



## Chlorinated Pesticides Residues in Environmental Compartments; Soil and Water contamination

Middle East Technical University, Department of Chemistry 06531, Ankara, TURKEY

KM SIFATULLAH & Semra G. TUNCEL

6. Ulusal Hava Kirliliği ve Kontrolü Sempozyumu-2015 7-9 Ekim 2015, İZMİR

## OUTLINE

Pesticides

Aim Of Study

Rules and regulations

The Green Technologies are Assessed for Future Agricultural Systems

Sampling and Analysis

**Results and Discussion** 

Conclusion

#### Pesticide

**Pesticide** is substance or mixture of chemical substances used for preventing, destroying or controlling pest, including human or animal disease.

Pesticides are classified as

#### 1-Organochlorine

2- organophosphate



The most important pesticides are herbicides, insecticides and fungicides.

## Aim of the study

- The aim of this study is to determine 17 organochlorinated pesticides in soil and water samples.
- To determine the distribution of organochlorine pesticides in water-soil.
- Produced data was used to determine pesticide pollution level.
- In addition, environmental risks of pesticides are evaluated.

## **Pillars of Environmental**

- Control of water and environmental contamination
- Protection of biodiversity
- Protection of endangered species
- Recycling
- Organic produce



## **Rules and regulations**

- Regulation (EC) No 396/2005 ; plant protection
- Directive 91/414/EEC ;plant protection
- Regulation (EC) No 1107/2009 ;plant protection
- Directive 2009/128/EC; sustainable use of pesticides
- Regulation 1185/2009/EC ; statistics on pesticide.
- Directive 2009/127/EC ; new equipment for pesticides spray.

Law No 5996 on veterinary services, plant health, food and feed, in force from 11 December 2010

Maximum Residue Levels (MRLs) are regulated in the Turkish Food Codex Maximum Residue Limits Regulation of 29 December 2011.

The MRLs for formetanate and malathion were aligned with the EU MRLs.

Law No 5957 of 26 October 2010, in force from 1 January 2012,

regulating the trade of, among others, fruits and vegetables allows exporters to purchase, after notifying, from producers.

- There are 20 official and 31 private laboratories authorised by MFAL for pesticide residue analysis in Turkey.
- Seven(7) of the official laboratories are not accredited to ISO 17025.
- From the authorised private laboratories for pesticides residues, eight(8) are not accredited under ISO 17025.
- Twelve(12) official laboratories are permitted to analyse pepper samples for EU export.

#### THE GREEN TECHNOLOGIES ARE ASSESSED FOR FUTURE AGRICULTURAL SYSTEMS



#### Water Consumption for Production



# Figure shows liters of water needed to produce one kilogram of product (or one liter for milk)

Source: World Development Report (2010), Development and Climate Change, p.149

#### SAMPLING AND EXTRACTION

In Ayaş 2 fields were choosen one with 500m<sup>2</sup> and another 1000m<sup>2</sup>.

Grid Method is used.

Samples were collected by dividing into equal squares and the samples are taken from the centers of each square.

## N 40,031230 32,26465 210 32,25289 40,03120 32,2589 .029300 32 Image @ 2014 DigitalGlobe © 2013 Basarsoff 40°01'41.29"K 32°15'32.23"D yükseklik 708 m göz hizasi 1.90 km 20103rüntü Tarihi: 6/5/2010

8 soil samples were collected from each field (Field 1 and Field 2) (n=16) 2 water samples (entrance and exit water) were collected for each field (n=4)

#### SAMPLING AREA



soil samples :ultrasonic bath extraction



#### Water samples:solid phase extraction system.



All samples were analyzed by using GC-MS system.

#### Extraction Recovery

% Extraction Recovery =(Cexp/Cthe)x100.

Cexp: Measured concentration of Surrogate Standard

Cthe: added concentration of Surrogate standard

Soil and Water was found as %47 and %58

Surrogate Standard:

SS1:2,4,5,6-Tetrachloro-m-xylene

SS2: Decachlorobiphenyl

#### Quality control/ quality assurance (QC/QA)

Accuracy: SRM 2261,2273 and 2275 were used for accuracy check. According to accuracy studies, % error values are changing between % 5.90-55.6.

Linearity: Calibration curves has also good linearity (r=0,99).

LOD is determined by using the response values where S/N=3. LOD values are 0.680-23,7  $\mu$ g/L for water, 0,370-25,7  $\mu$ g/kg for soil.

LOQ values are the three times LOD or S/N=10 of these values. Values under LOQ were identified as BLOQ.

#### Average pesticide concentrations

	Soil (µg/kg)	Water (µg/L)	
alpha-HCH	55.19	BLOQ	
beta-HCH	3,799	BLOQ	
gamma-HCH	$41.19 \pm 29.59$	BLOQ	
delta-HCH	BLOQ	BLOQ	
Heptachlor	$10.73 \pm 5.314$	BLOQ	
Aldrin	BLOQ	0.2539±0.01816	
Endosulfan I	BLOQ	$2.882 \pm 2.424$	
Heptachlorepoxide	$10.35 \pm 5.915$	BLOQ	
Endosulfan II	BLOQ	$1.826 \pm 0.7769$	
p.p'-DDE	$14.99 \pm \textbf{7.494}$	BLOQ	
Endrin	0.8152	BLOQ	
p.p'-DDD	BLOQ	0.1877±0.08120	
Endrin aldehyde	$219.1 \pm 116.9$	$8.005 \pm 3.808$	
p.p'-DDT	$12.70 \pm 26.64$	0.8792±0.1786	
Methoxychlor	BLOQ	BLOQ	





Pesticide concentrations in water (µg/kg)

17



Literature Comparison-SOil



Literature Comparison-water

## **Maximum Residue level (MRL) Values**

		MRL
	Water (µg/L)	(µg/L)*
alpha-HCH	BLOQ	
beta-HCH	BLOQ	
gamma-HCH	BLOQ	
delta-HCH	BLOQ	
Heptachlor	BLOQ	
Aldrin	0.2539±0.01816	
Endosulfan I	$2.882 \pm 2.424$	
Heptachlorepoxide	BLOQ	
Endosulfan II	$1.826 \pm 0.7769$	
p.p'-DDE	BLOQ	
Endrin	BLOQ	
p.p'-DDD	0.1877±0.08120	
Endrin aldehyde	$8.005 \pm 3.808$	
p.p'-DDT	0.8792±0.1786	
Methoxychlor	BLOQ	
Total Pesticide	14.04	0.5

		MRL (EU)
	Tomato (µg/kg)	
alpha-HCH	23.03±26.73	
beta-HCH	BLOQ	
gamma-HCH	BLOQ	0.00001
delta-HCH	BLOQ	
Heptachlor	BLOQ	0.00001
Aldrin	BLOQ	0.00001
Endosulfan	BLOQ	0.00005
Heptachlorepoxide	BLOQ	
Endrin	BLOQ	0.00001
Endrinaldehyde	8.302	
DDT	BLOQ	0.00005
Methoxychlor	BLOQ	0.00001

#### Soil to Water transition

#### Soil to Tomato transition



The investigation of pesticide transition from soil to water reveals that the highest % transfer ratio for pp-DDT (%69) and lowest ratio is for Endrine aldehyde (%37).



For soil to tomato transfer the values are % 42 (alpha-HCH) and %38(Endrine aldehyde).

#### Mexico, Morocco and Turkey Trading partner map



#### Top ten exporters of tomatoes in 2010



Country	Trade value (\$)	Trade quantity (kg)	per kg
Mexico	1,595,315,056	1,509,615,649	\$1.06
Morocco	571,284,039	784,964,560	\$0.73
Turkey	476,873,744	574,278,907	\$0.83
USA	373,626,415	224,278,636	\$1.67
Canada	356,415,730	166,869,630	\$2.14
France	355,117,720	189,462,000	\$1.87
Italy	287,182,488	128,797,318	\$2.23
Belgium	281,623,333	191,100,924	\$1.47
Jordan	232,376,618	371,257,022	\$0.63
Israel	73,635,000	66,567,807	\$1.11

#### Conclusion

Organochlorinated pesticides are banned in Turkey and around the world. Howverver, they can be still observed in environment.

Extraction Recovery: Water: 58, Soil: 47

Pesticide Concentration Range in Soil: 3.799-219.1

Pesticide Concentration Range in Water: 0.1877-8.005

The order of pesticide contamination is generally like soil>water.

Farmers should be informed about the over use of pesticides and health safety.

There should be an education about the proper use of pesticides at proper time during the plantation period.

In addition more efficient policies about pesticide use should be developed.

Thank you for your attention...