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Assessment of the sequestration strategy based on brown coal Shoptykol to reduce organochlorine pesticides transfer from contaminated soil to hen eggs

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Abstract. This study investigated the efficiency of a sequestration strategy using carbon-based materials to reduce the transfer of organochlorine pesticides (OCPs) from hens to eggs. Specifically, the potential of Kazakhstan-made Shoptykol coal was evaluated by applying 2% (by weight) of this material to OCP-contaminated soil obtained from Kyzylkairat (Almaty region, Kazakhstan). The experiment was conducted by exposure for 45 days of 18 hens, which were divided into three groups depending on their feeding conditions. Laying hens were fed diets containing 10% of soil: for the first group with control soil A, the second group with contaminated soil K, the third group with contaminated soil containing coal. Quantification of pesticide concentrations in egg yolks of laying hens was then performed by gas chromatography mass-spectrometry. Despite the supply of Shoptykol, no significant reduction in OCPs transfer was observed for compounds tested. Thus, the efficiency of Shoptykol coal in reducing the transfer of organochlorine pesticides to animals was not confirmed by our results.

1 Introduction

Organochlorine pesticides (OCPs) categorised as persistent organic pollutants (POPs) under the Stockholm Convention [1], have been widely used mainly as insecticides in agriculture. However, they were banned in developed countries in the 1970s because of their risks to human health and persistence in the environment [2]. OCPs have 4 main properties: persistence, bioaccumulation (increasing concentration in tissues as they move up the food chain), biomagnification (further concentration at higher trophic levels), long-range transport [3].

OCPs can enter farm animals and human from the environment by oral ingestion, inhalation and dermal absorption. For animals, the main route is through contaminated feed and soil. Poultry could ingest daily up to 10% soil in totally ingested dry matter in normal exploring conditions [3-5] whereas over 20% of soil has been reported in deteriorated conditions [6-7]. Therefore, soil could be one of the main vector of these environmental contaminants to farm animals and in food they produced (meat and eggs) especially when these animals were raised in areas with a historical contamination [4, 8, 9].

In the aftermath of a pollution incident, extensive damage to food supplies and production systems leads to significant economic and social repercussions in the affected region. However, these consequences should be minimized while ensuring consumer safety remains a priority. Rehabilitating contaminated areas for food production is essential for both commercial farms and private households. Commercial farms require tailored management and restoration strategies due to their extensive size compared to private holdings. Therefore, accurately assessing pollutant transfer and implementing efficient reduction measures are crucial for evaluating and mitigating risks in contaminated areas. Some studies of the last decades showed that different carbon rich materials such as activated carbons, biochars and charcoals have been applied as amendment in remediation of OCP contaminated soils and water [10-12]. The remediation of contaminated soils using these materials is based on desorption-adsorption processes, which ensure the long-term retention and trapping of contaminants in the soil matrix. This form of remediation is called sequestration strategy, and the material used to immobilize contaminants is called sequestration material.

In this study, we employed Kazakh-produced brown coal Shoptykol as a soil amendment to assess its potential in minimizing the transfer of OCPs from polluted soils from the Kyzylkairat village (Almaty region) to the eggs of laying hens. Through controlled experiments with laying hens, we aimed to gauge the effectiveness of this sequestration strategy. Our primary goal was to lower OCP concentrations in laying hen eggs by utilizing brown coal as a sequestration material.

2 Materials and methods

2.1 Materials

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In this study, as sequestration material was used non-porous brown coal Shoptykol. The physico-chemical characteristics of the Shoptykol described in study [13].

Two types of soil were used in the experiments: the first soil, labelled Kyzylkairat (K) soil from the settlement of Kyzylkairat (43°17'59.3"N 77°11'40.2"E) as contaminated soil described by [14] in the Almaty region and Antigen (A) soil, uncontaminated brown soil taken from the vivarium of "Antigen" LLP located in Kaskelen city (43°12'23.1"N 76°38'05.0"E). Soil sampling was carried out according to the prescribed standard [15].

Analytical standards for pesticides (2,4-DDD, 4,4-DDD, 4,4-DDT, 4,4-DDE, α -HCH, β -HCH, γ -HCH) were obtained from "Lezart" LLP (Kazakhstan) and ^{13}C -labelled β -HCH was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and used as an internal standard.

2.2 Scheme of experiment

The experimental scheme for the present study is shown in Figure 1.

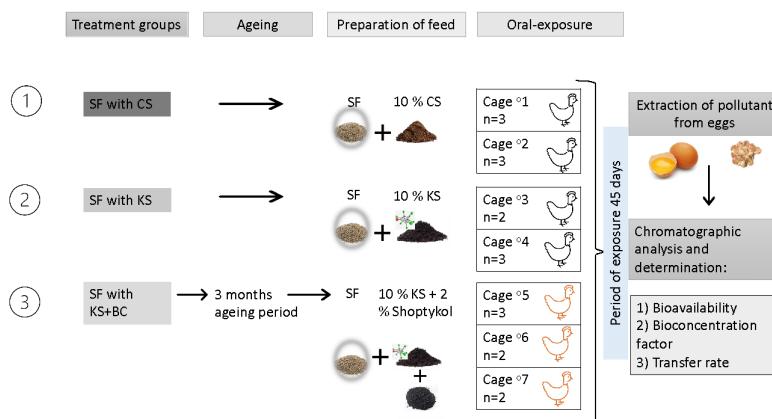


Fig.1. Experimental scheme of present study. Note: SF – standard feed, CS – Control soil, KS – Contaminated soil, BC – Brown coal.

Three randomly selected groups of laying hens received one of the three types of feed. During the exposure period (day 1 to day 45), the hens were given daily the feed containing soil. At the end of the adaptation period 2-3 eggs have been taken for analysis as a starting point and during the exposure period eggs were collected daily by cages.

This study was approved by the local ethical committee on the appropriate use of animal experiments (Resolution No. 132 dated 28 December 2016, based on the order of the Public Health of the Republic of Kazakhstan) and was conducted in strict compliance with the principles outlined in the Guidelines for the Care and Use of Laboratory Animals.

2.3 Creation of controlled conditions for keeping experimental hens

Laying hens from Leghorn and Loman Brown breeds were chosen for the study, totaling 18 hens from Kyzylkairat village (7 Loman Brown and 11 Leghorn). After a 51-day adaptation period, they were housed in groups of 2-3 cages (160x80 cm) equipped with individual feeders at Co Ltd "Antigen" vivarium. Three experimental groups were formed based on feeding conditions:

Group 1: Leghorn hens (3 per cage) fed with feed mixed with control soil A.

Group 2: Leghorn hens (3 in one cage, 2 in another) fed with feed mixed with contaminated soil K.

Group 3: Loman Brown hens (3 per cage) fed with feed mixed with soil K and coal Shoptykol. The mixture of coal (2% dry matter) and soil K were preliminary aged during 3 months before starting of the experiment with hens.

Finally, each hen daily received a 130 g of feed with 10% of soil included.

2.4 Determination of OCPs concentrations in soil

The extraction of soil samples was carried out with some modifications according to the method described in [16].

The extraction for egg samples was carried out according to the original QuEChERS principle established by Anastasiadis et al. with slight modifications [17] and was carried out as described elsewhere [18]. For each sample, the

analysis was carried out in 3 replicates. Quantitative analysis of experimental samples was carried out by GC-MS method.

2.5 GC-MS analysis

The determination of OCPs in the soil and egg samples was carried out using GC-MS (7890B, Agilent Technologies). Briefly, the mass spectrometer was set to a resolution of 10000 in electron ionisation mode (70 eV electron energy) (5975C, Agilent Technologies). An HP-5ms Ultra Inert capillary column (30 µm x 250 µm x 0.25 µm) from Agilent J&W (Agilent Technologies) in splitless mode was used. The GC temperature program for OCP analysis was: from 120 °C (1 min), 40 °C min⁻¹ to 220 °C (13 min). The total time was 16.5 minutes. The obtained signals were integrated using the Mass Hunter program (B 07.05.2479).

Pesticide concentrations in soil and egg samples was calculated using external and internal calibration methods. The linear equations derived from the calibration curves were used to calculate the concentration of the substance in the extract. Accordingly, pesticide concentration in soil was expressed as dry matter and in eggs as fat weight. Mean concentrations and standard deviations were calculated and presented in tables below.

3 Results and Discussion

Analysis of OCP concentration was conducted intermittently, with analyses performed for each egg collected during the adaptation period, given that not all hens laid eggs. Once the experiment commenced, analyses were conducted on days when hens laid eggs. Therefore, in the initial two weeks of the experiment, analyses were performed thrice, while in subsequent weeks, it was carried out once. A total of 142 eggs underwent analysis to determine OCP concentrations.

3.1 OCP concentration in soils

OCP concentrations in A and K soils are presented in Table 1. The soil A showed only background concentrations of DDT congeners (i.e; respecting regulatory thresholds) and low concentrations of HCH congeners. Contrarily, the concentrations in K soil were very high for DDT congeners: between 84 and 385 ppm meaning at least 800 times over regulatory thresholds. The concentrations of HCH, in soil K were quite variable depending on the considered congener: concentrations around the regulatory thresholds for gamma-HCH and delta-HCH, overpassing a threshold by a factor of 20 for alpha-HCH, and very consequent overpassing (300 times) for beta-HCH.

Table 1. Organochlorine pesticide concentrations in Kyzylkairat and Antigen soils, µg/g of dry matter.

OCPs	Antigen soil	Kyzylkairat soil	MRLs	
			RK	EU
α-HCH	0,2±0,05	1,1±0,2	0,05	0,1
β-HCH	0,03±0,004	15,5±0,9	0,05	0,1
γ-HCH	0,01±0,002	0,09±0,06	0,05	0,1
δ-HCH	0,08±0,01	0,2±0,01	0,05	0,1
4,4-DDE	0,04±0,02	385,7±6,5	0,1	-
2,4-DDD	0,08±0,09	85,3±0,05	0,1	-
4,4-DDD	0,01±0,001	293,2±7,77	0,1	-
4,4-DDT	0,06±0,03	83,7±2,4	0,1	0,1

MRL – Maximum residue limit

3.2 OCP concentration in experimental eggs

The results obtained in the *in vivo* experiment were confirmed by quantitative analysis of pesticide concentrations in eggs of hens of all groups, presented in Table 2.

In particular, the results of the control group showed that the concentration of 4,4 DDE measured at the beginning of the adaptation period is at a noteworthy level of 12.54 µg/kg. During the seven-week experiment, this concentration tends to increase, reaching an elevated value of 19.95 µg/kg.

Table 2. Mean concentrations of OCPs determined in eggs of hens from: (i) control group, (ii) exposed to K soil, (iii) exposed to K soil with coal, $\mu\text{g}/\text{kg}$ of egg fat mass.

Period of exposure	Treatment groups	OCPs							
		α -HCH	β -HCH	γ -HCH	δ -HCH	4,4-DDE	2,4-DDD	4,4-DDD	4,4-DDT
Adaptation	T1	0,8	0,3	1,2	0,0	12,5	0,0	0,2	0,0
	T2	0,5	0,2	0,8	0,8	7,9	0,0	0,1	0,4
	T3	7,9	3,7	12,5	2,3	2,5	0,0	1,1	0,2
Week 1	T1	1,1	0,4	4,9	1,4	9,8	0,1	0,1	0,2
	T2	2,0	1,0	3,6	1,3	11,9	0,1	0,3	2,2
	T3	4,6	2,5	7,0	1,9	5,0	0,1	0,6	1,2
Week 2	T1	1,2	0,6	8,9	0,6	8,7	0,1	0,1	0,2
	T2	3,6	1,1	3,7	0,8	24,0	0,2	0,7	6,7
	T3	9,9	4,4	12,1	1,6	14,0	0,4	0,7	2,1
Week 3	T1	1,4	0,5	4,2	0,0	8,5	0,0	0,2	0,0
	T2	2,2	1,6	3,3	0,1	27,6	0,3	0,4	3,3
	T3	24,9	11,2	22,2	2,7	59,7	1,7	2,0	3,5
Week 4	T1	0,3	0,1	2,7	0,0	3,6	0,0	0,2	0,0
	T2	1,6	1,5	3,6	0,1	29,2	0,2	1,2	3,2
	T3	25,5	11,8	22,3	3,9	35,5	1,3	1,9	9,2
Week 5	T1	NA	NA	NA	NA	NA	NA	NA	NA
	T2	NA	NA	NA	NA	NA	NA	NA	NA
	T3	22,5	3,1	12,6	0,8	57,2	1,2	0,7	8,0
Week 6	T1	0,4	0,0	4,0	0,0	8,7	0,0	0,2	0,0
	T2	5,1	1,7	2,5	0,1	13,4	0,2	0,9	2,7
	T3	33,8	4,4	22,9	2,5	101,4	1,5	2,3	11,0
Week 7	T1	3,4	0,0	1,6	1,0	20	0,1	0,2	2,0
	T2	4,8	7,2	0,8	1,4	122,3	0,9	2,1	22,1
	T3	12,0	2,7	11,7	1,6	91,1	1,8	2,7	9,2

T1 – control group, T2 – group of hens exposed to K soil, T3 – group of hens exposed to K soil with coal

The group exposed showed at the seventh week, compared to the adaptation period, the amount of α -HCH and β -HCH increased to 4.82 $\mu\text{g}/\text{kg}$ and 7.18 $\mu\text{g}/\text{kg}$ respectively. Notably, the concentrations of 4,4-DDE increased significantly, up to 122.25 $\mu\text{g}/\text{kg}$ in the last week of the experiment, exceeding MRL of Kazakhstan (100 $\mu\text{g}/\text{kg}$). This represented a factor of 15-fold increase compared to the level during the adaptation period. Moreover, 4,4-DDE, 2,4-DDE and 4,4-DDT showed a marked increase up to 2.07 $\mu\text{g}/\text{kg}$, 0.93 $\mu\text{g}/\text{kg}$ and 22.13 $\mu\text{g}/\text{kg}$, respectively, compared to their concentrations during the adaptation period.

The third group of eggs show that the concentrations of β -, γ - and δ -HCH isomers peaked at the third and fourth week.

The values of β -HCH, γ -HCH and δ -HCH were determined in the range of 11.24-11.80 $\mu\text{g}/\text{kg}$, 22.23-22.34 $\mu\text{g}/\text{kg}$ and 3.93 $\mu\text{g}/\text{kg}$, respectively. The highest concentration of α -HCH ranging from 24.91-33.77 $\mu\text{g}/\text{kg}$ was observed from week three to week six. Then a decrease was observed at the seventh week. Increased concentrations of 4,4-DDE and 4,4-DDT were observed from the second and fourth week and reached a maximum at the sixth week (40-fold increase for 4,4-DDE). The maximum concentrations of 2,4-DDD and 4,4-DDD were found in the seventh week with values of 1.77 $\mu\text{g}/\text{kg}$ and 2.72 $\mu\text{g}/\text{kg}$, respectively. These values were 1.7-2.4 times higher compared to the initial values during the adaptation period.

It was found that the use of Shoptkyol coal as a sequestering material has an insignificant effect on the concentration of OCP in eggs. This ineffectiveness of the used coal could be explained by the lack of heat treatment and insufficient porous structure. It contradicts to the results of previous similar studies [10], [11], [19] in which the use of activated carbon and biochar demonstrated effectiveness in reducing the transfer of OCP into animal tissues.

4 Conclusion

The study discovered that the sequestration strategy based on coal Shoptkyol showed almost no significant reduction of OCPs in eggs during exposure of laying hens. Thus, raw nature (coal without thermal or chemical treatment), and as consequence absence of porous surface could explain this absence of lowered bioavailability.

Further research is needed to observe if at level of body of laying hens situation is similar than with eggs. Globally for perspective also need to implement this strategy using thermally treated coal Shubarkol, which can adsorb effectively all the studied compounds, to validate effectiveness of this sequesterant in soil remediation.

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