

Factor analysis

Factor loading plot showed loadings for each OCP in the principal component plane (Factor 1 that shows the largest possible variance in the data set *versus* Factor 2 which is uncorrelated with Factor 1 and accounts for the next highest variance; Figure 8).

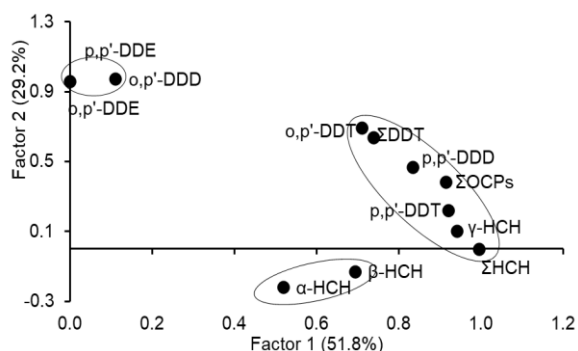


Figure 8. Loading plot of factor analysis based on concentrations of organochlorine pesticides.

Σ HCHs is sum of α -HCH, β -HCH, and γ -HCH.
 Σ DDTs is sum of p,p' -DDE; o,p' -DDE; p,p' -DDD,
 o,p' -DDD; o,p' -DDT and p,p' -DDT.
 Σ OCPs is the sum of all OCPs.

The circles indicate factors of high scores.

By processing, two factors were considered here, accounting for 81.0% of the total variance. Factor 1 explained 51.8% of the total variance and was mainly associated with p,p' -DDD (0.83), o,p' -DDT (0.74), p,p' -DDT (0.92), γ -HCH (0.94),

which were generally high correlated with the total concentrations of OCPs (Table 3). In Factor 1, α -HCH (0.52) and β -HCH (0.69) had medium loading, meaning that the HCHs appeared to have the similar contributions to OCPs and originated from the similar source. Factor 2 was associated mainly with the o,p' -DDE (0.97), p,p' -DDE (0.96) and o,p' -DDD (0.97). The fact that DDT isomers were the highest loading of all the factors, suggested that they appeared to have higher contributions to OCPs than other individual OCPs.

According to the relevance to both Factor 1 and Factor 2, these components can be represented by DDT and HCHs, respectively. The DDT and HCHs accounted for the highest loading for Factor 1, whereas the DDE and DDD isomers accounted for the highest loading for Factor 2 (Table 3). This finding suggested that DDT and HCHs showed larger contributions to OCPs possibly originating from the similar source.

Summarization of the obtained results revealed that the compositions of the contaminants indicated mainly the parent compounds with low levels of degradation products at most sites. The slow degradation rates of the pesticides for most sites and their low mobility in soil suggest that the contaminated sites are acting as continuous point sources of contamination for the environment.

Table 3

Pearson correlations of OCPs identified in the analysed samples.

	<i>o,p'</i> -DDE	<i>p,p'</i> -DDE	<i>o,p'</i> -DDD	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	Σ DDT	α -HCH	β -HCH	γ -HCH	Σ HCH
<i>o,p'</i> -DDE	1										
<i>p,p'</i> -DDE	0.98*	1									
<i>o,p'</i> -DDD	0.98**	0.97**	1								
<i>p,p'</i> -DDD	0.36**	0.40**	0.49**	1							
<i>o,p'</i> -DDT	0.55**	0.54**	0.68**	0.92**	1						
<i>p,p'</i> -DDT	0.097	0.11	0.26	0.94**	0.87**	1					
Σ DDTs	0.61**	0.62**	0.73**	0.94**	0.99**	0.85**	1				
α -HCH	-0.02	-0.02	0.00	0.15	0.12	0.16	0.12	1			
β -HCH	0.03	0.03	0.09	0.36**	0.33*	0.38**	0.32*	0.96**	1		
γ -HCH	-0.02	0.02	0.14	0.91**	0.79**	0.99**	0.78**	0.21	0.41**	1	
Σ HCHs	-0.02	0.01	0.12	0.82**	0.72**	0.89**	0.70**	0.58**	0.74**	0.92**	1

* ** Significant at probability $P < 0.05$ and $P < 0.01$, respectively.

This study should be considered as a first steppingstone (as a regional study) towards a major investigation on the main sources and levels of OCPs throughout the territory of the Republic of Moldova. The study has highlighted the area of Soroca district with high concentrations of some OCPs that could pose some potential human health concerns, which need addressing urgently. Thus, remediation measures are required to reduce the levels of the contaminants.

Conclusions

The OCPs compounds concentration was determined in urban and rural soils in the immediate proximity of former pesticides storages in the Soroca district, in the north-eastern part of the Republic of Moldova. The main findings revealed that the concentration of nine OCPs were up to 1954 mg/kg (average was 84 mg/kg). The level of contamination in the analysed samples was higher than the national maximum allowable concentration in soil (0.1 mg/kg for γ -HCH and DDTs). The highest concentrations were found within the former pesticides' storage points.

The HCH and DDT isomers and their degradation products were the most abundant contaminants, accounting for 79.4% of the total OCPs. Diagnostic ratios of DDTs residues and of HCHs isomers clearly unveiled a dominance of historical application of these compounds in soil. The most dominant OCP species were γ -HCH, followed by *p,p'*-DDT and *o,p'*-DDE isomer was present in smallest amount, that confirms the high persistence and slow degradation of the studied OCPs.

The compositions of the contaminants indicated mainly the parent compounds with low levels of degradation products at most sites. The slow degradation rates of the pesticides for most sites and their low mobility in soil suggest that the contaminated sites are acting as continuous point sources of contamination for the environment.

Acknowledgements

I would like to express my gratitude to my supervisors, Acad., Prof., Dr. Hab. Tudor Lupascu and Dr. Oleg Bogdevici for their continuous guidance and kind support.

This work was supported by the financial support by GEF and FAO contract FAO1-16 and ENPI project code MIS ETC 1676.

It is greatly appreciated the effort of the management of the Institute of Chemistry for equipping the Center of Ecological Chemistry and Environment Protection for core teaching and research work where this research work was carried out.

References

- Jayaraj, R.; Megha, P.; Sreedev, P. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary Toxicology*, 2016, 9(3-4), pp. 90-100. DOI: <https://doi.org/10.1515/intox-2016-0012>
- Kaur, R.; Mavi, G.K.; Raghav, S. Pesticides classification and its impact on environment. *International Journal of Current Microbiology and Applied Sciences*, 2019, 8(3), pp. 1889-1897. DOI: <https://doi.org/10.20546/ijcmas.2019.803.224>
- Ravichandra, N.G. *Agrochemicals in plant disease management*. Scientific Publishers, India, 2018, 556 p. <https://www.scientificpub.com/book-details/>

- [Agrochemicals-in-Plant-Disease-Management-HB-964.html](#)
- Chen, M.W.; Santos, H.M.; Que, D.E.; Gou, Y.Y.; Tayo, L.L.; Hsu, Y.C.; Chen, Y.B.; Chen, F.A.; Chao, H.R.; Huang, K.L. Association between organochlorine pesticide levels in breast milk and their effects on female reproduction in a Taiwanese population. *International Journal of Environmental Research and Public Health*, 2018, 15(5), pp. 931-953.
DOI: <https://doi.org/10.3390/ijerph15050931>
 - The Concern About POPs. Persistent Organic Pollutants Toolkit, 2008.
<http://www.popstoolkit.com/about/concern.aspx>
 - United Nations Environment Programme, Stockholm Convention on Persistent Organic Pollutants (POPs). Text and Annexes, 2009, Switzerland.
https://www.wipo.int/edocs/lexdocs/treaties/en/une-p-pop/trt_unep_pop_2.pdf
 - Spătaru, P.; Spînu, O.; Spătaru, T.; Povar, I. Analysis of the environment contamination sources with halogenated organic pesticides. *Akademios*, 2017, 1(44), pp. 42-47 (in Romanian).
<http://akademios.asm.md/taxview/97>
 - Government Decision of the Republic of Moldova No. 1155 of 20 October 2004 for approving National Strategy on reducing and eliminating persistent organic pollutants and the National Plan for implementing the Stockholm Convention on persistent organic by pollutants. Official Monitor no. 193-198 (29.10.2004), art. no. 1347 (in Romanian).
 - Inspectorate for Environmental Protection. Environmental protection in the Republic of Moldova, Yearbook-2018, Chisinau, 2019, 358 p. (in Romanian).
 - Regulation No. 100 of 18 January 2000 of the Ministry of the Environment and Territorial Planning regarding the estimation of damages for the prejudices caused to the environment. Official Monitor no. 112-114 (05.09.2000), art. no. 317 (in Romanian).
 - Instruction no. 383 of 8 August 2004 of the Ministry of Ecology and Natural Resources on the assessment of damage caused to soil resources. Official monitor no. 189-192 (22.10.2004), art. no. 383 (in Romanian).
 - Plesca, V.; Barbarasa, I.; Cupcea, L.; Melian, R. Inventory of POP pesticides polluted areas in Moldova. *International Conference Contaminated Sites*, Bratislava, 2013, pp. 75-80.
<https://contaminated-sites.sazp.sk/node/2>
 - Slobodnik, J.; Isac, A. WB/GEF Persistent Organic Pollutants (POPs) stockpiles management and destruction project. Koš, Slovak Republic, 2010, 251 p.
<http://www.moldovapops.md/app/includes/files/POPs%20MIS.pdf>
 - Duca, Gh.; Bogdevich, O.; Cadocinicov, O.; Porubin, D. The pollution spectrum of old pesticides storages in Moldova. *Chemistry Journal of Moldova*, 2012, 7(1), pp. 124-128.
DOI: [dx.doi.org/10.19261/cjm.2012.07\(1\).23](https://doi.org/10.19261/cjm.2012.07(1).23)
 - Gluga, O. Content of organochlorine pesticide residues in environmental components. *Intellectus*, 2015, 2, pp. 103-112 (in Romanian).
 - Sapozhnikova, Y.; Zubcov, E.; Zubcov, N.; Schlenk, D. Occurrence of pesticides, polychlorinated biphenyls (PCBs), and heavy metals in sediments from the Dniester River, Moldova. *Archives of Environmental Contamination and Toxicology*, 2005, 49(4), pp. 439-448.
DOI: <https://doi.org/10.1007/s00244-005-8011-8>
 - Ene, A.; Bogdevich, O.; Sion, A. Levels and distribution of organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in topsoils from SE Romania. *Science of the Total Environment*, 2012, 439, pp. 76-86. DOI: <https://doi.org/10.1016/j.scitotenv.2012.09.004>
 - Bogdevich, O.; Ene, A.; Cadocinicov, O.; Culighin E.; Nicolau, E.; Grigoras, M. The study of POPs contaminated sites in Danube River Basin of Republic Moldova for risk assessment and remediation actions. *Contaminated Sites Conference: Bratislava, Slovakia, 2016*, pp. 64-68.
<http://contaminated-sites.sazp.sk/node/58>
 - Government Decision of the Republic of Moldova no. 814 of 17 October 2017 on approval of the Management plan of the Dniester river basin district. Official Monitor no. 371-382 (27.10.2017), art. no. 942 (in Romanian).
 - ISO 18400-101:2017 - Soil quality — Sampling — Part 101: Framework for the preparation and application of a sampling plan. The International Organization for Standardization, 2017.
 - EPA Method 3500B, Organic extraction and sample preparation. Environmental Protection Agency, 1996.
<https://gtanalytical.com/epa-methods/>
 - Validation of analytical procedures: text and methodology Q2(R1). International Conference on Harmonization of technical requirements for registration of pharmaceuticals for human use, Step 4 version, November 2005.
<https://www.ich.org/page/quality-guidelines>
 - ISO 10382:2002 - Soil quality — Determination of organochlorine pesticides and polychlorinated biphenyls — gas-chromatographic method with electron capture detection. The International Organization for Standardization, 2002.
<https://www.iso.org/standard/32422.html>
 - Zhang, C.; Liu, L.; Ma, Y.; Li, F. Using isomeric and metabolic ratios of DDT to identify the sources and fate of DDT in Chinese agricultural topsoil. *Environmental Science and Technology*, 2018, 52(4), pp. 1990-1996.
DOI: <https://doi.org/10.1021/acs.est.7b05877>
 - Mungai, T.M.; Wang, J. Occurrence and toxicological risk evaluation of organochlorine pesticides from suburban soils of Kenya. *International Journal of Environmental Research*

- and Public Health, 2019, 16(16), pp. 2937-2950. DOI: <https://doi.org/10.3390/ijerph16162937>
26. Girones, L.; Arias, A.H.; Oliva, A.L.; Recabarren-Villalon, T.; Marcovecchio, J.E. Occurrence and spatial distribution of organochlorine pesticides in the southwest Buenos Aires using the freshwater snail *Chilina parchappii* as environmental biomonitor. *Regional Studies in Marine Science*, 2020, 33, p. 100898. DOI: <https://doi.org/10.1016/j.rsma.2019.100898>
27. Shunthirasingham, C.; Gawor, A.; Hung, H.; Brice, K.A.; Su, K.; Alexandrou, N.; Dryfhout-Clark, H.; Backus, S.; Sverko, E.; Shin, C.; Park, R.; Noronha, R. Atmospheric concentrations and loadings of organochlorine pesticides and polychlorinated biphenyls in the Canadian Great Lakes Basin (GLB): Spatial and temporal analysis (1992–2012). *Environmental Pollution*, 2016, 217, pp. 124-133. DOI: <https://doi.org/10.1016/j.envpol.2016.01.039>
28. Bogdevich, O.; Ene A.; Cadocinicov, O.; Culighin, E. The analysis of old pesticides and PAHs pollution sources in Low Danube region. *Journal of International Scientific Publications: Ecology & Safety*, 2013, 7(2), pp. 233-243. <https://www.scientific-publications.net/en/archive/>
29. Zhang, F.; He, J.; Yao, Y.; Hou, D.; Jiang, C.; Zhang, X.; Di, C.; Otgonbayar, K. Spatial and seasonal variations of pesticide contamination in agricultural soils and crops sample from an intensive horticulture area of Hohhot, North-West China. *Environmental Monitoring and Assessment*, 2013, 185(8), pp. 6893-6908. DOI: <https://doi.org/10.1007/s10661-013-3073-y>
30. Toxicological Profile for DDT, DDE, and DDD. US Department of Health and Human Services, Public Health Service, Agency For Toxic Substances And Disease Registry, Atlanta, GA, United States of America: 2002, 480 p. <https://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=81&tid=20>
31. Agapkina, G.I.; Brodskiy, E.S.; Shelepchikov, A.A.; Artukhova, M.B. Transformation and form of dichlorodiphenyltrichloroethane (DDT) applied to Moscow soils. *Moscow University Soil Science Bulletin*, 2017, 72(3), pp. 125-131. DOI: <https://doi.org/10.3103/S0147687417030024>
32. Ssebugere, P.; Wasswa, J.; Mbabazi, J.; Nyanzi, S.A.; Kiremire, B.T.; Marco, J.A.M. Organochlorine pesticides in soils from southwestern Uganda. *Chemosphere*, 2010, 78(10), pp. 1250-1255. DOI: <https://doi.org/10.1016/j.chemosphere.2009.12.039>
33. Pinkney, A.E.; McGowan, P.C. Use of the p,p'-DDD: p,p'-DDE concentration ratio to trace contaminant migration from a hazardous waste site. *Environmental Monitoring and Assessment*, 2006, 120, pp. 559-574. DOI: <https://doi.org/10.1007/s10661-005-9103-7>
34. Toxicological profile for alpha-, beta-, gamma-, and delta-hexachlorocyclohexane. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta, GA, 2005, 377 p. <https://www.atsdr.cdc.gov/toxprofiles/tp43.pdf>
35. Becker, S.; Halsall, C.J.; Tych, W.; Kallenborn, R.; Schlabach, M.; Manø, S. Changing sources and environmental factors reduce the rates of decline of organochlorine pesticides in the Arctic atmosphere. *Atmospheric Chemistry and Physics*, 2012, 12(9), pp. 4033-4044. DOI: <https://doi.org/10.5194/acp-12-4033-2012>
36. Da, C.; Liu, G.; Sun, R.; Yuan, Z.; Tang, Q.; Liu, H. Sources and risk assessment of organochlorine pesticides in surface soils from the nature reserve of the Yellow River Delta, China. *Soil Science Society of America Journal*, 2014, 78(3), pp. 779-786. DOI: <https://doi.org/10.2136/sssaj2013.12.0547>