

Monitoring of Pesticides in Drinking, Surface and Ground Water of Cyprus by Liquid-Liquid and Solid Phase Extraction in Combination with GC/MS and UPLC/MS/MS

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Abstract

Pesticides having different structures and biological activities are widely used for agricultural and non-agricultural purposes throughout the world. Monitoring of pesticides in water contribute to the protection of human health and the protection of environment too. Analysis of a big number of water samples each year is revealed a clear image for pollution by pesticides. Twenty-four pesticides are monitored in drinking, surface and ground waters of Cyprus according to the European legislation. During the last 4 years (2013-2016) 2860 samples were analysing using two different techniques of extraction and determination. Pesticides were separated at two groups according to their polarity and stability and determined using GC/MS and UPLC/MS/MS. The limit of quantification is 0.01 µg/L for those determined with UPLC/MS/MS and 0.01 - 0.03 µg/L for those determined with GC/MS. The results revealed that only 1.5% of the samples analysed found to contain some of these compounds at concentration over the limit of quantification. Only nine of the pesticides were found at the samples and those with the highest frequency were Chloropyrifos, Prosulfocarb and Simazine.

Keywords

GC/MS, UPLC/MS/MS, Pesticides, Water, Cyprus

1. Introduction

Pesticides are chemical compounds divided in many categories according to their use (e.g. insecticides, herbicides, rodenticides, etc.) or their chemical struc-

ture (e.g. organochlorines, organophosphorus, triazines, carbamates, triazoles, etc.). They are widespread for agricultural and non-agricultural use. Despite their benefits, most of them are hazardous for human health. They can be classified as carcinogenic, mutagenic, teratogenic, neurotoxic, endocrine disruptors and they can affect the skin, eyes, liver, kidneys, cardiovascular system, reproductive system etc. The effect of pesticides in human health depends on the chemical structure of the compound, the dose and the kind of exposure (e.g. inhalation, ingestion, epidermal) [1] [2] [3].

Pesticides contaminated ground and surface waters mainly by the use at agricultural fields. Direct run-off, leaching, careless disposal of empty containers and the washing of agricultural equipment are some of the ways which release pesticides at the environment. The concentration of pesticides at ground and surface waters affected by several parameters, like soil properties, the distance from the water, climate conditions, topography and of course the physicochemical properties of the compounds. The stability and the degradation rate of the pesticides in combination with their solubility in water and organic solvents influence their amounts in water [4] [5] [6] [7].

As a member of European Union, Cyprus has to monitor the drinking, surface and ground waters according to three European Directives: 1) Directive 98/83/EC on the quality of water intended for human consumption, 2) Directive 2013/39/ EU for the priority substances in the field of water policy and 3) Directive 2006/118/EC on the protection of groundwater against pollution and deterioration [8] [9] [10]. So, the State General Laboratory (SGL) of Cyprus which is the Official Laboratory for monitoring waters in Cyprus is preparing annual programmes in cooperation with other competent governmental authorities like Public Health Services of the Ministry of Health, Water Development Department and Geological Survey Department of the Ministry of Agriculture to control the quality of the water. Among the parameters that SGL is obliged to control are the pesticides, which constitute a big category of different compounds with different chemical properties. Twenty-four pesticides were chosen to be monitored, according to the demands of the regulations and Directives mentioned above [8] [9] [10]. Furthermore, in cooperation with the Ministry of Agriculture the authorized plant protection products were taken into consideration, in combination with those which are most widely used and expected to be found in water samples of Cyprus [11]. Also, the method covers only the monitoring of the target compounds and not any of their possible metabolites.

The selected pesticides were separated in two groups according to their chemical properties e.g. polarity and stability and analysed with the most efficient technique of extraction and determination. Validation of the developed methods, proved their suitability for routine analysis of water samples. Thirteen of the pesticides (Group A) which are the most polar, are extracted from all water samples using only Solid Phase Extraction (SPE) with C18 cartridges as the absorbent material and quantified with UPLC/MS/MS [12] [13]. Eleven pesticides

(Group B) are extracted using Liquid-liquid Extraction (LLE) based on dichloromethane as an extraction solvent for all water samples and SPE for ground and surface waters using also C18 cartridges. Their quantification achieved with GC/MS [14] [15] [16]. The pesticides chosen are shown at **Table 1** and **Table 2**. Also the Limit of Determination (LOD), the Limit of Quantification (LOQ) and the Legal limit (parametric value) of each compound in each matrix are presented

Table 1. List of pesticides quantified with UPLC/MS/MS.

GROUP A—UPLC/MS/MS				
	Drinking, Surface, Ground		Drinking, Ground	Surface
	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)	Legal Limit ($\mu\text{g/L}$)	
Carbofuran	0.003	0.01	0.1	
Diuron	0.003	0.01	0.1	0.2
Linuron	0.003	0.01	0.1	
Isoproturon	0.003	0.01	0.1	0.3
Kresoxym-methyl	0.003	0.01	0.1	
Flusilazole	0.003	0.01	0.1	
Penconazole	0.003	0.01	0.1	
Atrazine	0.003	0.01	0.1	0.6
Metribuzin	0.003	0.01	0.1	
Chlorfenviphos	0.003	0.01	0.1	0.1
Simazine	0.003	0.01	0.1	1
Prosulfocarb	0.003	0.01	0.1	
Propyzamide	0.003	0.01	0.1	

Table 2. List of pesticides quantified with GC/MS.

GROUP B—GC/MS						
	Drinking, Ground	Surface	Drinking, Ground	Surface	Drinking, Ground	Surface
	LOD ($\mu\text{g/L}$)		LOQ ($\mu\text{g/L}$)		Legal Limit ($\mu\text{g/L}$)	
Trifluralin	0.01	0.003	0.03	0.01	0.1	0.03
Chlorothalonil	0.01	0.01	0.03	0.03	0.1	
Alachlor	0.01	0.01	0.03	0.03	0.1	0.3
Chloropyrifos	0.01	0.003	0.03	0.01	0.1	0.03
Dicofol	0.01	0.01	0.03	0.03	0.1	
Iprodione	0.01	0.01	0.03	0.03	0.1	
Fenitrothion	0.01	0.01	0.03	0.03	0.1	
Formothion	0.01	0.01	0.03	0.03	0.1	
Diazinon	0.01	0.01	0.03	0.03	0.1	
Captan	0.01	0.01	0.03	0.03	0.1	
Folpet	0.01	0.01	0.03	0.03	0.1	

at these tables. The legal limit of each compound is defined by the European Directives mentioned above [8] [9] [10]. The methods used for the extraction and determination of the selected pesticides are developed by the laboratory of Environmental Chemistry I of SGL. They are fully validated [17] [18] [19] and accredited since 2013 according the ISO/IEC 17025:2005 [20].

The purpose of this study is to monitor and evaluate the quality of drinking, surface and ground waters of Cyprus and therefore the pollution of environment, concerning the concentration of pesticides during a four year period. Additionally, the results will indicate if there are areas with higher pollution levels by pesticides or any seasonal patterns that may occur during the year.

2. Material and Methods

2.1. Sampling

All the samples received in glass bottles from various parts of the country, according separate annual sampling plans for drinking, surface and ground water samples. Drinking water samples are collecting from residential areas or places with high consumption of water (e.g. picnic areas, camps). Surface water samples are collecting from, rivers, dams and lakes and ground water samples from boreholes. The number of drinking water samples is much higher than the number of surface and ground water samples, since is the final water that is going for human consumption.

The samples are stored in refrigerator below 10°C for a maximum period of seven days until the extraction. 250 mg of sodium thiosulfate is added only in drinking water samples for dechlorination.

2.2. Chemicals and Materials

The solvents used for the determination of pesticides of Group A are Acetonitrile LC-MS Chromasolv and Methanol LC-MS Chromasolv from FLUKA, Dichloromethane for HPLC and Formic Acid from Sigma-Aldrich. The solvents used for the determination of pesticides of Group B are Dichloromethane, Acetone, and Ethyl Acetate for pesticides residue analysis from FLUKA, Methanol and Hexane for GC residue analysis from SCHARLAU. Also sodium sulphate and sodium thiosulfate for pesticides residue analysis from MERCK are used.

The standards are obtained from Dr Ehrenstorfer as individual compounds. Kresoxim-methyl, Flusilazole and Prosulfocarb are bought in solid condition, Alachlor is bought in a 10 ml ampoule with concentration 10 ng/μl and the rest of them are bought in a 1 ml ampoule with concentration 100 ng/μl. The purity of all standards is more than 97%. The individual standards are stored under -18°C until their expiry date is mixing to make the appropriate mixtures for the stock solutions which are also stored under -18°C for one year.

2.3. Extraction

Group A

Pesticides of Group A are extracted using an automated SPE device with C18 cartridges. The cartridges are initially conditioned with 6 ml dichloromethane:methanol 1:1, followed by 3 ml methanol and finally with 3 ml Milli-Q water without let the cartridges to dry. Then 1 L of the sample is passed through the cartridges at a flow rate 15 ml/min and after that the cartridges are drying for 35 minutes under controlled flow of nitrogen. Finally the pesticides are eluted in 3 stages with 4 ml dichloromethane-methanol 1:1, followed by 2 ml and finally 2 ml of the same mixture. The eluate of each sample is evaporated to dryness under low stream of nitrogen in room temperature and dissolved again in 1 ml methanol.

Group B

Pesticides of Group B are extracted with two different methods of extraction. Surface and ground waters are extracted with SPE or LLE, and drinking waters are extracted only with LLE.

For LLE, 750 ml of water are extracted twice with 100 ml dichloromethane in separation funnels. The organic phases are collected and dried with the appropriate amount of anhydrous sodium sulphate and evaporated to 1 ml using a rotary evaporator. The temperature of the water bath should not exceed 28°C. 10 ml of hexane is added and is evaporated again to 1 ml. This stage is repeated and a final volume of 1 ml is collected.

For SPE, an automated extraction device is used for sample extraction. C18 cartridges are initially conditioned with 5 ml ethyl acetate followed by 5 ml dichloromethane. After each solvent, the cartridge is dried with a flow of nitrogen for 1 minute. Then, 10 ml of methanol passes through the cartridge which is finally conditioned with 10 ml of MilliQ water. 1 L of sample is then introduced into the cartridge at a flow of 20 ml/min and the cartridges are dried for 10 minutes under controlled flow of nitrogen. The elution is done in three stages. The first two stages include the use of 5 ml dichloromethane:ethyl acetate 1:1 and soaking the cartridge for one minute with the same mixture. The final elution is achieved with 10 ml dichloromethane:ethyl acetate 1:1. The water is removed from the eluate with anhydrous sodium sulphate. Finally the eluate is evaporated to 0.5 ml to an automated evaporation device under controlled temperature and flow of nitrogen. 10 ml of hexane is added and is evaporated again to 1 ml.

The extraction procedures for pesticides of both groups were developed in our laboratory, based on previous experience. Many trials took place including different sample flow, solvent volume and drying time of the cartridges (See **Figure 1**).

2.4. Instrumentation

Group A

Pesticides of Group A are determined using a UPLC coupled with Tandem Quadrupole Detector-TOQ with electrospray ionization source (ESI) by Waters company. The chromatographic column was ACQUITY UPLC BEH C18, with

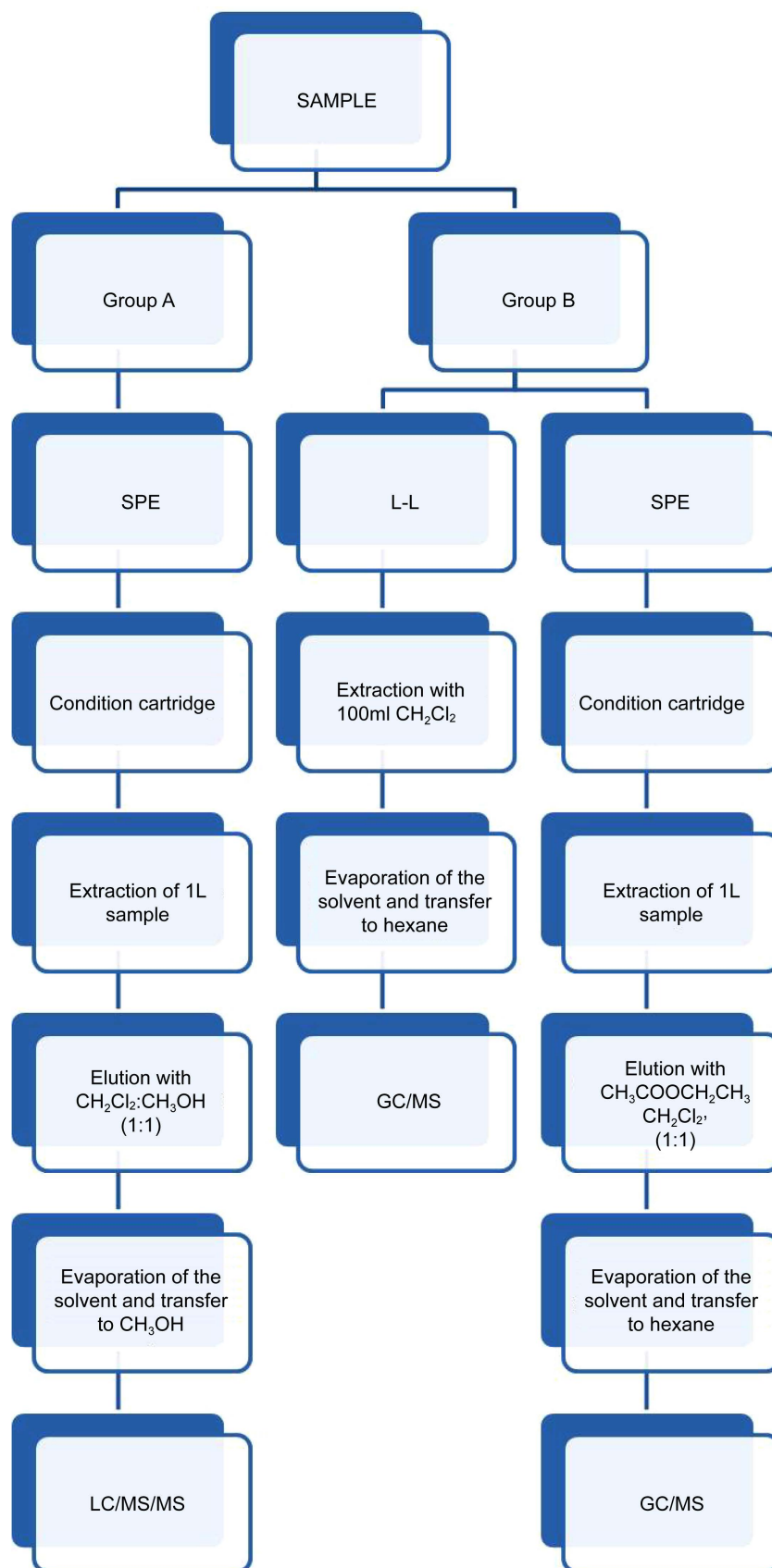


Figure 1. Extraction procedure of drinking, surface and ground water sample.

dimensions 1.7 μm \times 2.1 \times 100 mm and the precolumn was ACQUITY VANQUARD with dimensions 2.1 \times 5 mm. The temperature of the column was 65°C. As a mobile phase a solution of ammonium formate 5 mM and methanol was used at a flow of 0.3 ml/min. Injection volume was 5 μL . The duration of a single run was 35 minutes, while the pesticides are eluted up to 25 minutes. The initial composition of mobile phase was 75% ammonium formate and 25% methanol, changing to 15% - 85% respectively after all the pesticides have eluted. The mass spectrometer conditions include the Source temperature that was 120°C, the Desolvation Temperature was 300°C, Gaseous Gas Flow was 100 L/Hr, Desolvation Gas Flow was 800 L/Hr and Collision Gas Flow was 0.1 ml/min.

Group B

The determination of pesticides of Group B performed with an Agilent Gas Chromatograph coupled to an Agilent Mass Spectrometer with Triple Axis Detector. The chromatographic column used was a DB-5MS from Agilent Technologies with dimensions 30 m \times 25 mm \times 0.25 μm film thickness. Helium was used as a carrier gas. The initial temperature of the column was 60°C for 5 min, increased to 210°C at 15°C/min and held for 5 min. Then raise up to 250°C at 5°C/min and held for 5 min and finally to 300°C at 5°C/min and held for 13 min. The inlet temperature was 250°C and the injection volume was 2 μL using an autosampler. The mass spectrometer was working at Electron Impact mode. The transfer line temperature was 280°C, Quad temperature was 150°C and Ion source temperature was 230°C.

2.5. Qualitative and Quantitative Analysis

Group A

Quantitative and qualitative analysis of pesticides of Group A was performed using the Multiple Reaction Monitoring (MRM) mode. A calibration curve ranged between 5 - 100 ppb was used for the quantification of all pesticides. All the calibration standards were prepared from the initial stock solution applying all the appropriate dilutions. Isoproturon-D6 was used as IS at the concentration of 100 $\mu\text{g/L}$ to all calibration standards and samples. The qualitative determination of these compounds is based on the presence of two transitions of the parental ion to two product ions (**Table 3**) at the same retention time. One of the two product ions (written in bold) is used as a quantification trace for the compound, while the second product ion is used only for the qualitative identification of the compound.

Group B

The qualitative and quantitative determination is performed using the Selected Ion Monitoring (SIM) mode. The identification of the pesticides is based on the presence of the target ion and the two secondary ions of each compound (**Table 4**) in a specific ratio, in combination with the Relative Retention Time (RRT) of each compound. The RRT is calculated using Alachlor D13 as Internal Standard (IS). The quantification achieved using a calibration curve at range of 5

Table 3. Ions (m/z) used for the qualitative and quantitative determination at UPLC/MS/MS.

Compound	Parental Ion (m/z) > Product Ions (m/z)
Carbofuran	222.07 > 123
	222.07 > 165.1
Diuron	233.01 > 72
	233.01 > 159.9
Linuron	249.01 > 160
	249.01 > 182
Isoproturon	207.12 > 72
	207.12 > 165.10
Kresoxym-methyl	314.14 > 116
	314.14 > 206.10
Flusilazole	316.14 > 165.10
	316.14 > 247.1
Penconazole	284.2 > 70.1
	284.2 > 159
Atrazine	216.07 > 96.10
	216.07 > 174.01
Metribuzin	215.07 > 84.0
	215.07 > 187
Chlorfenviphos	359.07 > 155
	359.07 > 169.90
Simazine	202.07 > 96
	202.07 > 132
Prosulfocarb	252.12 > 91
	252.12 > 128
Propyzamide	256.05 > 172.9
	265.05 > 190
Isoproturon-d6	213.13 > 91
	213.13 > 171.1

Table 4. Ions (m/z) used for the qualitative and quantitative determination at GC/MS.

Compound	Target Ion	Secondary Ions	
Trifluralin	306	264	290
Chlorothalonil	266	264	109
Alachlor	160	188	237
Chloropyrifos	197	314	258
Dicofol	139	111	250
Iprodione	314	187	245
Fenitrothion	125	109	260
Formothion	93	125	170
Diazinon	137	179	152
Captan	149	117	107
Folpet	260	130	178
Alachlor D13	200	172	156,249

$\mu\text{g/L}$ - $150 \mu\text{g/L}$, regard only the response of the target ion of each pesticide. All the calibration standards and samples have the same amount of IS. Calibration standards are prepared by spiking extracted MilliQ water which followed the same extraction procedure as the samples, with the appropriate amount of stock solution in order to avoid the matrix effect.

3. Results

3.1. Validation

As mentioned above the methods were validated before applied for routine analysis of water samples. The repeatability (% RSD), trueness (% Rec) and uncertainty (% U) were calculated, using six spiked water samples at three spiking levels for all the water matrices as it seems at the **Tables 5-7**. %Recovery represents the average recovery of the six spikes of each compound. During the validation, the average % Recoveries for all pesticides at all matrices were within the acceptable limits of 50% - 120%, except Trifluralin when SPE extraction was applied. Additionally, % RSD and % U were lower than the maximum limits of 30% and 50% respectively for all compounds.

Table 5. Range of the % Recoveries and % RSD obtained from the spiked water samples for pesticides of Group A.

Spiking level	0.1 $\mu\text{g/L}$			0.03 $\mu\text{g/L}$			0.01 $\mu\text{g/L}$		
	% Rec	% RSD	% U	% Rec	% RSD	% U	% Rec	% RSD	% U
Matrix									
Surface Water	79 - 89	7 - 12	21 - 39	85 - 104	4 - 6	13 - 20	85 - 112	2 - 10	6 - 32
Ground Water	58 - 86	8 - 12	27 - 38	74 - 86	12 - 15	39 - 48	75 - 92	7 - 11	21 - 36
Drinking Water	74 - 87	3 - 13	10 - 41	73 - 97	9 - 15	30 - 48	71 - 99	1 - 11	5 - 35
MilliQ Water	66 - 91	2 - 7	6 - 24	81 - 102	4 - 15	12 - 48	60 - 91	4 - 10	12 - 33

Table 6. Range of the % Recoveries and % RSD obtained from the spiked water samples for pesticides of Group B (L - LExtraction).

Spiking level	0.13 $\mu\text{g/L}$			0.053 $\mu\text{g/L}$			0.027 $\mu\text{g/L}$		
	% Rec	% RSD	% U	% Rec	% RSD	% U	% Rec	% RSD	% U
Matrix									
Surface Waters	63 - 118	5 - 14	10 - 43	52 - 101	7 - 16	23 - 50	64 - 114	10 - 16	31 - 50
Ground Water	87 - 113	4 - 15	12 - 49	72 - 110	3 - 16	10 - 50	69 - 114	5 - 16	16 - 50
Drinking Water	54 - 102	5 - 15	16 - 49	53 - 98	5 - 15	16 - 48	76 - 125	3 - 15	10 - 48
MilliQ Water	62 - 117	9 - 15	27 - 47	71 - 105	2 - 7	8 - 22	70 - 106	2 - 16	7 - 50

Table 7. Range of the % Recoveries and % RSD obtained from the spiked water samples for pesticides of Group B (SPE Extraction).

Spiking level	0.1 $\mu\text{g/L}$			0.05 $\mu\text{g/L}$			0.03 $\mu\text{g/L}$		
	% Rec	% RSD	% U	% Rec	% RSD	% U	% Rec	% RSD	% U
Matrix									
Surface Waters	51 - 105	4 - 16	13 - 50	54 - 94	7 - 16	22 - 50	50 - 93	3 - 15	8 - 47
Ground Water	45 - 104	5 - 11	15 - 35	54 - 119	3 - 14	10 - 43	49 - 120	4 - 8	11 - 26
MilliQ Water	45 - 116	2 - 14	8 - 46	50 - 95	4 - 10	11 - 31	53 - 97	5 - 14	16 - 45

3.2. Monitoring of Water Samples

During the four year period, 2013-2016, 2860 water samples were analysed. 1544 of them were drinking water samples, 802 were ground water samples and 514 were surface water samples. Pesticides were detected at concentration higher than the LOQ at 42 samples, which constitute 1.5%. At 36 samples, the concentration of pesticides was between the LOQ and the legal limit and at only 6 samples the concentration was higher than the legal limit. LOQ, LOD and Legal Limit of each pesticide are presented at **Table 1** and **Table 2**. Furthermore, 24 of the samples with concentration higher than the LOQ were surface waters, 15 were ground waters and only 3 of them were drinking water as it seems to **Table 8**. Also, the most important outcome of this study was that none of the drinking water samples were found to contain any of the selected pesticides at concentration over the legal limit.

Nine of the twenty four pesticides were identified and quantified. These were Chloropyrifos, Prosulfocarb, Simazine, Diouron, Diazinon, Iprodione, Dicofol, Chlorothalonil and Penconazole. Chloropyrifos found at more samples than any of the other pesticides. It was determined at 17 samples which mean 38%, while prosulfocarb and simazine determined at 9 samples each which constitute 21% as it seems to **Table 9**.

Only one of the samples found to contain two different pesticides, in contrast with the rest of them at which we detected only one of the pesticides each time. This was a seasonal river at which we determined chlorpyrifos at concentration

Table 8. Total results of monitoring drinking, ground and surface waters.

	Drinking Water	Ground Water	Surface Water	Total
Number of Samples	1544	802	514	2860
Concentration > LOQ	3	13	20	36
Concentration > Legal Limit	0	2	4	6

Table 9. Number of samples at which pesticides were determined.

Pesticides	Number of samples found
Chloropyrifos	16
Prosulfocarb	9
Simazine	9
Diouron	2
Diazinon	2
Iprodione	2
Dicofol	1
Chlorothalonil	1
Penconazole	1

0.021 µg/L and diazinon at concentration 0.134 µg/L (Diazinon does not belong to the priority substances).

Chlorpyrifos determined at fourteen surface waters, all of them seasonal rivers at different areas of Cyprus and at two water samples which derived from Paphos waste treatment plant and intended to enrich one of the aquifers of Cyprus, at the west of the island. The concentrations found were 0.010 µg/L to 0.090 µg/L. At six of these samples, the concentration of chlorpyrifos was over the legal limit (0.03 µg/L), while at the rest of the samples the concentration was between the LOQ and the legal limit.

Prosulfocarb's concentrations vary between 0.03 µg/L to 0.522 µg/L. It was found at five seasonal rivers, one dam, one ground and two drinking waters. Prosulfocarb does not belong to the priority substances, so there is not legal limit at surface waters. The ground water was a borehole at the district of Paphos with concentration 0.320 µg/L. At the two drinking water samples the concentrations were 0.054 µg/L and 0.034 µg/L well below the legal limit (0.1 µg/L).

Simazine was found in six ground water samples, four located in Limassol district and two located in Famagusta district. In the first case simazine concentrations varied between 0.012 µg/L and 0.033 µg/L, with the compound to be determined for two constant years (April of 2015 and April of 2016) at the area of Trachoni, for three constant years (November of 2013, April of 2015 and November of 2016) at Asomatos area and for two constant samplings (April and May of 2016) at Akrotiri area. In the Famagusta area, simazine concentrations varied between 0.011 and 0.025 µg/L.

Other pesticides determined was dicofol, in a drinking water sample, in concentration 0.032 µg/L and diuron at a seasonal river and in the water from the Paphos waste treatment plant, with concentration 0.015 µg/L and 0.017 µg/L respectively. Diazinon determined in the water from the Paphos waste treatment plant also at a concentration 0.11 ppb and in a seasonal river at concentration 0.134 ppb, whereas Chlorothalonil and Penconazole were only found once in ground water (0.152 µg/L) and in a seasonal river (0.023 µg/L) respectively.

4. Discussion

Water quality is very important for human's health but is affected by a variety of pollutants. Among these pollutants, pesticides can cause direct or indirect effects to human's health and to the environment. The presence and the concentration of pesticides in waters depends mainly by the used amounts of plant protection products, the meteorological conditions in combination with the physicochemical properties which can affect the environmental fate of these compounds and even the size of the dams or rivers affecting their concentration.

The results confirm the good quality of water in Cyprus. Surface and ground waters are most exposed to pesticides, due to their location. Dams and rivers are locate outside of the cities, in most mountainous and agricultural areas and bo-reholes in places at which agriculture is one of the main activities. However, the

majority of these waters are clean from pesticides. This is probably due to the application and implementation of the National Action Plan 2013-2017, which provides instructions and guidelines to the users, distributors and advisors about the use and handling of plant protection products [21].

Additional, the good quality of drinking water is confirmed, since pesticides determined at only three samples at concentration over the LOQ but below the Legal Limit. This is expected, because the majority of drinking water is derived from surface and ground water which are free from pesticides.

Our laboratory receives water samples during the whole year, from various sampling points according the European Directives mentioned above. Thirty-two of the samples found to contain pesticides, were collected and analyzed between the months January to May. The half of them came to the laboratory at April. One sample came at January, seven samples at February, five samples came at March and three samples at May. Among the rest of the samples, one came at June, one sample came at July, two samples came at October, four samples came at November and three samples came at December. We did not detect any of the pesticides at the samples came at August and September. This fact is in accordance with the precipitation patterns of Cyprus. During the second half of Autumn and at Winter, rainfall is increased and more frequent than the rest of the year, which leads to increased leaching of pesticides to rivers and dams the months of winter and spring. In contrast, there is not an important pattern concerning the areas that the positive samples came from. All the samples at which we determine any of the pesticides, except the drinking water samples, collected from locations with increased agricultural activity but in different areas of Cyprus.

The three pesticides that determined more times than the others, (chlorpyrifos, prosulfocarb and simazine) are in general stable at soil and water concerning the temperature and pH. Chlorpyrifos reported half-lives in soils vary between 7 - 120 day and its low mobility does not allow it to be transferred easily from soil to water. Although, chlorpyrifos found in waters is probably a result of soil-bound chlorpyrifos from eroding soil. Also, it is stable against hydrolysis in natural waters at pH 5 - 9. Its hydrolysis rate increases with increase of temperature and pH [22] [23] [24] [25] [26].

Prosulfocarb is also stable at waters and soils at natural conditions. There is no significant hydrolytic degradation at pH 5, 7 and 9 at 25°C and 40°C. Additionally, it resists to photolysis at soils with half-life 97 days and to aqueous photolysis with a half-life at 25 - 30 days [26] [27].

Simazine is stable at neutral, weakly acidic and weakly alkaline matrices like soil and water. It was observed to have 145 days half-life at pH 4 which is the lowest pH that can be found at aquatic environments. Reduce of simazine's concentration by direct photodecomposition is not important, but the temperature and the moisture of soil are the main parameters that can affect its half-life. Even it has low leaching potential, it can be found in rivers and ground waters at pre-

precipitation periods [22] [26] [28].

5. Conclusions

The combination of two extraction methods and two instrumental techniques seems to be reliable, sensitive and effective for the qualitative and quantitative determination of pesticides in the drinking, surface and ground waters of Cyprus. The LOQs of the two methods, which are in accordance with the European legislation, allow detecting the presence of pesticides even in low concentrations. The results prove the good quality of waters in Cyprus. Only few of the surface and groundwater samples found to contain any of the pesticides and the absence of pesticides in concentration over the legal limit at drinking water confirm the good practices applied about the use of pesticides.

To our knowledge there is not any other study about the determination of pesticides in waters of Cyprus for so long period. However, the monitoring of pesticides can be considered complete with the determination of the metabolites of some of the pesticides, which constitute a future goal for our laboratory.

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