Persistent Organic Pollutants in Lebanon Conference
Research Vice rectorate – USJ

Saint Joseph University 9 May 2019

An overview of chemical pollutants contamination in Lebanon: Challenges and case study for water and food

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Lebanese University – Faculty of Public Health

Background

- National Council for Scientific Research (CNRS)
  - Lebanese Atomic Energy Commission (CLEA)
    - ➢ Laboratory for Analysis of Organic Compounds (LACO)

❖ Monitoring program since 2006:

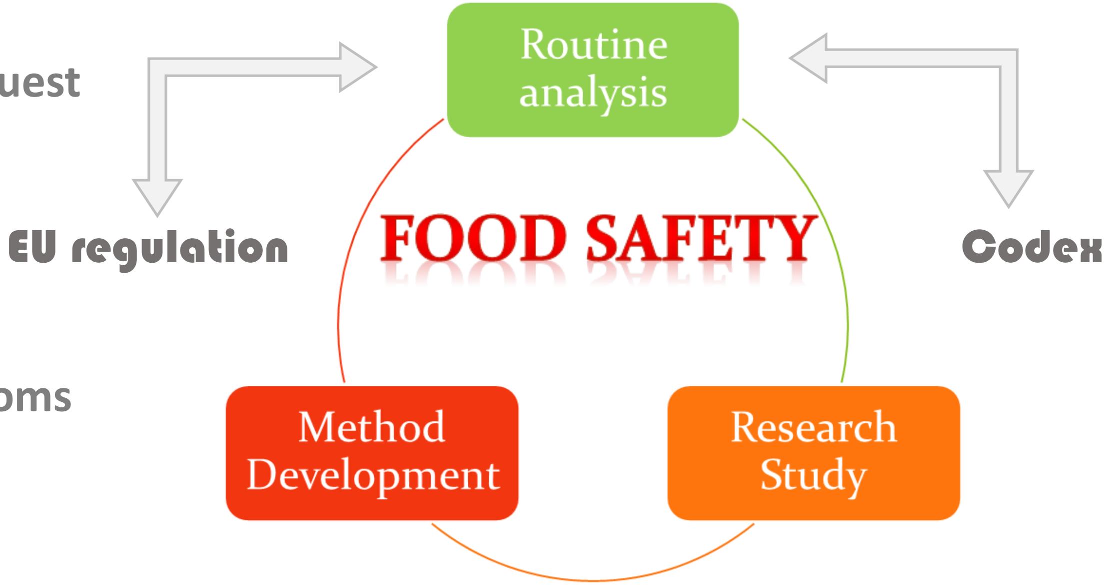
Pesticides and veterinary drugs in Food

- Ministry of environment (200 samples)
- Ministry of agriculture (300 samples)
- Ministry of Economy (900 samples)

- Develop analytical techniques based ministries request

- Provide technical advises for many labs

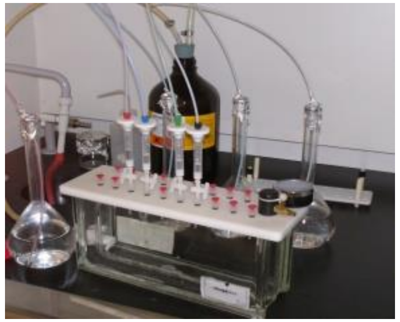
- Analysis of Unknown compound for Lebanese customs



Background Collaborations/Partners

➢ Laboratory for Analysis of Organic Compounds (LACO)

- **Analysis of more than 100 pesticides residue in fruit/vegetables and water using GCMS and LCMSMS**
- **Analysis of 16 PAHs in grilled meat water, soil and sediment**



- **Analysis of aliphatic hydrocarbons in water**
- **Analysis of PCBs in water and sediment**

- **Development of a multiclass method for the determination of veterinary drugs and Hormones residues in water and in food producing animals (Milk, Beef, Chicken, Honey) using LCMSMS**

  (EU Directive 96/23/EC)

  (EU Directive 2002/657/EC)

- **Transformation of Pesticides and Antimicrobials by chlorine and UV Lights in water: Kinetics and by-products identification.**

Collaborations/Partners

Oniris
École Nationale Vétérinaire, Agroalimentaire et de l'Alimentation Nantes Atlantique

IAEA
International Atomic Energy Agency
Atoms For Peace

The University of California 1868
Let There Be Light

UCB Lyon 1

anses
French agency for food, environmental and occupational health safety

Université Bordeaux 1
Sciences Technologies

ulp
Université Louis Pasteur Strasbourg

Université Paris-Sud 11

LPTC

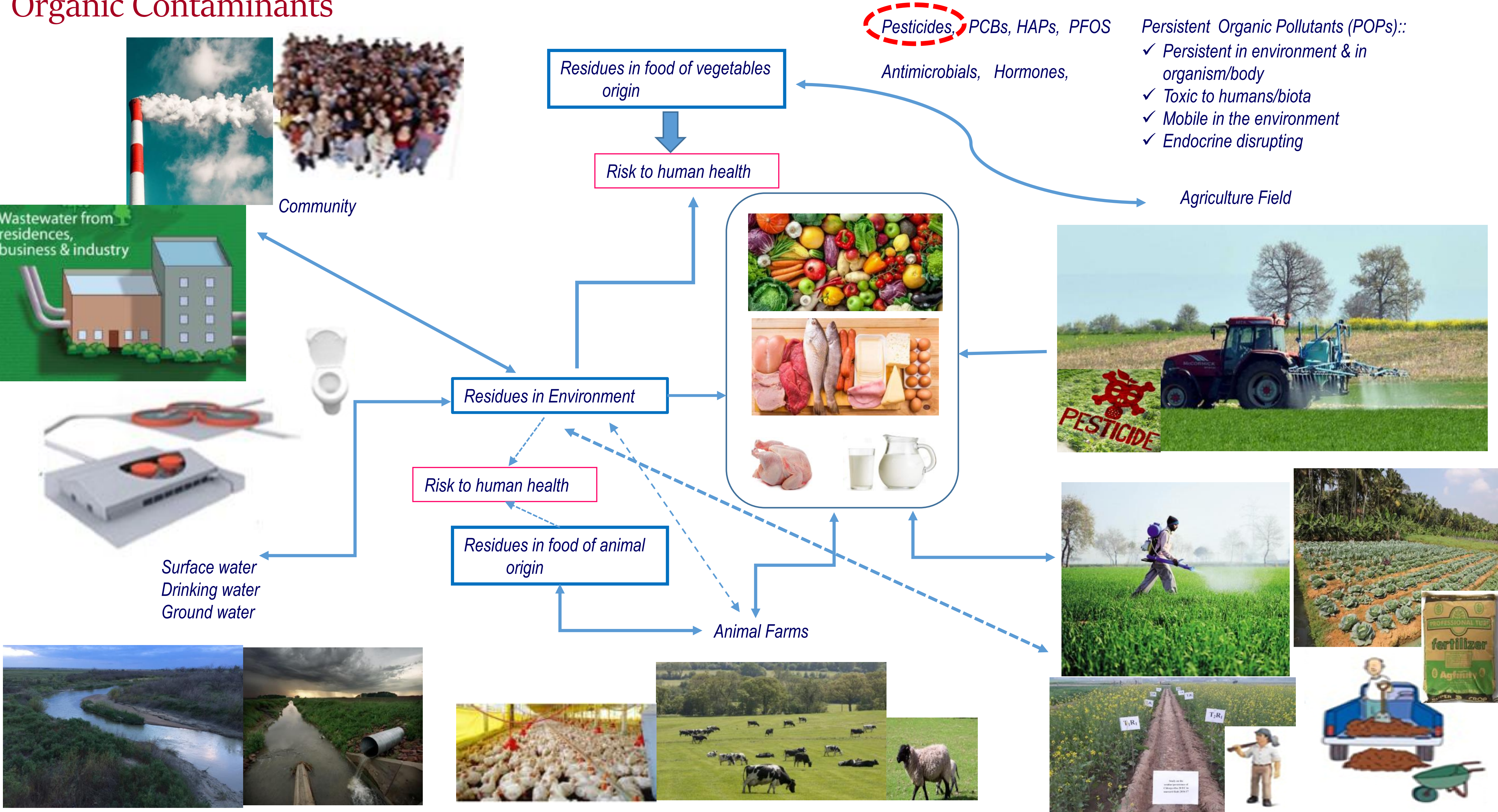
Università degli Studi di Teramo

American University of Beirut 1866

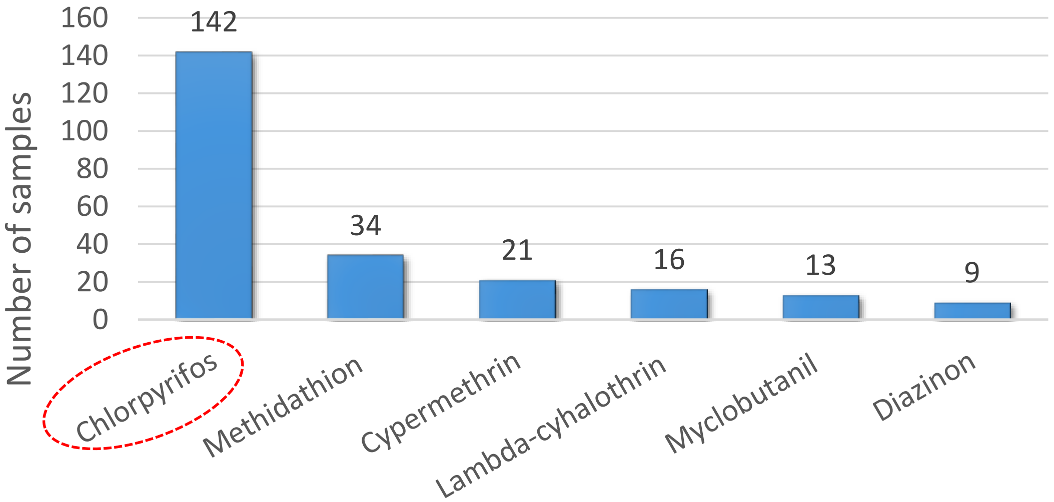
Clermont Université

Ud'A
Università degli Studi "G. d'Annunzio" Chieti - Pescara

Organic Contaminants



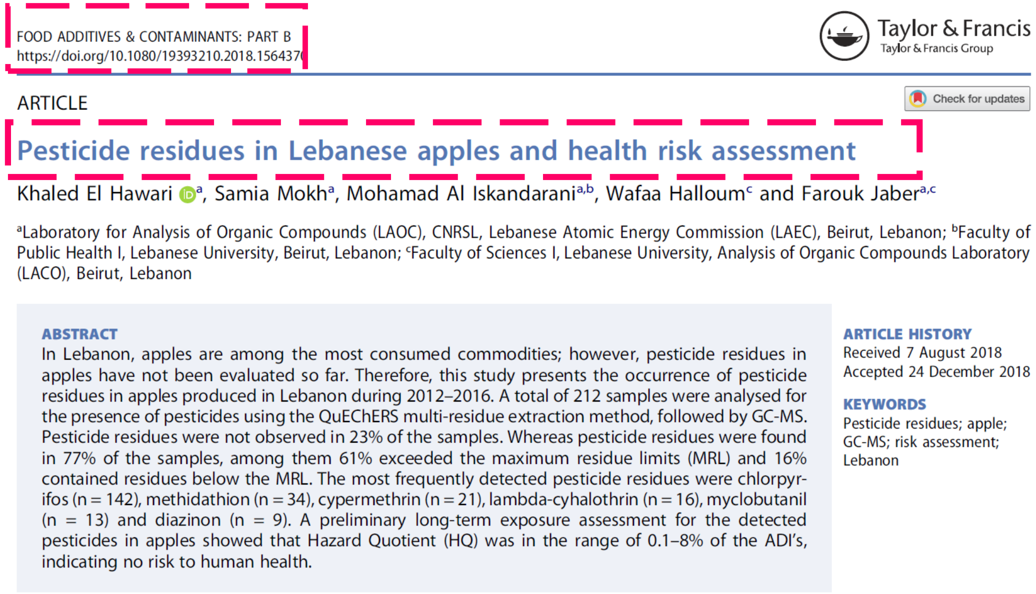
Pesticides in Apples



- *212 apple samples locally collected from producers*
- *Collection was carried out between 2012-2016*
- *QuEChERS EN 15622 method for sample preparation was adopted*
- *GC-MS multi residue quantitative method for detection & quantification of 40 pesticides*

* *EFSA in 2015 recommended to lower the existing MRLs for chlorpyrifos in apple and other commodities based on the new toxicological data and health risk assessment*

Ref: EFSA Journal 2015;13(6):4142, 41 pp. doi:10.2903/j.efsa.2015.4142.



FOOD ADDITIVES & CONTAMINANTS: PART B
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ARTICLE

Check for updates

Pesticide residues in Lebanese apples and health risk assessment

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ABSTRACT

In Lebanon, apples are among the most consumed commodities; however, pesticide residues in apples have not been evaluated so far. Therefore, this study presents the occurrence of pesticide residues in apples produced in Lebanon during 2012–2016. A total of 212 samples were analysed for the presence of pesticides using the QuEChERS multi-residue extraction method, followed by GC-MS. Pesticide residues were not observed in 23% of the samples. Whereas pesticide residues were found in 77% of the samples, among them 61% exceeded the maximum residue limits (MRL) and 16% contained residues below the MRL. The most frequently detected pesticide residues were chlorpyrifos (n = 142), methidathion (n = 34), cypermethrin (n = 21), lambda-cyhalothrin (n = 16), myclobutanil (n = 13) and diazinon (n = 9). A preliminary long-term exposure assessment for the detected pesticides in apples showed that Hazard Quotient (HQ) was in the range of 0.1–8% of the ADI's, indicating no risk to human health.

ARTICLE HISTORY
Received 7 August 2018
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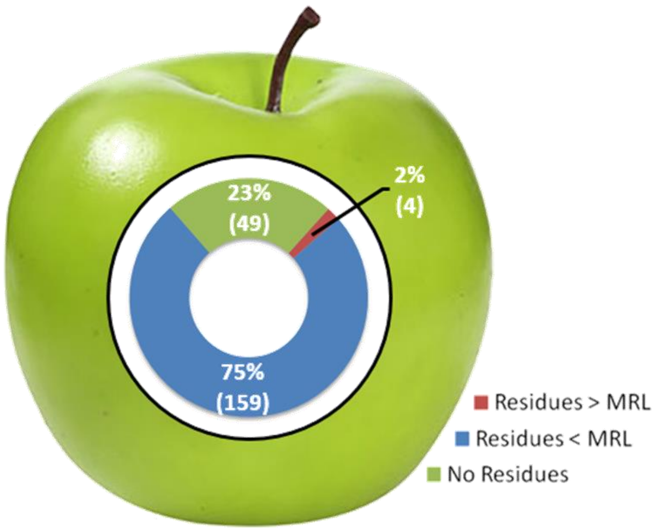
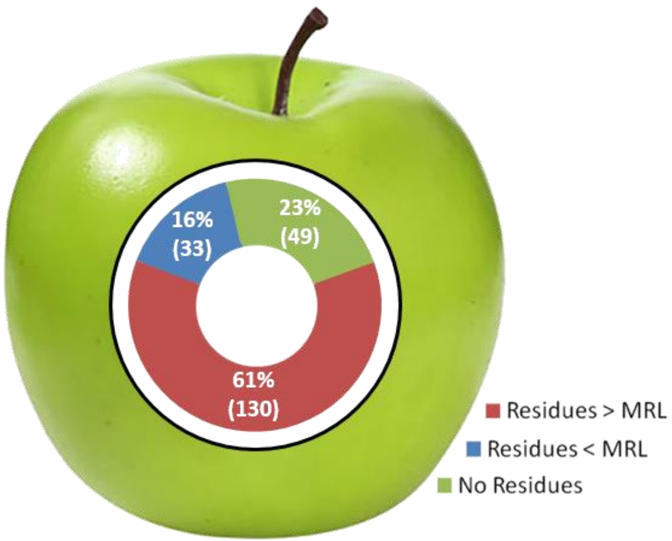
KEYWORDS
Pesticide residues; apple; GC-MS; risk assessment; Lebanon

- ***CODEX-MRLs***



- ***EU-MRLs***

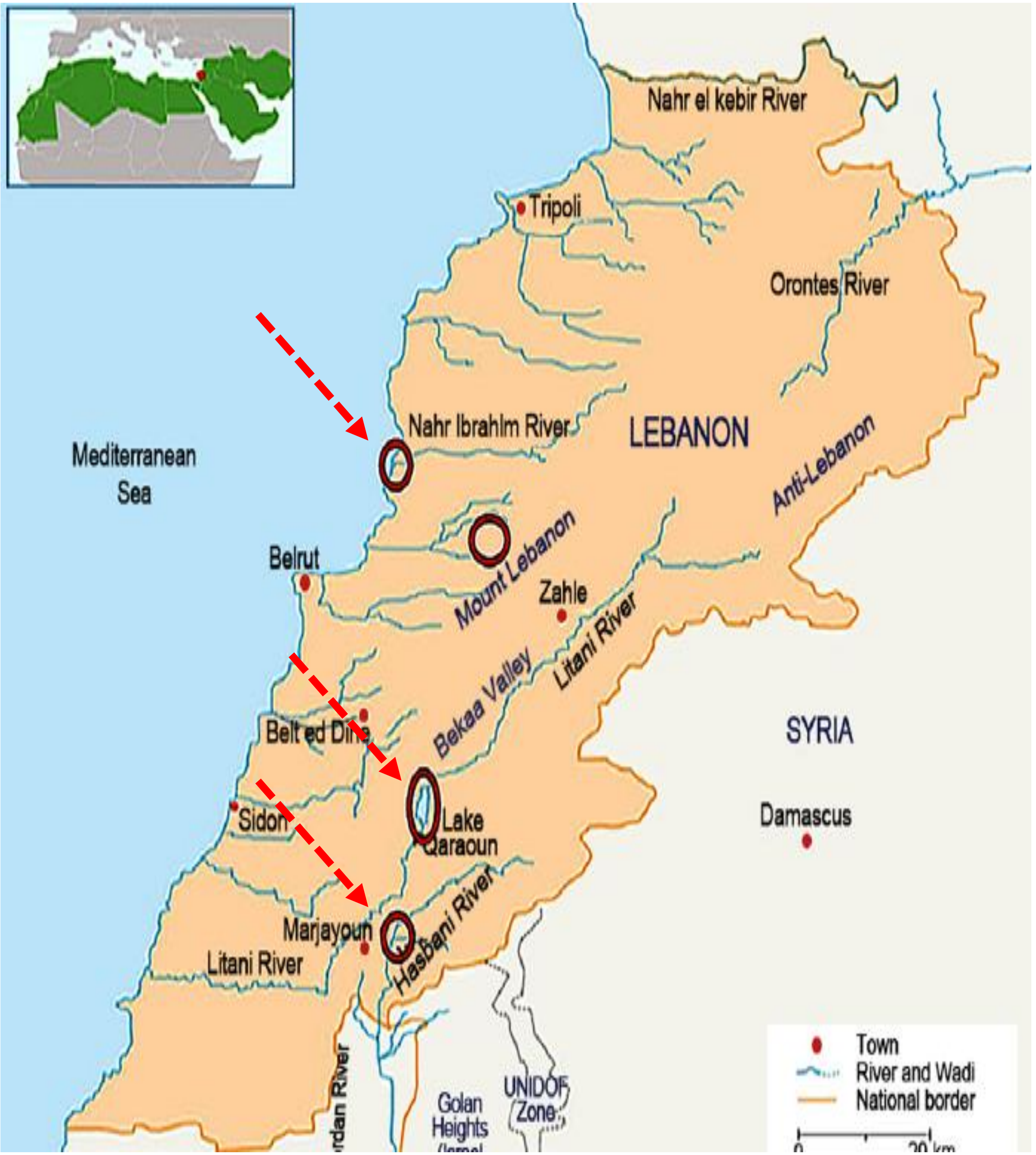


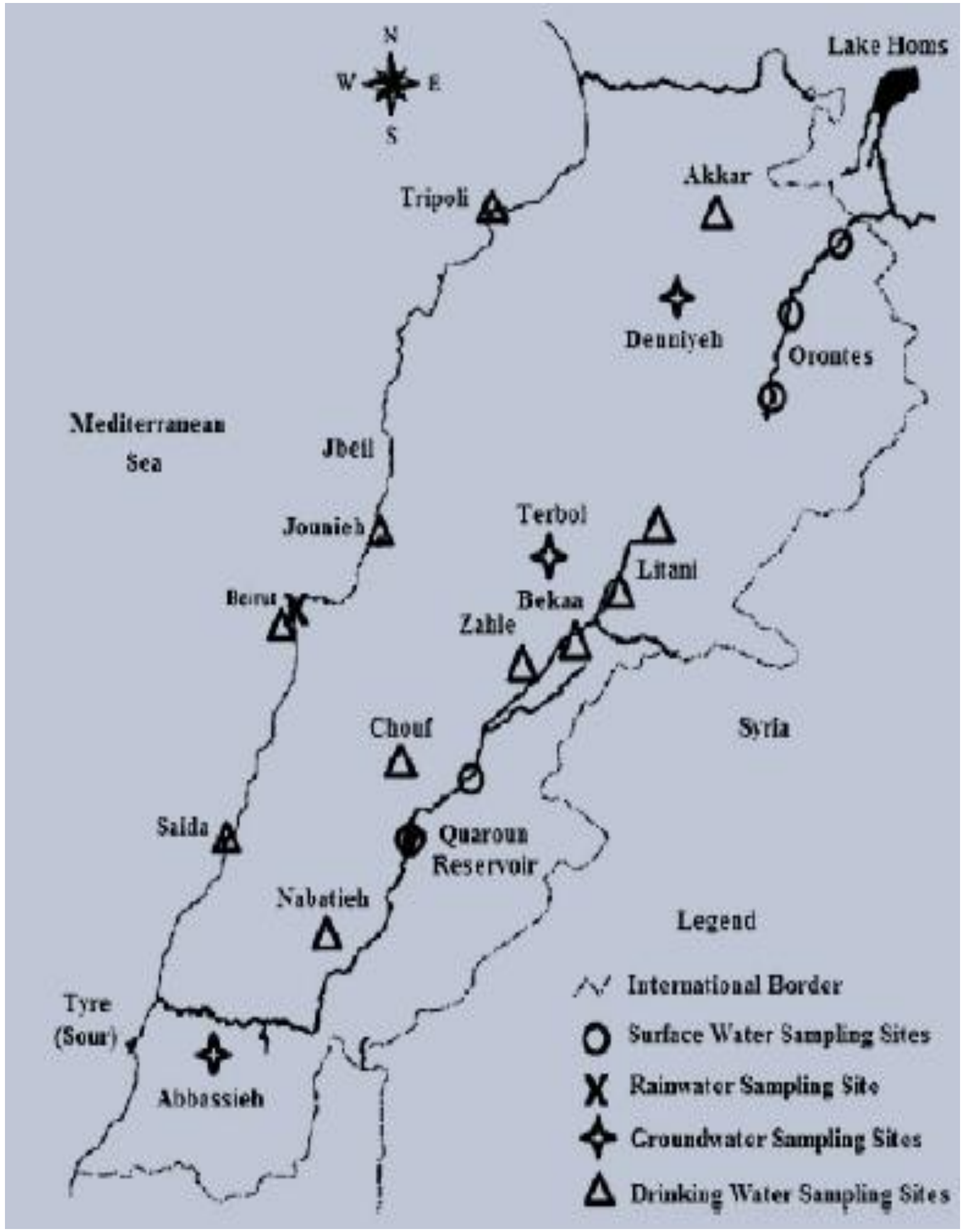
Pesticides in Water (Surface Water, Ground Water, Drinking Water and Rain Water)

	Class	Chemical class	CAS RN	Log kow		Class	Chemical class	CAS RN	Log kow
Alachlor	Herbicide	Chloroacetamid	15972-60-8	3.09	Malathion	Insecticide	OP	121-75-5	2.75
Atrazine	Herbicide	Triazine	1912-24-9	2.7	Mecarbam	Insecticide	OP	2595-54-2	2.29
Azoxystrobin	Fungicide	Strobilurine	131860-33-8	2.5	Mepanipyrim	Fungicide	Pyrimidine	110235-47-7	3.28
Boscalid	Fungicide	Carboxamide	188425-85-6	2.96	Metalaxyl	Fungicide	Phenylamide	57837-19-1	1.65
Bromopropylate	Acaricide	Benzilate	18181-80-1	5.4	Methamidophos	Insecticide	OP	10265-92-6	-0.79
Carbaryl	Insecticide	Carbamate	63-25-2	2.36	Methomyl	Insecticide	Carbamate	16752-77-5	0.09
Carbendazim	Fungicide	Carbamate	10605-21-7	1.48	Methoxychlore	Insecticide	OC	72-43-5	5.83
Carbofuran	Insecticide	Carbamate	1563-66-2	1.8	Parathion	Insecticide	OP	56-38-2	3.83
Chlorfenvinfos	Insecticide	OP	470-90-6	3.8	Penconazole	Fungicide	Triazole	66246-88-6	3.72
Chlorpyrifos	Insecticide	OP	2921-88-2	4.7	Phenthoate	Insecticide	OP	3/7/2597	3.69
Clodinafop-propagyl	Herbicide	APP	105512-06-9	[illegible]	Phosmet	Insecticide	OP	732-11-6	2.96
DDE-pp*	Insecticide	OC	50-29-3	6.9	Pirimicarb	Insecticide	Carbamate	23103-98-2	1.7
Diazinon	Insecticide	OP	333-41-5	3.69	Procymidone	Fungicide	Dicarboximide	32809-16-8	3.3
Dimethoate	Insecticide	OP	60-51-5	0.704	Propyzamide	Fungicide	Benzamide	189278-12-4	5.5
Dimethomorph	Fungicide	Morpholine	110488-70-5	2.68	Pyridaben	Insecticide	Pyridazinone	96489-71-3	6.37
Endosulfanβ	Insecticide	OC	115-29-7	4.75	Quinalphos	Insecticide	OP	13593-03-8	4.44
Ethoprofos	Insecticide	OP	13194-48-4	2.99	Simazine	Herbicide	Triazine	122-34-9	2.3
Fenpropathrin	Insecticide	Pyrethroides	39515-41-8	6.04	Tebuconazole	Fungicide	Triazole	107534-96-3	3.7
Flusilazole	Fungicide	Triazole	85509-19-9	3.87	Thiamethoxam	Insecticide	Neocotinoid	153719-23-4	-0.13
Heptachlor	Insecticide	OC	76-44-8	5.44	Triadimenol	Fungicide	Triazole	55219-65-3	3.18
HCB*	Fungicide	OC	118-74-1	3.93	Triazophos	Insecticide	OP	24017-47-8	3.55
Hexaconazole	Fungicide	Triazole	79983-71-4	3.9	Trifluralin	Herbicide	Dinitroaniline	1582-09-8	5.27
Imidachlopride	Insecticide	Neocotinoid	138261-41-3	0.57					

OP: Organophosphorous; OC: Organochlorine; APP: Aryloxyphenoxypropionate; DDE-pp: Dichlorodiphenylethane (metabolite of DDT); HCB: Hexachlorobenzene

Pesticides in Water (Surface Water, Ground Water, Drinking Water and Rain Water)





Pesticides in Water (Surface Water, Ground Water, Drinking Water and Rain Water)

- ***PASSIF SAMPLING (POCIS)***

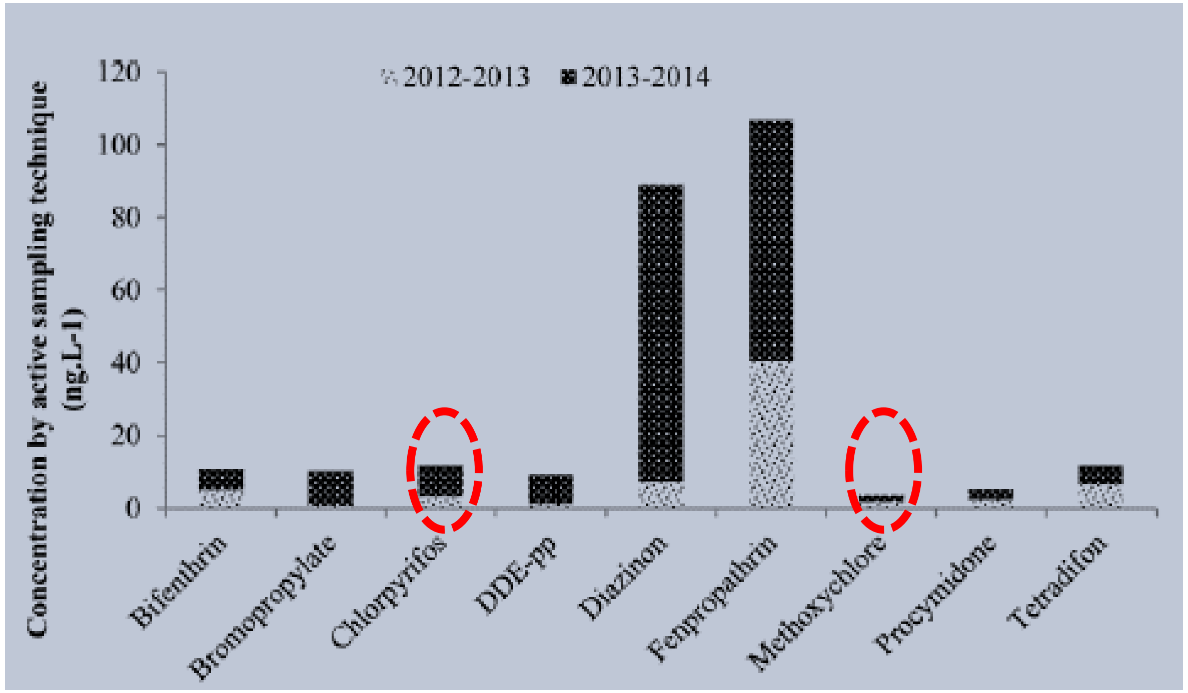
The POCIS was built using Oasis® HLB bulk sorbent (average particle diameter: 60 µm) and polyethersulfone (PES) SUPOR 100 membranes (0.1 µm, 90 mm diameter)

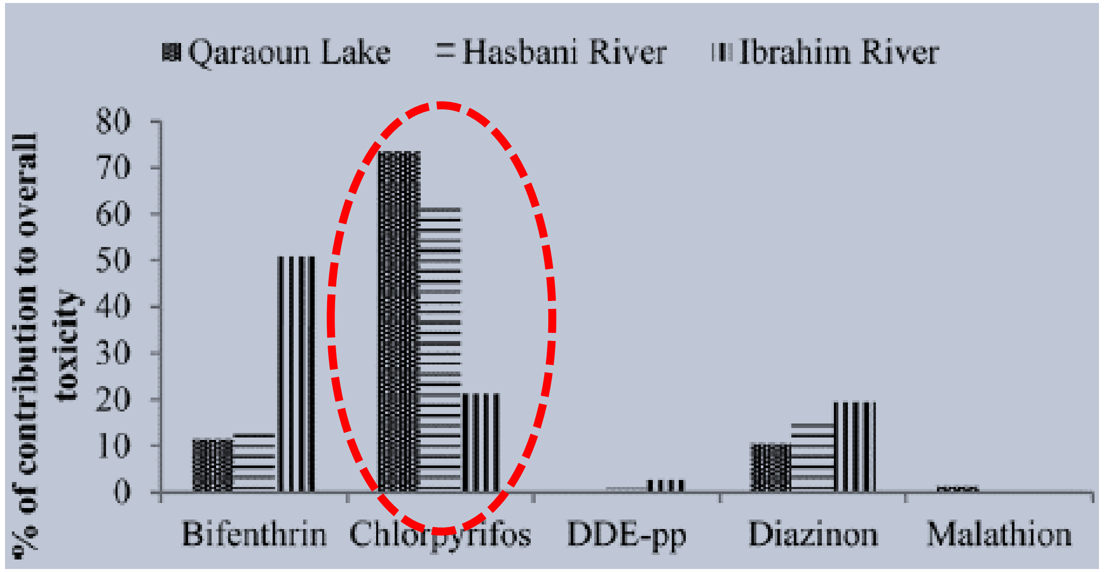
PRC: DIA-d5

POCIS + PRC

- ***SPOT SAMPLING***

Pesticides in Water (Surface Water, Ground Water, Drinking Water and Rain Water)





The potential ecotoxicological impact of the measured pesticides on aquatic organisms in surface waters was assessed by applying a recently developed index: the Short term Pesticide Risk Index for the Surface Water System (PRISW-1) proposed by Finizio et al. (2001).

	LOD (ng·L^{-1})	LOQ (ng·L^{-1})	Ibrahim River TWA concentrations (ng·L^{-1}) (n = 72)		Qaraoun Lake TWA concentrations (ng·L^{-1}) (n = 36)		Hasbani River TWA concentrations (ng·L^{-1}) (n = 36)		R,
			Average	Range	Average	Range	Average	Range	
Alachlor	0.05	0.7					0.75	nd–4.47	
Atrazine	0.03	0.28		<LOQ	0.96	0.28–1.62	0.80	0.47–1.12	
Azoxystrobin	0.14	1		<LOQ		<LOQ		<LOQ	
Carbaryl	0.23	1.22	1.69	0.17–13.26	2.61	nd–12.73	1.29	nd–2.50	
Carbendazim	0.12	0.24	2.58	0.26–13.63	8.72	1.81–21.23	4.73	0.93–23.07	
Carbofurane	0.46	1	1.13	nd–1.58		<LOQ		<LOQ	
Chlorfenvinfos	0.04	0.23		<LOQ					
Chlorpyrifos	0.02	2	3.55	nd–24.64	27.90	2.08–124.69	19.02	nd–20.34	
DDE-pp	0.29	0.5	23.16	nd–137.66	1.73	nd–8.63	15.43	nd–31.79	
Diazinon	0.11	1	34.89	nd–97.13	42.71	1.38–110.83	50.73	1.36–50.73	
Dimethoate	0.04	0.05	2.72	nd–14.32	2.18	0.16–4.54	9.65	0.3–54.46	
Dimethomorph	0.3	1.58		<LOQ					
Ethoprofos	0.04	0.19					1.92	nd–11.36	
Hexaconazole	0.17	1.28			0.39	nd–0.94	0.42	nd–2	
Imidacloprid	0.19	1.12	1.65	nd–5.95	1.69	nd–2.19	6.59	nd–32	
Malathion	0.21	0.39			3.94	nd–19.69			
Metalaxyl	0.1	0.82	0.91	nd–2.37	2.51	0.81–6.11		<LOQ	
Methomyl	0.11	1.11		<LOQ	1.05	nd–4.95	3.56	nd–20.34	
Penconazole	0.01	0.17		<LOQ	0.24	nd–0.42	1.62	nd–8.38	
Phosmet	0.24	1.32			2.31	nd–11.57	4.47	nd–26.84	
Pirimicarb	0.02	0.03	0.50	nd–3.27	0.17	0.05–0.51	0.07	nd–0.15	
Propyzamide	0.07	0.16			22.23	6.15–51.37			
Simazine	0.01	0.32		<LOQ	1.65	nd–7.11			
Tebuconazole	0.27	1.14				<LOQ	1.17	nd–7	
Thiamethoxam	0.28	1.05	0.42	nd–1.38		<LOQ			
Triadimenol	0.18	2.11			4.62	nd–9.44			

Pesticides in Water (Surface Water, Ground Water, Drinking Water and Rain Water)

Pesticide	LOQ ($ng.L^{-1}$)	Drinking water		Ground water ($ng.L^{-1}$)		Surface water ($ng.L^{-1}$) (Litani River and Quaroun Lake)		Surface water (Orontes River)		Rain water ($ng.L^{-1}$)	
		Av	Range	Av	Range	Av	Range	Av	Range	Av	Range
Alachlor (H)	0.7					1.8	nd–5.8				
Aldrin (I)	0.1	0.6	nd–1.1	0.4	nd–0.7						
Bifenthrin (I)	0.1	0.1	nd–0.9			5.2	nd–33.7		< LOQ		
Bromophos-ethyl	0.1	0.3	nd–1.4								
Bromopropylate	0.1					0.6	nd–1.5		< LOQ	0.4	nd–3.3
Cadusafos (I, N)	0.1	0.6	nd–3.6	0.5	nd–1.5						
Chlorpropham (H)	1.0					12.4	nd–34.6				
Chlorpyrifos (I)	2.0					3.2	nd–7.1			4.0	nd–13.8
Cyprodinil (F)	0.1									0.2	nd–1.7
DDD (I)	0.5	0.8	nd–1.2	1.6	0.9–2.2	1	nd–3.4				
DDE (I)	0.5	1.2	nd–3.3	1.1	0.7–1.3	1.1	nd–2.7		< LOQ		
Diazinon (I,A)	1.0	4.2	nd–15.3	2.2	1.7–2.4	7.49	2.8–9.7	4.1	1.2–8.9	15.8	1.8-61.8
Dichlorovos (A)	1									1.9	nd–19.6
Dieldrin (I)	0.5	0.7	nd–1.3	0.6	nd–1.5						
Endosulfan sulfate	0.5					5.3	nd–9.2				
Fenpropathrin (I)	0.5					40.6	nd–220.1		< LOQ	0.65	nd–6.1
Hexachlorobenzene	0.1	1.7	nd–4.5	1.5	1.2–1.6				< LOQ	0.5	nd–2.5
Kresoxim-methyl	0.5	1.7	nd–12.3								
Lindane (I)	0.5					7.8	nd–9.5				
Metalaxyl (F)	1.0			4.8	nd–14.5						
Methoxychlor (I)	0.8					1.8	nd–4.7		< LOQ	3.4	nd–6.4
Pendimethalin (H)	1.0					7.3	nd–9.7				
Procymidone (F)	0.5	1.6	nd–5.7			2.5	nd–6.0		< LOQ	0.7	nd–2.9
Pyrimethanil (F)	0.1									0.5	nd–4.5
Quintozene (F)	0.1	0.5	nd–1.5								
Tecnazene (F)	0.1	0.5	nd–1.7	0.4	0.3–0.7						
Tetradifon (A)	0.1	1.3	nd–4.4	0.2	nd–0.5	6.6	nd–8.6		< LOQ	0.8	nd–8.3
Trifluralin (H)	0.1	0.3	nd–1.5	0.3	0.2–0.4						

A acaricide, F fungicide, H herbicide, I insecticides, N nematicide, nd not detected, < LOQ detected but not quantified

Bull Environ Contam Toxicol
DOI 10.1007/s00128-013-1071-y

Occurrence of Pesticide Residues in Lebanon's Water Resources

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Monitoring of 45 Pesticides in Lebanese Surface Water using Polar Organic Chemical Integrative Sampler (POCIS)

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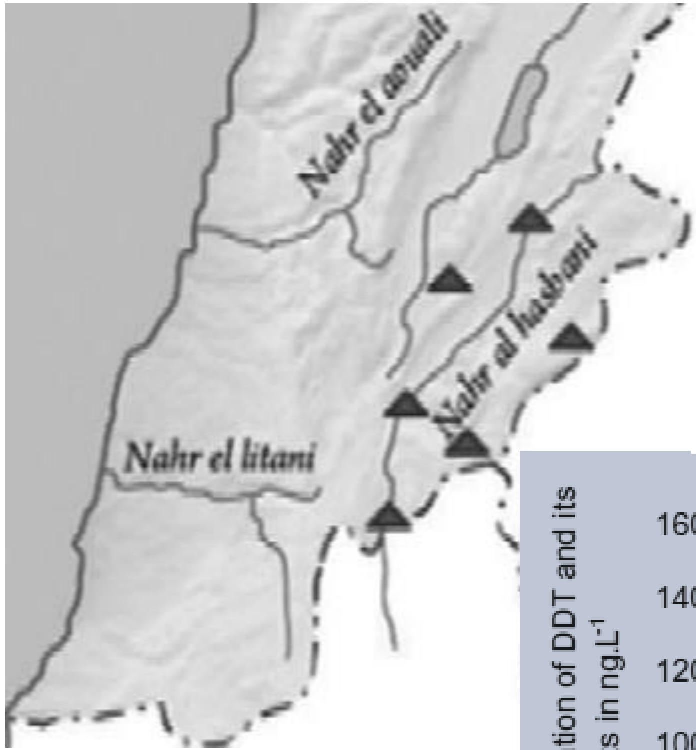
STOCKHOLM CONVENTION
UNEP
Protecting human health and the environment from persistent organic pollutants

***Pesticides**: Aldrin, DDT, Dieldrin, Hexachlorobenzene,*

Pesticides in Rivers (Surface and Ground Water from South Litani)

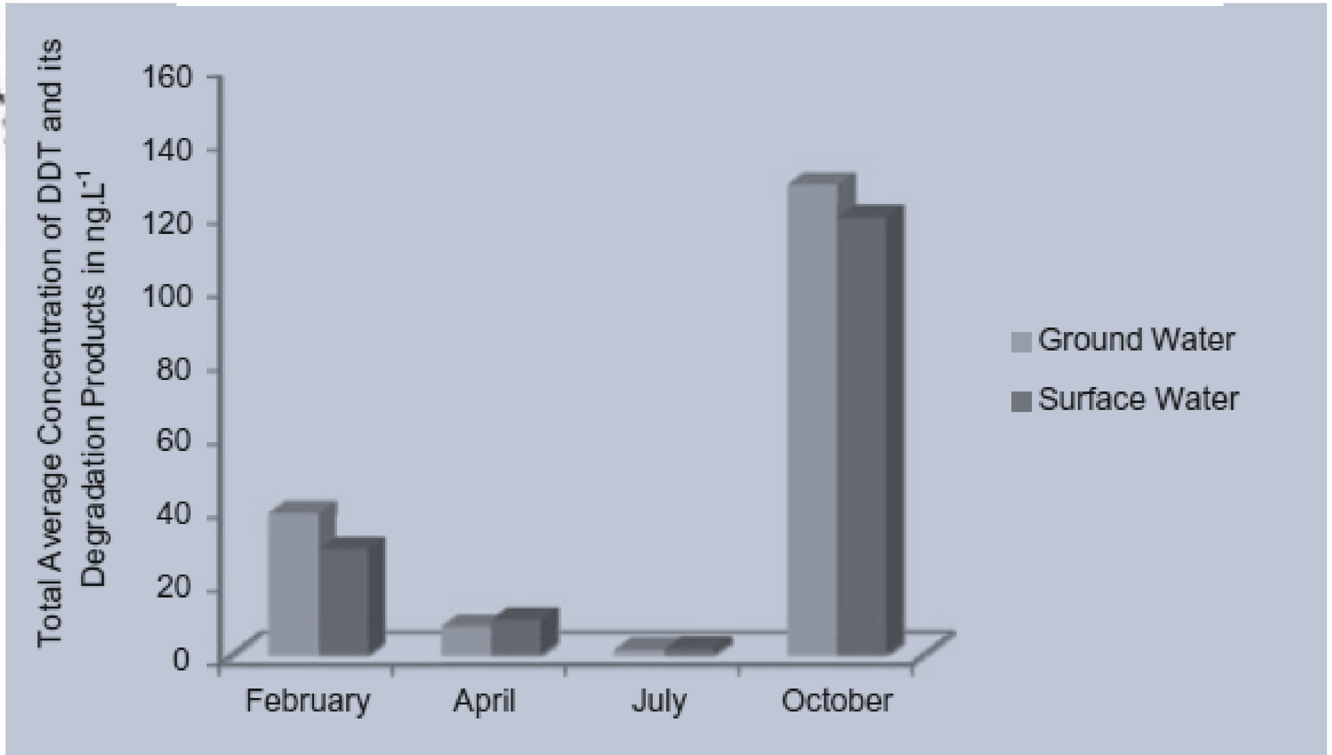


- *Water samples from different water bodies in South Litani region were taken during four seasons of the year 2012. Surface water samples from Hassbany and Wazani River at two distinct points, 3 km apart approximately, were collected at 30 cm deep during all seasons.*
- *groundwater samples were taken from three wells located in urban regions at approximately 100 m depth.*
- *Water samples from either Derdara Lake (Khyam) or NebaaJawz (Shebaa) were collected at the nearest point that can be reached from the original source.*

Chemical Speciation & Bioavailability, 2015
Vol. 27, No. 2, 62–70, http://dx.doi.org/10.1080/09542299.2015.1023092

Occurrence and levels of pesticides in South Lebanon water

Half-life 3-10 years



DDT and their metabolites:

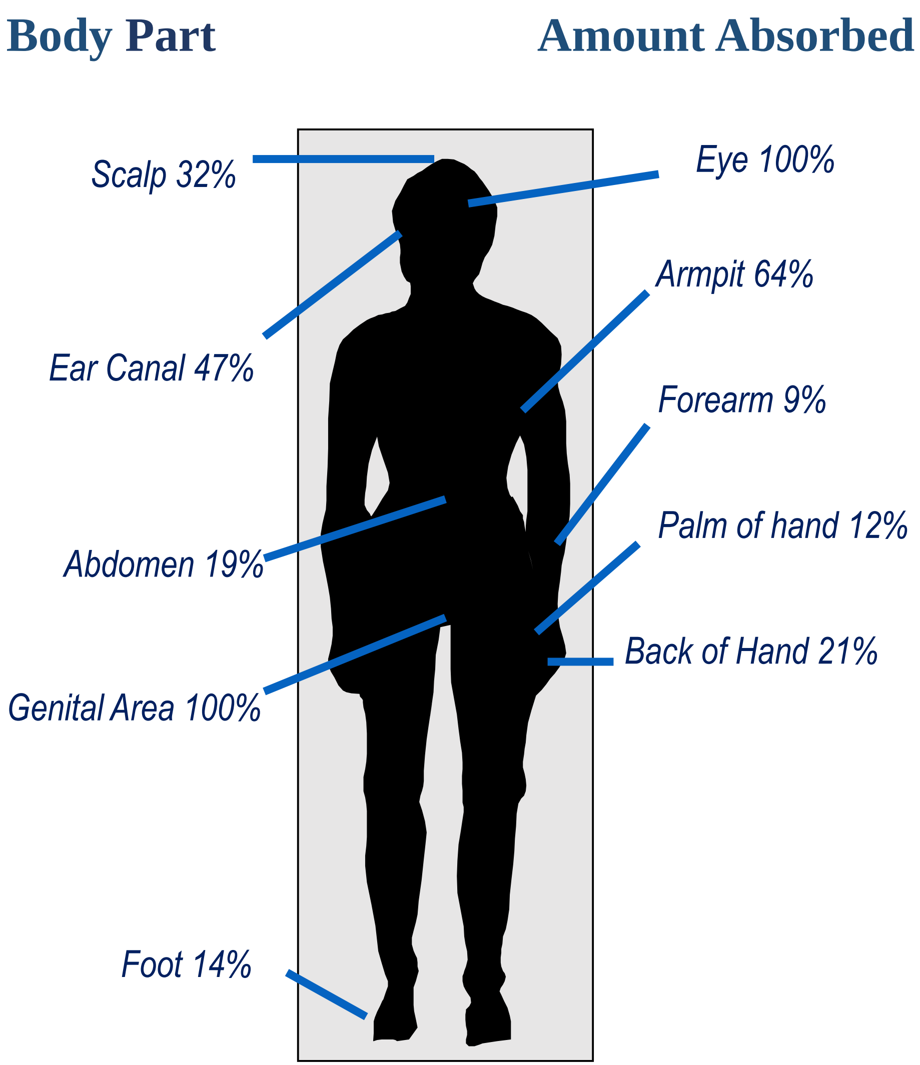
Insects : Death

Fish: Reproductive effects
Neurotoxin effects

Birds: Eggshell thinning

Mammals: Localized liver and kidney damage
Neurotoxin effects
Teratogenic effects (mice)
Carcinogenic effects are likely

Absorption, Effects and Toxicities of Pesticides



Organophosphates: *affect the central nervous system (brain) and peripheral nervous system (nerves found outside of the brain or spinal cord). Organophosphates attach themselves to the enzyme (acetylcholinesterase- AChE) that stops nerve transmission. Therefore, there is suppression of AChE and continuous electrical nerve transmission.*

Carbamates: *Disturbs the peripheral nervous system (short acting)*

Organochlorines*: Disturbs the central nervous system (Long acting)*

Pyrethroids: *irritant to eyes, skin, and respiratory tract*

- ***Reproduction***
- ***Teratogenicity (birth defects)***
- ***Mutagenicity (altering genes)***
- ***Carcinogenic***
- ***Neurotoxicity***
- ***Immunosuppression***
- ***Endocrine disruption***

Volodymyr Lushchak et al, 2018

Recommendations

- *Washing fresh fruits and vegetables before eating helps remove surface residues*

- *Processing usually reduces residues, but may sometimes concentrate residues*
- *Cooking reduces residues*

- *Grow your own produce (Private Garden)*
- *Use non-toxic methods for controlling insects in the home and garden*
- *Use a Bio-pesticides biodegradable and eco friendly to the environment (Research study). EX: Essential oils rich in phenols are also used as food preservatives in the food and flavoring industry, and ascaridol is widely used as a worm killer. The role of essential oils and their compounds is highlighted as a green approach and a potential alternative to synthetic pesticides*

- *Traditional method to eliminate herbs (Don’t use herbicides)*
- *Awareness by Public media, Education, Government*

Conclusions

- *From 212 samples of apples, 16% of the analysed samples showed no residues, 23% contained residues at or below the MRL, and 61% exceeded the MRL. The most commonly found pesticide residues exceeding the EU legal limits was chlorpyrifos, methidathion, and lambda-cyhalothrin. Multiple pesticide residues (up to five different pesticides) were detected in 22.6% of all individual apple samples.*

- *Reporting the occurrence of 28 pesticides, from the most widely used pesticides in Lebanon, at variable levels in water samples from different sources including drinking water, ground water, surface water and rainwater.*

- *The most frequently detected pesticides in groundwater and drinking water samples were diazinon (organophosphate insecticide and acaricide), DDE and DDD (degradation products of DDT organochlorine insecticide), hexachlorobenzene (fungicide), aldrin, dieldrin and tetradifon (organochlorines insecticides and acaricides) quantified at low levels (5 ng L-1 for each compound except for diazinon). The frequently detected organochlorine pesticides are classified as persistent organic pollutants (POPs) and they have been prohibited to be used in Lebanon since 1992.*

- *For groundwater samples, the highest individual concentration was recorded for Metalaxyl. This compound, mainly used as systemic fungicide, is moderately stable under normal environmental conditions (with a half-life of 400 days) and mobile at the same time. It is used on many food and feed crops, and on non-food, residential and greenhouse crops such as tobacco, ornamental plants, trees, shrubs and vines.*

- *In Litani river and the lake of Quaraoun, the maximum individual pesticide concentrations were measured for fenpropathrin insecticide (220.1 ng L-1), chlorpropham herbicide (34.6 ng L-1) and bifenthrin insecticide (33.7 ng L-1). In addition, eight insecticides, lindane, endosulfan sulfate, chlorpyrifos, diazinon, methoxychlor, tetradifon, DDE and DDD, two herbicides, alachlor and pendimethalin, one acaricide was detected. Some of the detected pesticides are included in the US-EPA and the European priority pollutant lists (EU 2001; US-EPA 1995),*

- *In Orontes river samples, only diazinon was detected and quantified at a level up to 8.9 ng L-1. Other pesticides like hexachlorobenzene, methoxychlor, DDE, fenpropathrin, bifenthrin, bromopropylate, procymidone and tetradifon were detected but not quantified due to their low levels.*

- *The occurrence of diazinon in rainwater at high levels might be related to the amount of insecticides, in particular diazinon, used indoor to control cockroaches, ants, silverfish, fleas and other insects in residential buildings and outdoors on a large scale by the municipality of Beirut.*

WORKING TEAM

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CNRS
المجلس الوطني للبحوث العلمية
National Council for Scientific Research

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Questions