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ESTIMATION OF RADIATION BACKGROUND AND ANALYSIS OF ORGANOCHLORINE PESTICIDE RESIDUES IN SOIL FROM TARTAR, AZERBAIJAN BY GC

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Abstract: In this study, for the purpose of evaluating the radioecological risks in the liberated territory of Tarter region, radiation background measurements were performed at 22 security points and the average value typical for the area was determined to be 6-7 μR/hour. Residues of organochlorine pesticides were investigated in soil from a former plantation area in Tartar District, Azerbaijan. Analysis was carried out to determine the concentration of 16 pesticides (Alpha BHC, Beta BHC, Gamma BHC, Delta BHC, Heptachlor, Aldrin, Heptachlor Epoxide Isomer B, Alpha Endosulfan, 4,4' DDE, Dieldrin, Endrin, Beta Endosulfan, 4,4' DDD, Endrin Aldehyde, Endosulfan Sulfate, 4,4' DDT) by gas chromatography (Varian CP 3800). It was determined that residues of 4,4' DDT and its metabolites 4,4' DDE and 4,4' DDD remained on the upper surface of the soil even though the latest possible usage period of pesticides in the investigated field was more than 29 years ago.

Keywords: radiation background, pesticides, soil, contamination, Azerbaijan, Karabakh

1. Introduction

Pesticides are a group of chemicals used for the destruction of insects, weeds, fungi, bacteria, *etc*. Most the pesticides can destroy a wide variety of pests or weeds, but some are developed against specific pests or pathogens [1]. There are many different pesticides in use today with very different modes of action and levels of toxicity [2]. As common persistent organic pollutants (POPs), organochlorine pesticides (OCPs) have received great attention worldwide due to their high toxicity, chemical durability, and biological concentration. These chemicals were once widely used in agricultural production and pest control universally [3] [4].

Although the human health effects after exposure to OCPs are not adequately understood it has been considered that these contaminants have an endocrine-disrupting activity and that they have also been implicated in the etiology of various diseases and endocrine-related disorders, such as pancreatic cancer, breast cancer, non-Hodgkin's lymphoma, leukemia, uterine cancer, liver cancer, sexual precocity, cryptorchidism, and low sperm concentration [5] [6]. DDT has been used extensively worldwide as an insecticide for agriculture. Due to concern about its toxicity, the use of DDT is banned in most countries. However, in some developing countries, DDT is still used in quantities ranging from a few to several thousand tons. Due to the ability of OCPs to accumulate in body tissues, their long half-life of elimination from the body, and emerging evidence of potential toxicity to human health, many countries throughout the world went on to ban many of the agents within the OCP family [7].

The exceptional stability of organochlorine pesticides results in the contamination of the natural environment for long years, and yet they are still used in certain regions of the world. There is an apparent need for both monitoring of their residues and the development of methods for their removal or decomposition [8].

It is known that Radiation can be referred as the energy in motion or energy in the form of waves or particles. Radiation is present everywhere around us in many forms. The overall radiation from various sources on a specific location on earth's surface refers to the background radiation level of that zone. Exposure to background radiation is an inescapable feature of the environment. Large doses of ionizing radiations, very much larger than background level, can cause a measurable increase in cancers and leukemia (blood cancer) after some years of delay. At very high levels, radiation can cause sickness and death within weeks of exposure [9].

This study aimed to investigate possible residues and degradation products of OCPs in the former crop field and to evaluate possible health risks due to reusing that area for plantation.

2. Materials and Methods

A portable dosimeter – identifinder was used to quantify the total radiation level at different places of investigation area. For the purpose of evaluating the radioecological risks in the liberated territory of Tarter region, radiation background measurements were performed at 22 security points and the average value typical for the area was determined to be 6-7 μR/hour

Sample collected from the surface (0-10 cm) layer of the former crop field soil located in Chayli village of Tartar District, Azerbaijan, and brought to the laboratory. The mentioned area wasn't used for plantation purposes due to this territory was under the occupation of the Armenian army, meaning the possible usage period of OCPs in that area was more than 29 years ago.

The concentration of 16 OCPs was determined in this study: α-, β-, γ- and δ- (HCH), p,p'-DDE, p,p'-DDD, p,p'-DDT, aldrin, dieldrin, endrin, α-, β- endosulfan, endosulfan sulfate, endrin aldehyde, heptachlor, and heptachlor epoxide-B. Pesticide standards (including 2,4,5,6-Tetrachlor-M-Xylene and decachlorobiphenyl) (purity > 97.0%) and other reagents, were purchased from LGC and Sigma-Aldrich. The mixed stock solution for calibration of the GC/ECD, containing all OCPs, was prepared in n-hexane.

Solvents used in the extraction and cleanup procedures including methylene chloride and acetone exchanged for n-hexane before analysis. All solvents were in chromatographic quality grade and each solvent was free of phthalates. EPA Method 8081B [10] was used as the base method for the determinations of OCPs. For extraction process EPA Method 3550C [11] (ultrasonic extraction), for clean-up EPA Methods: 3660 (sulfur cleanup) [12] and 3630 (Silicagel cleanup) [13] was used for preparation of samples.

OCP concentrations in soil samples were determined using GC/ECD system. The measurement procedure was carried out under the following conditions:

Gas chromatograph (GC) Varian 3800 (Varian, Inc. (USA)), detector - ECD (63Ni), on a column 30 m x 0.250 mm x 0.25 μm, phase DB-5MS, temperature programming was used. The oven temperature was programmed starting at 80ºC staying steady for 0.5 min, followed by increases of 26ºC/min to 175ºC, then 6.5ºC/min to 235ºC, and then 15ºC/min to 300ºC and held 6 min. The injection port was at 250ºC splitless mode, and the detection operated at 340ºC. Nitrogen (purity ≥ 99.999%) was used as carrier gas at a constant flow rate of 3.0 mL/min, whereas nitrogen (purity ≥ 99.999%) was employed as makeup gas at a flow of 27 mL/min. The system was operated by GC Solution Star Workstation software [5][14][15].

3. Results and Discussion

Radiation background measurements carried out in liberated area of Tartar district showed that the exposure dose rate of radiation varies in the range of 3.2 - 12.7 μR/h. The observed values are lower than the average radiation background value for Azerbaijan (14 μR/h) and do not pose a radiation risk for the population.

The concentrations of OCPs in soil sample (C) were calculated using chromatogram via the following equation:

$$C_n = \frac{A_n x V_{extr} x D}{CF x M_{samp}} \quad (1)$$

Where: C_n - concentration of the compound of interest in a solid sample, μg/kg; A_n - peak area of the compound of interest; V_{extr} - the volume of extract, ml; D - dilution factor; CF - calibration factor of analyte; M_{samp} - dry mass of sample taken for extraction, g.

Calculated concentrations of investigated OCPs are given in Table 1.

Table 1

The concentration of OCPs in soil from former crop field

Compound	**CAS-number**	**Concentration (μg/kg)**
Alpha-BHC	319-84-6	-
Beta-BHC	319-85-7	-
Gamma-BHC	58-89-9	2.17
Delta-BHC	319-86-8	-
4, 4 ' - DDT	50-29-3	4.48
4, 4 ' - DDE	72-55-9	67.70
4, 4 ' - DDD	72-54-8	3.17
Aldrin	309-00-2	-
Dieldrin	60-57-1	-
Heptachlor	76-44-8	6.38
Heptachlor Epoxide Isomer B	1024-57-3	-
Endosulfan I (Alpha)	959-98-8	-
Endosulfan II (Beta)	33213-65-9	-
Endosulfan Sulfate	1031-07-8	-
Endrin Aldehyde	7421-93-4	-

As can be seen from Table 1, Alpha BHC, Beta BHC, Delta BHC, Aldrin, Heptachlor Epoxide Isomer B, Alpha Endosulfan, Dieldrin, Endrin, Beta Endosulfan, Endrin Aldehyde, Endosulfan Sulfate were not detected in the analyzed sample. Residues of the widely used carcinogenic compound - 4, 4 ' - DDT and its metabolites (4, 4 ' – DDE and 4, 4 ' – DDD) remain in the soil of the former crop field. The half-life of DDT in the soil can vary between 2 and 15 years, depending on the soil acidity and temperature [16]. Considering the last usage period of this compound was more than 29 years of age, it can be said that it mostly degraded to its metabolites and that is the reason why the low content of DDT remains in the investigated sample. The concentration of 4, 4 ' - DDE was determined to be more than 15 times higher than 4, 4 ' – DDD's concentration, indicating degradation of 4, 4 ' - DDT mainly results in forming of 4, 4 ' – DDE. In our previous research, residues of OCPs in former pesticide storage located in Salyan, Azerbaijan were investigated (Table 2). The concentration of 4, 4 '-DDD in the soil of former pesticide storage was more than 2 times higher than 4, 4 '-DDE's concentration, contrary to the result of the present research. There are multiple pathways in the literature for the transformation of DDT to its metabolites, and metabolites to each other via bacteria and fungis that live in different conditions [17]. The difference between the results of mentioned research can be explained as differences between properties of investigated soils and conditions for living organisms that degrade 4, 4 ' – DDT, 4, 4 ' – DDE, and 4, 4 ' – DDD.

Table 2

Results from previous research (soil from Dayikand, Salyan, Azerbaijan)

Compound	**Concentration (µg/kg)**
Alpha-BHC	1.83
Beta-BHC	12.9
Gamma-BHC	3.66
Delta-BHC	2.13
4, 4 ' - DDT	104
4, 4 ' - DDE	70.2
4, 4 ' - DDD	191
Aldrin	0.84
Dieldrin	8.99
Heptachlor	26.1
Heptachlor Epoxide Isomer B	2.84
Endosulfan I (Alpha)	4.73
Endosulfan II (Beta)	7.53
Endosulfan Sulfate	10.1
Endrin Aldehyde	1.66

4. Conclusion

The finding of this shows a variation of radiation level. Comparatively large values of radiation counts at high altitude and low values at river side. There is no any abnormal value of

radiation counts for all sample places. So, there is, generally, no significant risk of public exposure to the background radiation for sample places.

Samples collected from the surface layer of the former plantation soil located in Chayli village of Tartar District, Azerbaijan were analyzed for 16 OCPs via gas chromatography. The result of the analysis showed that residues of some of the investigated organochlorine pesticides (Gamma-BHC, Heptachlor, 4, 4 '-DDT, 4, 4 ' – DDE, and 4, 4 ' – DDD) remain in the soil from Chayli village. This indicates that reusing that area for plantation purposes may cause health problems due to the transfer of residues of OCPs to plants, and then to the human body. Also, for overall evaluation of soils that can be used as plantation areas after the de-occupation of Azerbaijan territories (in Karabakh and surrounding regions) are very important estimation pollution. Monitoring and scientific research works are of particular importance to measuring OCP (and any other pollutants) contents of soils. The using pesticides was not controlled for 30 years in that area. Measuring their content in soils would also allow investigating the degradation processes of OCPs.

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ОЦЕНКА РАДИАЦИОННОГО ФОНА И АНАЛИЗ ОСТАТКОВ ХЛОРОРГАНИЧЕСКИХ ПЕСТИЦИДОВ В ПОЧВЕ ИЗ ТАРТАР, АЗЕРБАЙДЖАН, МЕТОДОМ ГХ

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Резюме: В данном исследовании с целью оценки радиоэкологического риска на освобожденной территории Тартерского района были проведены измерения радиационного фона в 22 безопасных пунктах и определено среднее значение, характерное для района, равное 6-7 мкР/час. Остатки хлорорганических пестицидов были исследованы в пробе почвы, взятой с бывшей плантаций в Тертерском районе Азербайджана. Был проведен анализ для определения концентрации 16 пестицидов (альфа-БГХ, бета-БГХ, гамма-БГХ, дельта-БГХ, гептахлор, альдрин, эпоксидный изомер Б гептахлора, альфа-эндосульфан, 4,4'-ДДЭ, дильдрин, эндрин, бета-эндосульфан, 4, 4'-ДДД, альдегид эндрина, сульфат эндосульфана, 4,4'-ДДТ) с помощью газового хроматографа (Varian CP 3800). Установлено, что 4,4’-ДДТ и его метаболиты 4,4’-ДДЕ и 4,4’-ДДД остались в верхнем слое почвы, несмотря на то, что последний возможный период применения пестицидов на исследуемом поле был более 29 лет назад.

Ключевые слова: радиационный фон, пестициды, почва, загрязнение, Азербайджан, Карабах.

AZƏRBAYCANIN TƏRTƏR ƏRAZİSİNDƏ RADİASİYA FONUNUN QİYMƏTLƏNMƏSİ VƏ QX VASİTƏSİLƏ GÖTÜRÜLƏN TORPAQ NÜMUNƏSİNDƏ XLORÜZVİ PESTİSİDLƏRİN QALIQLARININ ANALİZİ

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Xülasə: Bu tədqiqatda Tərtər rayonunun işğaldan azad edilmiş ərazisində radioekoloji risklərin qiymətləndirilməsi məqsədilə 22 təhlükəsiz məntəqədə radiasiya fonunun ölçülməsi aparılıb və ərazi üçün xarakterik olan orta qiymət 6-7 μR/saat müəyyən edilib.Azərbaycanın Tərtər rayonu ərazində yerləşən keçmiş əkin sahəsindən götürülən torpaq nümunəsində xlorüzvi pestisidlərin qalıqları tədqiq olunmuşdur. 16 pestisidin (Alpha BHC, Beta BHC, Gamma BHC, Delta BHC, Heptaxlor, Aldrin, Heptaxlor Epoxide Isomer B, Alpha Endosulfan, 4,4’ DDE, Dieldrin, Endrin, Beta Endosulfan, 4,4’ DDD, Endrin Aldehid, Endosulfan Sulfat, 4,4’ DDT) konsentrasiyalarını müəyyənləşdirmək məqsədilə qaz xromatoqrafı (Varian CP 3800) vasitəsilə analiz həyata keçirilmişdir. Ərazidə mümkün olan son istifadə zamanının 29 ildən çox olmasına baxmayaraq torpağın üst səthində 4,4’ DDT və onun parçalanma məhsulları olan 4,4’ DDE və 4,4’ DDD-nin qalıqlarının mövcud olduğu müəyyən edilmişdir.

Açar sözlər: radiasiya fonu, pestisidlər, torpaq, çirklənmə, Azərbaycan, Qarabağ