Annals of Agrarian Science

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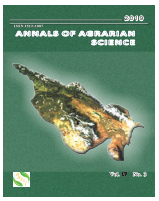

Studying residual pesticides in agricultural lands of the republic of armenia

A. Hovhannisyan, L. Sahakyan, O. Belyaeva, G. Tepanosyan, M. Beglaryan, D. Pipoyan, A. Saghatelyan

Center for Ecological-Noosphere Studies NAS RA 68, Abovian Str.,, Yerevan, 0025, Republic of Armenia

Received: 12 February 2019; accepted: 15 May 2019

A B S T R A C T

In Armenia like other former Soviet states synthetic and particularly organochlorine pesticides were first introduced in the mid XX century and remained in wide use for almost 20 years, up to the 1970s. After the USSR disintegration numerous pesticide storage facilities throughout Armenia were left unmanaged and presently semi-collapsed and abandoned repositories are found in almost all marzes (provinces) of the country. However, no complex, in-depth researches of residual pesticides were ever done in the country, isolated studies had a limited character. The given research is a long-term one and is aimed at detection of residual pesticides in Armenia's agricultural lands and assessment of residual pesticide contamination in system 'agricultural soil-irrigation water-fruits and vegetables'. To assure and control the quality of field and lab works the CENS staff have developed respective SOPs (standard operating procedures) and QA/QC (quality assurance and quality control) plans. Chromatographic analyses were done by a gas chromatograph-mass spectrometer (GC-MS) Trace DSQ (Thermo Electron Corporation, USA). This paper considers a part of initial research results obtained for Armenia's 5 out of 10 marzes (provinces) in 2014 and 2015. Data generated from this research have indicated that in all the five studied marzes agricultural soils and those of abandoned pesticide storage sites are contaminated with residual DDT which exceeds national MAC (maximum acceptable concentration) by several tens of times. None of banned residual pesticides were detected in irrigation water and fruit and vegetable samples. Presently, the research is underway.

Keywords: Organochlorine pesticides, DDT (sum), Agricultural land, Pesticide contamination, Pesticide storage facility, Banned pesticides.

*Corresponding author: Astghik Hovhannisyan; e-mail address: astghik.hovhannisyan@cens.am

Introduction

It is known that all organochlorine pesticides decay very slowly and hence remain in the environment for a long time. It is also known that due to good migration [1] and bioaccumulation properties pesticides travel into different environmental compartments vis. soils [2, 3], water [4, 5], vegetation [2, 3, 6] and penetrating into food chain ultimately affect human health [4, 3, 7]. In 2001 the Stockholm Convention [8] included those pesticides in the list of persistent organic pollutants to the environment, thus banning both their production and application in agriculture. In 2003 Armenia, too, joined the Convention.

The Republic of Armenia (latitude $38^{0}50' - 41^{0}18'$ N, longitude $43^{0}27' - 46^{0}37'$ E) is a landlocked highland country located in the South Caucasus. A major portion of its total area (29 743 sq.km) belongs to agricultural lands (68.8 %) [9, 10]. In Armenia like other former Soviet states synthetic emphasizing organochlorine and organophosphate pesticides were first introduced in the mid XX century and remained in wide use for almost 20 years, up to the 1970s [11]. Since the 1990s, after the USSR disintegration numerous pesticide storage facilities throughout Armenia have remained unmanaged and presently semi-collapsed and abandoned repositories are found in almost all marzes (provinces) of the country [12]. The fact that pesticide storage fas

cilities are potential sources of environmental pollution is demonstrated particularly by recent researches [13, 14]. It should be stressed that though the issue is topical to Armenia, nonetheless little pesticide research has been done in the country since the 1990s. Moreover, the studies had a limited character and did not include in-depth and complex monitoring investigations particularly in system "agricultural soils-irrigation water-fruits and vegetables". It should mentioned that GAP (Good Agricultural Practice), has not been introduced in Armenia so far and that no data are available regarding pesticide contamination of agricultural crops. This particular research was implemented in the frames of a "Monitoring of residual pesticides in food produced in the Republic of Armenia, 2014-2018" Program designed to fill in the mentioned gaps and covering all the 10 marzes of Armenia. The research goal was detecting residual pesticides in Armenia's agricultural lands and assessing pesticide contamination in system "agricultural soils-irrigation water-fruits and vegetables".

Material and methods

The research covered 13 settlements located in 5 out of 10 marzes.

Selection of plots of agricultural land was done based on the size and productivity. The studied materials were samples of agricultural soils, irrigation waters, fruits and vegetables.

The research included implementation of both field and lab works in compliance with SOPs and QA/QC plans developed by the CENS staff consistent with national and international standards, methods and directives (Tab. 1, 2). Sampling was done in 2014 and 2015. Specimens of fruits (peach, plum, apple, fig, persimmon, pomegranate, pear, apricot, quince) and vegetables (potato, pepper, cabbage, beetroot) were gathered in the harvesting period from relatively large plots of agricultural land-orchards and fields; samples of soil were taken from the same orchards and fields; water was sampled from local irrigation canals. One should stress that when sampling soil, special attention was given to former pesticide storage sites.

Table 1. *Standards, orders, guidance and directives used in SOPs and QA/QC plans*

Kind of samples	Standards	Order	Guidance	Directives
Agricultural soils	ISO 10381-1:2002 ISO 10381-2:2002 ISO 103081-4:2003	Order № 01–Ա of the Minister of Health RA as of January 25, 2010 "Hygienic requirements to soil quality" № 2.1.7.003–10: About approval of sanitary regulations and norms"	US EPA. Field sampling guidance document #1205. Soil sampling.	-
Irrigation water	ISO 5667-1:2006 ISO 5667-2:1991	-	-	US EPA OSWER Directive #93240.0-05
Fruits and vegetables	ISO 874:1980	-	CAC/GL 41-1993 CAC/GL 33-1999	Commission Directive 2002/63/EC

Wholly, over the studied period 152 fruit and vegetable, 146 soils, 22 water samples were collected. Additionally, 6 soil samples were taken from some of former pesticide storage sites found in four out of five studied marzes.

Lab analyses were carried out at the Central Analytical Laboratory CENS accredited by ISO IEC 17025. Prior to extraction all the samples underwent pre-treatment. Extraction of the fruit, vegetable, agricultural soil and irrigation water samples was done to indicate the presence of 17 forbidden pesticides [15]: aldrin, DDT (sum), dieldrin, 1,2-dichloroethane, endrin, captafol, heptachlor, HCH (sum), methyl parathion, methamidophos, mirex, parathion, pentachlorophenol (PCP), toxaphene, chlordane, chlordecone, phosphamidon. All the reagents and solvents we used were of analytical grade and included twenty (20) different pesticide standards ordered from AccuStandard (New Haven, USA). Working standard solutions were made by dilution of the stock standards and mixtures of standards of different concentrations and were used mostly for the screening of the pesticide residues and metabolites. The volumetric glassware was teflon stoppered. Chromatographic analyses were done by a gas chromatograph-mass spectrometer (GC-MS) Trace DSQ (Thermo Electron Corporation, USA) (Tab. 2).

After thorough analyses the obtained data were collated with national MACs for soil (0.1 mg/kg) [16] and then compiled into a respective database.

Results and discussion

None of 17 banned pesticides (aldrin, DDT (sum), dieldrin, 1,2-dichloroethane, endrin, captafol, heptachlor, HCH (sum), methyl parathion, methamidophos, mirex, parathion, pentachlorophenol (PCP), toxaphene, chlordane, chlordecone, phosphamidon) were detected in sampled irrigation waters, fruits and vegetables. In 13.6% of agricultural soil samples we detected residual DDT only, the contents of which widely varied 0.0028 to 7.32 mg/kg (Tab.3).

DDT was not found in agricultural soil samples collected from settlements of Azatan (Shirak marz), Deghdzavan (Tavush marz), Meghri, Karchevan, Agarak (Syunik marz). The largest share of contaminated samples (54.5%) belongs to Armaviri mars, where DDT concentrations exceeded MAC (0.1 mg/kg) by 1.5-73.2 times (Tab.3). It is noteworthy that DDT and its metabolites were found out mainly in soil sampled from orchards except one sample collected from potato field in village of Akhurian. In this respect one should note that according to Harris M. et.al [17], pesticides remain in orchard soils for a longer time as compared to field soils. The impact of physical factors on orchard soils (soil treatment, direct sun rays, extensive moisture loss, erosion) is limited, this contributing to bioaccumulation properties of persistent pesticides.

Table 2. *Standards and methods of analyses of agricultural soil, irrigation water, fruit and vegetable samples*

Kind of samples	Standards	Methods
Agricultural soils	AST ISO 10382-2005 ISO 11465:1993 ISO 14507:2003 US EPA 3546	microwave extraction (MWE), GC-MS
Irrigation water	AST ISO 6468-2005 US EPA 608 US EPA 625	Liquid-Liquid Extraction (LLE), GC-MS
Fruits and vegetables	AST EN 12393-2-2011 AST EN 12393-3-2011 GOST R 30349-1996 GOST R 30710-2001	GC-MS

Table 2. *Concentrations of DDT (sum) in agricultural soils of 5 studied marzes*

n/n	Marzes	Studied settlements	The total amount of samples per settlement	The amount of contaminated samples	Share of contaminated samples, %	DDT range, mg/kg
1	Ararat	Qaghtsrashen	36	3	8.33 %	0.0028 - 4.165
		Narek	10	2	20 %	0.013 - 0.778
		Jrashen	10	4	40 %	0.44 - 5.36
2	Armavir	Khanjian	13	6	46.15 %	0.15 - 7.32
3	Shirak	Akhurian	12	1	8.3 %	0.424
		Azatan	14	*n/d**	*n/d*	*n/d*
4	Tavush	Haghtanak	19	1	5.26 %	0.103
		Ptghavan	12	2	16.67 %	0.29 - 0.483
		Deghdzavan	9	*n/d*	*n/d*	*n/d*
5	Syunik	Syunik rural community	5	1	20 %	0.654
		Meghri	9	*n/d*	*n/d*	*n/d*
		Karchevan	2	*n/d*	*n/d*	*n/d*
		Agarak	1	*n/d*	*n/d*	*n/d*
TOTAL		13	152	20	13.6 %	*n/d* - 7.32

*Note: *- not detected*

DDT was detected only in three soil samples collected from pesticide storage facilities found in the four out of five studied marzes. Its concentrations varied rather widely: between 0.09 and 46.49 mg/kg. The highest concentration 46.49 mg/kg which exceeded national MAC by 469.9 times, was established in one soil sample taken from an abandoned pesticide storage facility in Ararati marz (Jrashen village). The lowest contents of DDT (sum) 0.09 mg/kg which did not overstep national MAC was detected in one of two former pesticide storage sites in Armavir marz (Khanjian village). DDT detected in one soil sample from Ptghavan village (Tavush marz) exceeded national MAC by 10.1 times. No residual DDT was detected in soil samples collected from Akhurian and Deghdzavan villages located respectively in Shirak and Tavush marzes and one out of two former pesticide storage sites in Khanjian village (Armavir marz) (Fig.).

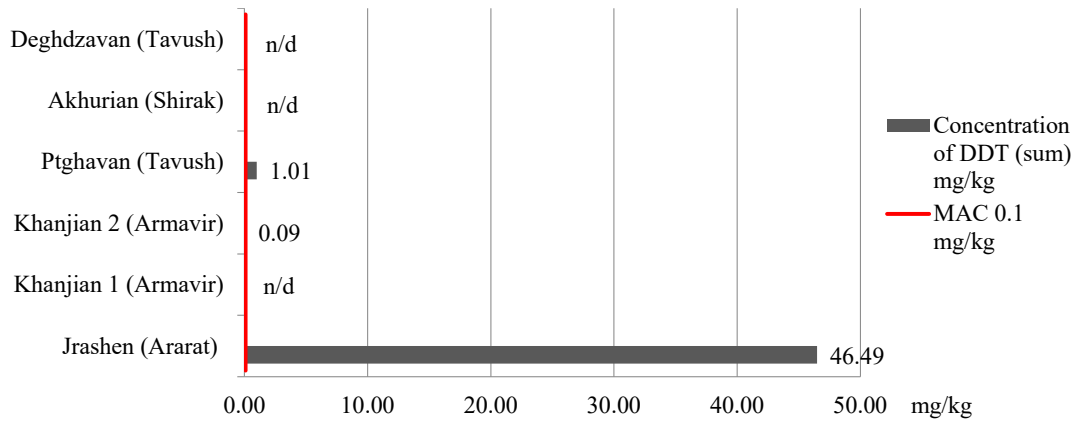

Fig. *Concentrations of DDT (sum) in soil samples collected from 6 former pesticide storage facilities*

Conclusion

The research results for 2014-2015 support a conclusion that irrigation water and fruit and vegetable samples collected from five studied marzes selected for this research are not contaminated with banned residual pesticides. Agricultural soil samples are contaminated with residual DDT only. In some soil samples DDT concentrations exceed national MAC by several times. Residual DDT which exceeds national MAC by several tens of times is detected in three marzes: Ararati, Armaviri, Tavushi. Presently the research is underway.

Acknowledgment

The research results considered in this paper were obtained in the frames of a target Program "Monitoring of residual pesticides in food produced in the Republic of Armenia, 2014-2018" funded by the State Committee for Science to the Ministry of Education and Science RA.

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