



The Impact of Organochlorine Pesticides, Which Reached the Soil 25 Years Ago, Depending on Their Use

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Abstract

This paper is part of an integral study of the dynamics of organochlorine pesticide residues (-DDT and its degradation products: -DDE and -DDD, α -, β -, γ - and δ -HCH, -HAP, -BPC) introduced 25 years ago in soils of different uses (natural biocenoses, arable land, grassland, floodplains, etc.); distribution, metabolism and isomerization in the upper soil layer of a former huge orchard covering more than 2000 ha.

Keywords: Distribution, Metabolism and Isomerization of Halogenated Compounds, Organochlorine Pesticides, Soil.

Introduction

Soil is a complex environment with highly heterogeneous physical, chemical and biological properties. The characteristic horizontal and vertical distribution of textural and structural elements in soil and differences in physicochemical properties lead to significant variations in sorption, desorption, transport and soil permeability. In this sense, soil acts as a "temporary or permanent sink" for any chemical that reaches its surface. Organochlorine pesticides are ubiquitous contaminants whose presence in the environment poses an eminent threat due to their resistance to degradation and the toxicity of some of their components. [1].

Due to their strong hydrophobic (lipophilic) properties, these toxic compounds are usually found associated with soil

organic matter and lipid tissues of pedobionts. The proportion of applied pesticides that reaches the target pest has been found to be less than 0.3%, leaving more than 99% as ballast in other parts of the environment. [2].

In this article we are not going to analyze the ways in which organochlorine pesticides are formed and penetrate into the soil, but we are going to focus on the fate of those pesticides that entered the soil more than 25 years ago. Assessing the current state of the soil, which fortunately remains the only national asset, we can say with certainty that it is deplorable, as a result of the relatively recent approval of "intensive technologies" in our country, the spread of grandeur in the field of specialization and concentration of agricultural production, including in the field of chemistry. In order to convince ourselves of this fact, we will quote just one figure: between 1978 and 1989, about 0.4 million tonnes of pesticides (by weight) were used in the Republic! [3].

The negative impact of chemicals, whatever their origin, on environmental factors, and in particular on soil health, is of particular concern today because of the problems arising from their ubiquity, persistence and xenobiotic action, which ultimately either strongly inhibits the microbiological activity of pedobionts (with the necessary consequences) or, as a result of washing off the soil surface or infiltration, pollutes surface waters and seriously affects the quality of groundwater.

This paper is part of an integrated study on the dynamics of organochlorine pesticide residues introduced 25 years ago into soils of different uses (natural biogenesis, arable land,

grassland, floodplains, etc.), their distribution, metabolism and isomerization in the upper soil layer. The main objective of this study was to assess the influence of land use (such as agricultural land, grassland in close proximity to agricultural land, chemical dumps and/or preparation stations for solutions used in the chemical treatment of agricultural crops) and underwater sediments (from ponds and/or rivers where residues of organochlorinated pesticides were probably deposited) on their content and distribution in the soils of a former huge orchard covering more than 2000 ha.

Materials and Methods

According to the work plan, different areas were selected depending on the use of the soil. Soil samples were taken using the "satellite" method. The average sample was obtained by mixing nine separate samples of the same volume. The samples were collected from: arable land, forest biocenoses, orchards, the area of the storage and preparation of solutions for processing agricultural crops, pastures in the immediate vicinity of agricultural land, and underwater sediments (depth: 0-20 cm, 20-40 cm and 40-60 cm). Soil samples were taken with a pedological drill. (Fig. 1).



Figure 1. Location of soil/sediment sampling sites.

Methods used for the determination of organohalogenated pesticide residues:

Analyses were carried out at the Institute for Environmental Chemistry and Ecotoxicology in Schmallenberg, Germany. The soil samples were dried at T 30°C and the particle fraction larger than 2 mm was separated. The organochlorine compounds analyzed included p,p'-DDT and its breakdown products p,p'-DDE and p,p'-DDD, α -, β -, γ - and δ -hexachlorocyclohexane (HCH), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were extracted from soil using toluene in a Soxhlet apparatus to which the internal standard was added. Concentration and purification of the extract was performed by gel chromatography using Biobeads S-X3. The mixture cyclohexane+dichloromethane (1+1, v/v) was used as eluent. The fraction remaining in the residue after concentration was cleaned using adsorbing chromatography and then separated polycyclic aromatic hydrocarbons (PAHs). For the determination of halogenated compounds, gas chromatography with ECD and MS detection (GC-ESD, GC-MS) was used according to the method. [4].

Results and Discussion

Due to the misuse of DDT (dichlorodiphenyltrichloroethane) in the not too distant past of our Republic and its ubiquitous nature, as well as its metabolites (dichlorodiphenyldichloroethylene - DDE; dichloro-diphenyl-

dichloro-ethane - DDD), these pesticides were detected in 1994 in all the soils studied according to their use (forest ecosystem, river meadow, grassland, arable land (fruit orchards), the territory of the chemical deposit and the plant for the preparation of tartar solutions and in underwater sediments). Their contents are shown in Table 1.

Table 1. Concentration of organochlorine compounds in soil layer 0-60 cm, [µg/kg dry sub.], 1994 year

Place of samples collection	Depth, cm	$\sum y,p'$ DDX	$\sum HCH$ - iso	$\sum PCB$	PAH	HCB
Land, chemical warehouse, v. Vărativ, Râşcani district	0-20	10426.0	125.7	n.d.	800.1	n.d.
Land, chemical warehouse, v. Vărativ, Râşcani district	20-40	2378.5	42,7	n.d.	222.1	n.d.
Land, chemical warehouse, v. Vărativ, Râşcani district	40-60	3788.0	43.8	n.d.	536.1	n.d.
Fruit cenoses (plum), v. Vărativ, Râşcani district	Litter (dry vegetation)	85.5	20.4	6.4	567.4	n.d.
Fruit cenoses (plum), v. Vărativ, Râşcani district	0-20	181.1	1.3	n.d.	1261.4	n.d.
Fruit cenoses (plum), v. Vărativ, Râşcani district	20-40	60.8	n.d.	n.d.	79.3	n.d.
Fruit cenoses (plum), v. Vărativ, Râşcani district	40-60	2.9	n.d.	n.d.	7.8	n.d.
Fruit cenoses (apple), v. Vărativ, Râşcani district	0-20	65.4	20.1	n.d.	64.3	n.d.
Fruit cenoses (apple), v. Vărativ, Râşcani district	20-40	31.3	6.8	n.d.	27.4	n.d.
Fruit cenoses (apple), v. Vărativ, Râşcani district	40-60	1.6	n.d.	n.d.	11.4	n.d.
Sediment, Ciuhur river, v. Vărativ, Râşcani district	0-20	27.1	1.0	n.d.	139.6	n.d.
Sediment, Ciuhur river, v. Vărativ, Râşcani district	20-40	49.9	2.4	n.d.	265.1	n.d.
Grassland (hârtop), v. Vărativ, Râşcani district.	0-20	39.7	n.d.	n.d.	65.8	n.d.
Grassland (hârtop), v. Vărativ, Râşcani district.	20-40	18.1	n.d.	n.d.	19.1	n.d.
Grassland (hârtop), v. Vărativ, Râşcani district.	40-60	n.d.	n.d.	n.d.	4.9	n.d.
Forest biocenoses, v. Ivancea, Orhei district	litter	181.7	16.4	10.6	1280.6	0.8
Forest biocenoses, v. Ivancea, Orhei district	0-20	125.0	n.d.	1.9	240.6	n.d.
Forest biocenoses, v. Ivancea, Orhei district	20-40	6.8	n.d.	n.d.	17.4	n.d.
Forest biocenoses, v. Ivancea, Orhei district	40-60	8.1	n.d.	n.d.	15.9	n.d.
Dniester river floodplain (Vadul lui Vodă)	litter	61.5	4.0	20.3	608.4	n.d.
Dniester river floodplain (Vadul lui Vodă)	0-20	226.7	2.1	0.6	478.8	n.d.
Dniester river floodplain (Vadul lui Vodă)	20-40	161.6	n.d.	0.6	301.3	n.d.
Dniester river floodplain (Vadul lui Vodă)	40-60	18.4	n.d.	1.8	102.2	n.d.

Note: 1. n.d. – nonderminable. Limit of determination - 0,5 mg/kg dry sub.;
2. $\sum y,p'$ DDX = sum. o,p DDT; p,p DDT; o,p' DDE; p,p' DDE; o,p DDD; p,p' DDD;
3. $\sum HCH$ – iso = sum. α , β , γ , δ – HCH;
4. $\sum BPC$ = sum. PCB (28, 52, 101, 138, 153, 170 and 180);
5. PAH = sum. PAHs;
6. HCB = Hexachlorobenzen.

Summary concentrations of organochlorine compounds (sum-DDX, sum-HCH, sum-BPC and HCB) in the repeatedly investigated soil layer (a. 2019) are presented in Table 2.

Table 2. Concentration of organochlorine compounds in soil layer 0-60 cm, [mg/kg dry sub.], year 2019

Place of sample collection	Depth, cm	$\sum y, p'$ DDX, mg/kg dry sub.	$\sum$ HCH-iso, mg/kg dry sub.	$\sum$ BPC, mg/kg dry sub.	HCB, mg/kg dry sub.
Land, chemical warehouse, v. Văratice, Râșcani district	0-20	0.5//500 μg/kg	<0.1	<0.01	<0.03
Land, chemical warehouse, v. Văratice, Râșcani district	20-40	0.4//400 μg/kg	<0.1	<0.01	<0.03
Land, chemical warehouse, v. Văratice, Râșcani district	40-60	<0.1	<0.1	<0.01	<0.03
Fruit cenoses (plum), v. Văratice, Râșcani district	0-20	<0.1	<0.1	<0.01	<0.03
Fruit cenoses (plum), v. Văratice, Râșcani district	20-40	<0.1	<0.1	<0.01	<0.03
Fruit cenoses (plum), v. Văratice, Râșcani district	40-60	<0.1	<0.1	<0.01	<0.03
Sediment, Ciuhur river, v. Văratice, Râșcani district	0-20	<0.1	<0.1	<0.01	<0.03
Sediment, Ciuhur river, v. Văratice, Râșcani district	20-40	<0.1	<0.1	<0.01	<0.03
Sediment, Ciuhur river, v. Văratice, Râșcani district	40-60	<0.1	<0.1	<0.01	<0.03
Grassland (hârtop), v. Văratice, Râșcani district.	0-20	<0.1	<0.1	<0.01	<0.03
Grassland (hârtop), v. Văratice, Râșcani district.	20-40	<0.1	<0.1	<0.01	<0.03
Grassland (hârtop), v. Văratice, Râșcani district.	40-60	<0.1	<0.1	<0.01	<0.03
Dniester river floodplain (Vadul lui Vodă)	litter	<0.1	<0.1	<0.01	<0.03
Dniester river floodplain (Vadul lui Vodă)	0-20	<0.1	<0.1	<0.01	<0.03
Dniester river floodplain (Vadul lui Vodă)	20-40	<0.1	<0.1	<0.01	<0.03

Note: 1. n.d. – nonderminable. Limit of determination - 0,1 mg/kg dry sub.; (y, p' DDX; HCH); 0,01 mg/kg dry sub. (PCB); 0,03 mg/kg dry sub. (HCB);
2. $\sum y, p'$ DDX = sum. o, p DDT; p, p DDT; o, p' DDE; p, p' DDE; o, p DDD; p, p' DDD;
3. $\sum$ HCH – iso = sum. $\alpha, \beta, \gamma, \delta$ – HCH;
4. $\sum$ PCB = sum. PCB (28, 52, 101, 138, 153, 170 and 180);
5. PAH = sum. Polycyclic aromatic hydrocarbons (PAHs);
6. HCB = Hexachlorobenzen.

The analytical results obtained show the presence of low correlated concentrations of $\sum$ HCB and $\sum$ PCB (both in 1994 and in 2019). Only low concentrations of these substances were found in 1994, namely 0.8 μg/kg (forest litter, MAC of HCB equal to 0.03 mg/kg) and 1.2 μg/kg (fruit litter). Analogues and PCBs (20.3 μg/kg, MAC equal to 0.06 mg/kg) were detected in the litter sample collected in the Dniester floodplain, Vadul lui Vodă.

The highest content of $\sum$ HCH-iso, equal to 125.7 μg/kg in the horizon 0-20 cm (1994), was found in the soil sample collected in the area of the chemical deposit and the treatment

solutions preparation plant (v. Văratice, Râșcani district), as a result of the intensive use of this insecticide in the agrophytopharmacy of the orchards (over 2000 ha of orchards). Due to its high volatility and lower persistence in the soil compared to other organochlorine compounds, HCH accumulates only in the shallow horizons of the soil, and over time (2019) the concentration of HCH-iso is lower than the non-detectable limit - 0.1 mg/kg (MAC of HCH equal to 0.1 mg/kg).

DDX compounds (DDT and its metabolites) were found in all analyzed soils. Summary levels of organochlorine compounds, depending on soil depth, showed different

distribution patterns between samples. Soils from natural biocenoses (forest, grassland) contain a maximum concentration in the upper layer of the soil (0-20 cm), while in the case of agricultural soils, relatively homogeneous concentrations of contaminants were found in the middle and lower horizons 0-40 cm, in some cases (orchards) the contamination reaches up to 60 cm. [5].

DDX levels (DDT and its metabolites) are high in the case of chemical deposits, extremely high (16.60 mg/kg in the 0-60 cm soil layer in 1994, or more than 166 times the MAC. However, even after 25 years (in 2019), although the concentration of $\Sigma y, p'$ DDX in the 0-40 cm layer of the soil has decreased by a factor of 21, there are still amounts that threaten the health of the soil biota (0.13 mg/kg in the 0-40 cm layer of the soil) and, of course, of humans through the plants that grow here and the grass grazed by animals (the area of about 4 ha is abandoned and left fallow). Note that all the DDX "left in the soil" is not metabolized and refers to the o,p-DDT and p,p-DDT compounds.

This again demonstrates the high stability and long "life" of organochlorine compounds. This indicates the high adsorption capacity of DDX by soils, especially arable soils, and of course the persistence of organochlorines over time. It was found that the content of y,p'-DDX compounds was (1994) about 1.5-2.0 times higher in agricultural soils than in forest ecosystems due to the systematic use of these compounds on arable soils. Over 25 years, some amounts of DDX residues have not been detected in the soils of fruit orchards (plum, v. Văratice, Râșcani district) (the content is more < 0.1 mg/kg (detection limit, DIN ISO method 10382: 2003-05), with 0.24 mg/kg recorded in the 0-60 cm soil layer in 1994).

Elevated concentrations of DDX were found in the 0-20 cm litter and soil layer of forest biocenoses and even in underwater sediments (their geoaccumulation). This shows that organochlorine compounds are transported through water in parallel with atmospheric transport. [6].

Regarding soil contamination with DDT compounds and its metabolites, we have found that most of it is concentrated in the litter and soil layer 0-20 cm (forest biocenoses), while arable soils are contaminated with these compounds to a depth of over 40 cm. It was found that the degree of metabolism of DDT to DDE and DDD also differs according to soil use. For example, we found that the degree of metabolism of DDT in the soil of grassland between orchards is low ($Gm-DDT = 0.34$), which proves that 66% of $\Sigma y, p'$ DDT are the compounds o,p'-DDT and p,p'-DDT and that this pesticide probably enters daily into the milk of domestic animals grazing here.

The main role in the degradation and metabolism of DDT is played by the soil, due to its own biological activity, but also by crops in the case of agricultural pesticides. The agro-ecosystem does not have a mechanism for "eliminating" toxic substances, but through its structure and functions it has a great capacity to degrade any organic product that enters one of its components

(e.g. in the soil, as in our case). This is mainly due to the biological activity of the biota metabolism, especially the microbiota, which plays the main role in the processes of metabolism and degradation of xenobiotics. It should be noted that DDT only undergoes structural changes as a result of metabolism.

DDT derivatives (DDD and DDE), on the other hand, break down very slowly and have the same spectrum of toxicity as DDT. DDD is much less stable, but more toxic to micropedobionts than DDT. The metabolites DDE and DDD are similar substances in terms of their physico-chemical properties, but DDE is the metabolite of DDT found in vertebrates, invertebrates, plants and microorganisms, while the metabolite DDD, formed as a result of reductive dechlorination of DDT and partly from DDE, is the basic metabolite in the aquatic environment. [7].

Conclusions

- ❖ The results of this study indicate that, despite the ban on the use of organochlorine pesticides in the 1980s, increased concentrations of DDT and HCH were present in 1994 in both natural (forest, meadow) and agricultural (orchard, grassland) soils; their presence in significant quantities represents a real threat to the food chain of ecosystems.
- ❖ The analytical results show correspondingly low concentrations of ΣPCB and ΣHCB . The presence of HCB in all investigated soils was not highlighted in 1994 and 2019. Low concentrations of 0.8 $\mu g/kg$ and 1.2 $\mu g/kg$ HCB and 20.3 $\mu g/kg$ PCB were found only in forest litter.
- ❖ The surface layers of natural and agricultural soils showed the highest levels of the analyzed organochlorine pesticides. The highest content of HCH-iso, equal to 125.7 $\mu g/kg$ in the horizon 0-20 cm (1994), was found in the soil sample taken from the area of the chemical warehouse and the treatment solutions preparation plant (v. Văratice, Râșcani district), as a result of the intensive use of this insecticide in the agrophytopharmacy of fruit trees. Due to its high volatility and lower persistence in the soil compared to other organochlorine compounds, HCH accumulates only in the superficial horizons of the soil, and over time (2019) the concentration of HCH-iso is lower than the non-detectable limit - 0.1 mg/kg.
- ❖ DDX compounds (DDT and its metabolites) were found in all the soils investigated (1994). Total levels of organochlorine compounds showed different distribution patterns between samples, depending on soil depth. Soils in natural biocenoses (forest, grassland) showed a maximum concentration in the 0-20 cm layer, whereas in agricultural soils relatively homogeneous concentrations of contaminants were found in the middle and lower horizons 0-40 cm, and in some cases (orchards) contamination reaches up to 60 cm.

- ❖ In the case of the chemical store and treatment plant, DDX levels were extremely high in 1994 (16.60 mg/kg in the 0-60 cm soil layer, or more than 166 times the MAC of DDT in soil).
- ❖ Although DDT has long been banned for use, it "still has" an impact on the environment and human health due to its long persistence and accumulation through the food chain. Even after more than 25 years (since 1994) there are still (in 2019) the areas of former chemical storage and preparation of treatment solutions, according to some national data in the Republic of Moldova, over 1500 such areas contaminated with organochlorine residues in quantities that threaten the health of soil biota and, of course, humans through the plants growing there. However, due to the depollution/decontamination capacity of micropedobionts, the soils studied, both natural and agricultural, have been "cleaned" over time (25 years) from the residues of organochlorine insecticides that were massively and recklessly used in the past.
- ❖ The results of this study suggest that there is still insufficient information on the fate of organochlorine pesticide residues in the soils of natural ecosystems in our country, including those in protected natural areas and recreational areas, and that natural soils should not be overlooked when assessing sources and/or monitoring the presence of organochlorine pesticides. Particular attention should also be paid to monitoring the quality of surface waters, especially underwater sediments (geo-storage of pollutants), for the presence of organochlorines.

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