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Bioconcentration of DDT and its Isomers in Carrots Grown in the Rural Community of Aramus in the Kotayk Region of Armenia

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ABSTRACT

In soil and carrot samples collected in the frame of this research from the same carrot beds in the rural community of Aramus, residual DDT and its isomers p,p′-DDT, p,p′-DDD, o,p′-DDT and p,p′-DDE were detected. In all soil samples, the total concentration of DDT exceeded maximum allowable concentration (MAC). In carrot samples, three isomers out of four were detected: p,p′-DDT, o,p′-DDT and p,p′-DDE, the total concentrations of which did not exceed MAC. The DDT/DDE ratio has indicated that the detected concentrations of DDT are due to historical usage of these pesticides. The bioconcentration factor (BCF) values vary in the range of 0.02-0.37.

Introduction

Residues of organochlorine pesticides (OCPs) and particularly dichlorodiphenyltrichloroethane or DDT, and its isomers are most commonly found in the environment since they came into wide use in pest control and for combating the disease pathogens in domestic animals and humans from the last half of XX century (Kafilzadeh, 2015). Despite their effectiveness, DDT and its isomers do rank among Persistent Organic Pollutants (POPs) (Commission of the European Communities, 2007) as these pesticides can persist in soils for a long time and when migrating in the environment, they accumulate in living organisms and finally enter food chains (Okoffo, et al., 2016). Being a hydrophobic organic compound, DDT has high affinity to soil organic matter, that causes this chemical to accumulate in organic-rich upper humic soil horizons (Li, et al., 2018). Due to its lipophilicity, DDT accumulates in animal and human tissues (Kafilzadeh, 2015) and as a consequence often provokes intoxication. This chemical as such does not cause specific diseases, instead, it depresses the immune system, the mechanism of which has been studied insufficiently so far. The main targets for DDT to affect are the reproductive organs and liver (Jallow, et al., 2017, EFSA, 2006), besides, this compound ranks among potential carcinogens for humans (IARC, 2015).

Residual DDT is detected in both animal-based food (milk, meat, fat, fish, etc.) (Kotinagu & Krishnaiah, 2015, Liu, et al., 2010) and fruits and vegetables (Chourasiya, et al., 2014). Out of vegetables, this chemical is most frequently found in root and tuber crops (carrot and beet roots, potato, etc.) due to their immediate contact with soil

(Mikes, 2009). Both absorption and accumulation of DDT are mainly influenced by three factors: 1 - crop species, 2 - presence and concentration of DDT in soils and the aging time of its application and 3 - soil quality, e.g. the content of organic matter and agricultural conditions, the irrigation system (Li, et al., 2018). Hence, it is important to conduct monitoring to identify OCPs in the environment and assess their migration- and bioaccumulation-associated risks.

Armenia ranks among states, who used large quantities of DDT as insecticide (Sargsyan V. & Sargsyan A., 2006). Taking into consideration ecological issues associated with the usage of OCPs, in 2001 Armenia joined the Stockholm Convention and in 2003 ratified it undertaking to ban OCPs including DDT (UNEP, 2017). It should be stressed that information about OCPs emphasizing pesticides in Armenia's agricultural soils and crops is incomplete and consequently no relevant risk assessment has ever been done in the country. To address the gaps, the Center for Ecological-Noosphere Studies (CENS) NAS RA implemented a state target program "Monitoring residual pesticides in foods produced in the Republic of Armenia" (2014-2018). The Program was designed to determine residual pesticides in soils, irrigation water and locally grown fruits and vegetables in the largest rural communities - fruit and vegetable producers - located in the marzes of the country.

In this particular research the data of aforesaid state program (Hovhannisyan, et al., 2018; Tepanosyan, et al., 2019) was used and it was done in the frame of base financing program of CENS NAS RA with a purpose to calculate the coefficient of DDT bioconcentration in carrot roots.

Materials and methods

The carrot bed soils and carrot roots were sampled on a random basis, in 2017 in rural community of Aramus located in Kotayk region following SOPs developed by the research group in compliance with ISO (ISO, 1980, 2002a), US EPA (US EPA, 1999) standards and FAO Guidance on Sampling Methodology (FAO, 2009). In total, 7 soil and 7 carrot samples were collected. Each composite soil sample was composed of 8-10 sub-samples, while composite carrot samples consisted of 12 carrot roots each. The samples were all placed into plastic packages and transported at 4 ^{0}C to the Central Analytical Laboratory CENS (accredited by ISO: 17025) to be then analyzed for residual DDT. The following isomers were detected and quantified: o,p′- DDT, p,p′- DDT, o,p′- DDE, p,p′- DDE, o,p′- DDD, p,p′- DDD.

Prior to lab measurements, the samples underwent pretreatment as follows: soil samples were dried, sieved (<2mm) and then pounded in an agate mortar consistent with ISO 11464 (ISO, 2006). The carrot samples for a complete cleanup were thoroughly washed by tap water, rinsed by deionized water and then dried on filter papers.

The subsequent extraction and cleanup of the pretreated soil samples was done by a microwave extractor (Start E, Milestone, Italy) in the acetone-hexane solution (1:1) with the following program: Pace 1-10 min., 1000 W, 120 ^{0}C, Pace 2-20 min., 1000 W, 120 ^{0}C. Then the sample containers were cooled to a room temperature, and the solutions were filtered (ASTM D6010-12) (Tepanosyan, et al., 2019).

The extraction of the shredded carrot samples was done in a separating funnel with sodium chloride solutions, sulfuric acid and distilled water (EN 12393-2:2008). The filtrates were then refined by column chromatography with silica gel. The eluate derived was concentrated to 2 mL with a rotary evaporator. The solution derived was then used for residual DDT to determine by a gas chromatography technique.

To determine residual DDT and its isomers in soil and carrot samples, a Trace GC Ultra gas chromatograph (Thermo Electron Corporation, USA) equipped with an automated injector (Combi PAL; CTC Analytics AG, Switzerland) and a mass spectrometric detector (Trace DSQ; Thermo Electron Corporation, USA) was employed. As carrier gas helium was used (1mL/min). For the quality of analytical work to assess, standard solutions of DDT and its isomers were prepared based on AccuStandard ISO 6468-PEST standards (New Haven, USA) (Hovhannisyan, et al., 2018).

The sensitivity of the method was evaluated based on the Limit of Quantification (LOQ) and Limit of Detection (LOD) which made 0.0006 mg/kg and 0.00006 mg/kg, respectively, whereas Relative Standard Deviation (RSD %) was varying from 1.1 % to 3.5 % (Tepanosyan, et al., 2019).

The level of DDT and its isomers bioaccumulation in the carrot was determined by formula (Li, et al., 2018) in the following way:

$$BCF=Cp/Cs,$$

where *BCF* is the bioconcentration factor, *Cp* – the concentration of a pesticide in a plant; *Cs* – the concentration of a pesticide in soils.

The statistical analysis of data obtained was done based on the Microsoft Excel (MS Office 2016) program.

Results and discussions

The results of lab analyses have indicated that 14 soil and carrot samples all contain at least a single DDT isomer (Hovhannisyan, et al., 2018, Tepanosyan, et al., 2019). This can unambiguously be explained by the fact of deposition of the given pesticide in agricultural soils (Jallow, et al., 2017) because as early as several decades ago this chemical was used in enormous quantities nationwide (Sargsyan V., Sargsyan A., 2006). According to literature sources, residual OCPs in soils can be absorbed by plants emphasizing root and tuber crops which sit immediately in the soil (Mikes, et al., 2009). Due to osmotic pressure, residual pesticides travel from soil to plants and accumulate in their vegetative organs (Wang, 2011).

In all soil samples residual ∑*DDT* exceeded the maximum allowable concentration (MAC) 0.1 mg/kg in soils. The most frequently detected isomers included *p,p'-DDT, p,p'-DDE* and *o,p'-DDT*, whereas *p,p'-DDD* was only detected in a single sample (Tepanosyan, et al., 2019). The coefficient of variation (*Cv*) for isomers made 26 - 73.2 %, for ∑*DDT - 32.0 %* (Table 1).

The samples of carrot - as distinct from those of soils - contained the residues of three isomers namely *p,p'-DDT, o,p'-DDT, p,p'-DDE* (Hovhannisyan, et al., 2018). For all carrot samples, ∑*DDT* did not exceed *MAC* and *MRL* for carrot-0.1 mg/kg and 0.05 mg/kg respectively established by the EEC and EC, but for a single sample, which showed insignificant excess of residual ∑*DDT* against *EC MRL* alone. In this case, the coefficient of variation (*Cv*) for *DDT* isomers varied 49.2 to 62.7 %, amounting to 78.5 % for ∑*DDT* (Table 2).

The data obtained suggest that ∑*DDT* concentrations in soils are far higher than those in carrot. An explanation is that the organic matter sorption ability of plants is too limited, so, the higher the concentration of soil organic matter, the higher the concentration of a contaminant in roots and tubers (Trapp & Legind, 2011).

Table 1. The detected residual DDT and its isomers in the soil samples (n=7)***

Isomers	Detection frequency, %	Average value, mg/kg	Standard Deviation, (SD)	Coefficient of variation, (Cv), %	Range, mg/kg
p,p'-DDT	100	0.047	±0.026	54.2	0.02 - 0.093
p,p'-DDD	14.3	-*	±0.007	-	n/d** - 0.017
o,p'-DDT	85.7	0.018	±0.013	73.2	0.007 - 0.041
p,p'-DDE	100	0.293	±0.076	26.0	0.191 - 0.413
∑*DDT*	100	0.358	±0.114	32.0	0.218 - 0.565

Note: **- no data, ** n/d – not detected.*

*** Tepanosyan, et al., 2019.

Table 2. The detected residual DDT and its isomers in carrot root samples (n=7)*

Isomers	Detection frequency, %	Average value, mg/kg	Standard Deviation, (SD)	Coefficient of variation, (Cv), %	Range, mg/kg
p,p'-DDT	57.1	0.00096	±0.00056	58.1	0.00062 - 0.00132
o,p'-DDT	28.7	0.014	±0.007	49.2	0.013 - 0.016
p,p'-DDE	100	0.018	±0.011	62.7	0.007 - 0.042
∑ *DDT*	100	0.023	±0.018	78.5	0.007 - 0.058

*Hovhannisyan, et al., 2018.

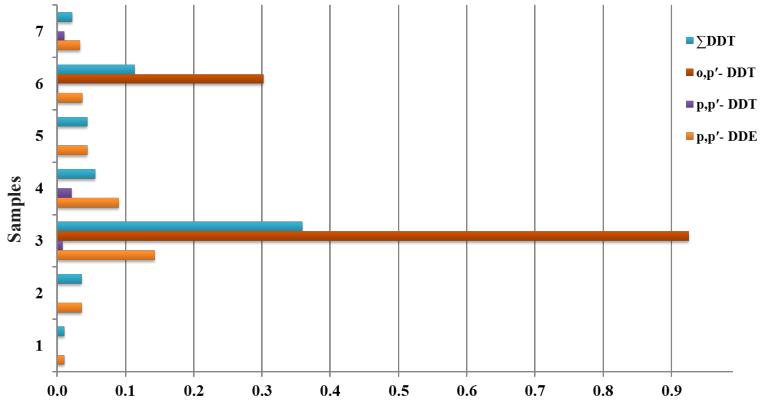

Figure 1. The coefficient of bioaccumulation for ∑DDT and individual isomers in the sampled carrot (*composed by the author*).

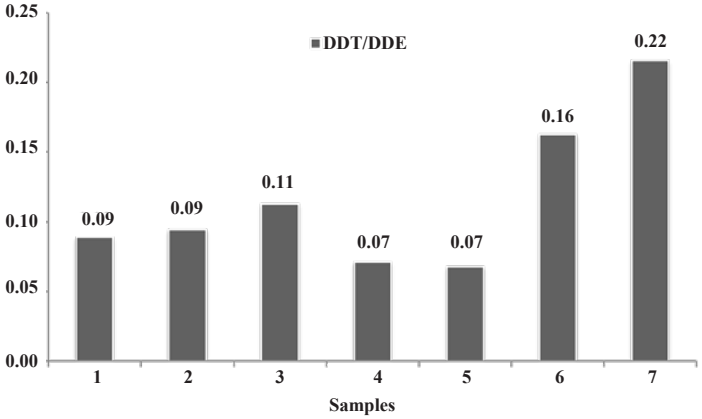

Figure 2. The DDT/DDE correlation in soil samples (*composed by the author*).

Calculation of the *BCF* allows predicting the level of bioaccumulation of organic matter by different organisms (Gao, et al., 2005). *BCF* ∑*DDT* varied 0.02 to 0.37 given the standard deviation ±0.12 and on the average made 0.10. The bioconcentration data are given in Figure 1.

The indices obtained were lower than those reported by Gao H. J., et al., 2005 where mean *BCF of* ∑*DDT* in carrot was 0.80.

Different researches (Gao, et al., 2005, Tao, et al, 2008) suggest that the ratio of concentrations of *DDT* isomers in soils is indicative of the time of the application of this chemical on the given site. To define *DDT* application timescales in Aramus community, a calculation was made in the correlation of *DDT/DDE* concentrations in the sampled soil, too. According to some researchers (Gao, et al., 2005), should *DDT/DDE* correlation be >1, it is indicative of a recent introduction of *DDT*.

For all samples, this correlation is below 1, this being indicative of a historical application of *DDT* on the studied site (Figure 2).

Conclusion

Conclusions derived from this particular research are as follows: the residual *DDT* in soils sampled from carrot beds across the rural community of Aramus exceeded *MAC* several tens of times. The ratio *DDT/DDE* showed the historical usage of this pesticide in that territory. Meanwhile, the residual *DDT* in the sampled carrot roots did not exceed the national MAC, but for a single sample, which showed insignificant excess against *MRL* set by the European Commission. However, there was bioaccumulation of *DDT* from soil into carrot, due to data obtained from *BCF* calculation. The presence of *DDT*

highlights the need for extensive monitoring entirely in Armenia to identify potential environmental risks and health risks to the population.

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