IDENTIFICATION OF PESTICIDES IN GROUNDWATER SITUATED UNDER GREENHOUSE AGRICULTURE PRODUCTION AND DROPPING IRRIGATION, USING GC/MS PULSED SPLITLESS INJECTION

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Abstract

The aim of this stady was to investigate the quality of groundwater situated under a topsoil where greenhouses and dropping irrigation system are used in tomato production. A GC -MS method was applied using pulsed splitless injection with pressure of 50 psi and purge flow to split vent of 1.5 minutes[1], for the screening of the most friquently used pesticides such as benalaxyl, chlorpyrifos, malathion, pirimifos methyl, methomyl, metribuzin, penconazole, triadimenol, pyrimethanil, and buprofezin. Seventy eight groundwater samples were collected from the region of Strumica, an agricultururally vulnerable area regarding pesticide application, during 2014 - 2015. Slightly modified liquid-liquid extraction was performed using dichloromethane as a solvent.[2] The obtained results show negligible pollution of groundwater with investigated pesticides. Only 5% of investigated samples were polluted with pesticides in concentrations which doesn't exceed the national maximum concentration limit. The analysis showed the presence of pyrimethanil and chlorpyrifos in maximum concentrations of 0,0299 ± 0,00026 µg/l and 0,133 ± 0,00929 µg/l, respectively. The main reason for this negligible pollution of groundwater with pesticides is considered to be the use of greenhouses and the dropping irrigation system in agriculture production which doesn't allow high quantity of water to be able to pass from the soil surface downward to the aquifers.

Keywords: GC/MS, pulsed splitless injection, pesticides, groundwater, dropping irrigation.

Introduction

Previously, it was considered that the period of time needed for pesticides to leach in to the groundwater is very long and it takes approximately one meter per year for a pesticide to reach the aquifer.[3] Recent investigations showed that the process of leaching depends of various factors like chemical and physical characteristics of the pesticide which defines it as a leacher or a non leacher. In 1986 US EPA published a list of characteristics according to which some pesticides are classified as high potential leachers: water solubility greater than 30 ppm, distribution coefficient (Kd) lower than 5, soil organic carbon-water partitioning coefficient (Koc) from 300 to 500, Henry's Law constant less than 10^{-2} $atm^{-1} \cdot m^{-3} \cdot mol$, hydrolysis half-life greater than 25 weeks, photolysis half-life greater than one week, field dissipation half-life greater than 3 weeks and negative charge fully or partially at ambient pH.[4] Considering this chemical and physical characteristics of substances several indexes are created indicating leaching potential of substances. One of the mostly used index for the evaluation of pesticides leaching ability into the groundwater called Groundwater Ubiquity Score (GUS) was introduced by Gustafson in 1989[5] but non of them consider agro-ecological and geochemical characteristics of the region like soil permeability, rainfall precipitation, crop variety, management practices and other. Geology and ecology of the region like soil type, soil moisture, depth of the aquifer, soil porosity, soil texture, soil organic matter content, soil clay content, local climatic conditions etc. as well as agriculture management practices like rate of application, timing of application, method of application, irrigation practice, cultivation practice etc. are also involved in the process of leaching and will determined if there are suitable conditions for pesticide leaching in to the groundwater. Thus, different agro-ecological, climatic and geochemical characteristics of regions contribute in differences of the quality of groundwater regarding pesticide contamination so, pesticides found in some region may not be present in other region where are used, although they poses leaching possibilities.

Table 1. Method validation parameters

	Quantifier ion	Qualifier ions	RRT	RSD	R%	R^2	equation	LOD *µg/l*	LOQ *µg/l*
Methomyl	105	58, 88	0.185	11.20	127	0.95	y = 0.33 · x + 0.0129	0.55	5.5
Pyrimethanyl	198	199, 77	0.565	3.14	125	0.96	y = 0.2972 · x - 0.3101	0.09	0.9
Pirimicarb	166	72, 238	0.601	2.89	109	0.95	y = 0.2162 · x – 0.2155	0.01	0.1
Metribuzin	198	103, 144	0.638	2.46	94	0.98	y = 0.581 · x – 0.0847	0.08	0.8
Pirimiphos methyl	290	276, 305	0.695	3.47	108	0.96	y = 0.1107 ·x – 0.1031	0.03	0.3
Malathion	125	173, 93	1.04	8.60	120	0.98	y = 0.777 ·x – 0.0978	0.54	5.4
Chlorpyrifos	197	97, 199	0.726	6.34	130	0.98	y = 0.294 · x – 0.197	0.33	3.3
Penconazole	159	248, 161	0.799	7.14	117	0.97	y = 0.1749 · x – 0.1845	0.01	0.1
Triadimenol	112	168, 57	0.822	5.00	120	0.96	y = 0.0761 · x – 0.0888	0.19	1.9
Buprofezine	105	106, 172	0.899	2.92	106	0.96	y = 0.0702 · x – 0.0582	0.53	5.3
Benalaxyl	148	91, 206	0.966	4.52	112	0.95	y = 0.158 · x – 0.133	0.02	0.2

Materials and methods

Sampling

Groundwater samples were collected from boreholes located in an intensive agriculture production area in the Strumica region (villages Borievo, Kuklish, Monospitovo, Prosenikovo, Dabile, Sachevo, Robovo, Piperevo and Dobrejtci), according to the EPA guidelines for groundwater sampling.[6] Each sample was collected from a single borehole located in the agriculture field. A total number of 78 groundwater samples were collected in 2014-2015. The boreholes are shallow with depth between 16 – 25 m. According to the lithological composition of the Strumica basin, the discovered thickness of the basal lithozone ranges from 20-50 m.[7]

Chemicals and materials

Certified chemical standards (purity 95 – 99%) and solvents with HPLC grade were obtained from Sigma Aldrich. Pesticide stock solutions and working standards were prepared in acetone. Hexane was used as solvent for column injection.

Extraction

The extraction of pesticides from water was made using continuous Liquid – Liquid Extraction (LLE) and dichloromethane (DCM, 40 ml) as a solvent. Water (1l, HPLC pure) was salted out with sodium chloride (NaCl, 66 g) and the extraction process was carried out using separating funnel. Water was spiked with pesticide standards in concentration of 100 ng/l. Triphenyl phosphate (TPP) was used as an internal standard in concentration of 50 ng/l. The extract was evaporate until dryness and reconstructed in 100 µg/l of hexan.[8]

Apparatus and GC- MS conditions

Analysis were performed on gas chromatograph Agilent 6890N coupled to a mass spectrometer and equipped with JAS UNIS split/splitless injector series 7683B. Glass wool liner type (JAS 90323L) with single restriction, 88 mm long and 3mm ID, was used in all experiments. For the separation of analytes DB-5ms Supelco column was used with helium as a carrier gas. The oven temperature ramped from 60ºC for 2 min. to 150ºC with increment of 25ºC for 0 min., ramped to 200 with increment of 3ºC for 0 min., ramped to 280 with increment of 20 ºC for 10 min., for a total run time of 41.8 min. The temperature of the injector was 250 ºC, the temperature of the MS quadrupole was 150ºC and the injection volume was 1µl. Sim method was created for the analysis of pesticides (Table 1). Blank sample and pure sample in hexan as

Results

Agro-ecological and geochemical characteristics of the Strumica region

The research was conducted during 2014 – 2015 in the alluvial part of the Strumica valley related with the Strumica river delta in southeast part of the Republic of Macedonia represented by gravels and sands.[9] The main activity in the region is early greenhouse tomato production. The climate is submediterranean with influence of east continental climate. The average annual temperature during the investigated period was 13.1 ºC. The highest average monthly temperature was observed in July, 23.9 ºC and the lowest in January of 1.7 ºC. The average annual precipitation where 604 mm. Maximum precipitations were observed in April (125.5 mm), July (344 mm) and September (100,7 mm) in 2014 and in October (2015).[10, 11]

The main source of water for irrigation in the investigated region is groundwater. Groundwater type is compact with water level under pressure and well, capacity of 10-20 L/s.[9] Groundwater in the investigated region is classified as highly vulnerable regarding the poor technical condition, no flow regulation in the convey structures, unregulated use, and the decrease of precipitation.[12] Groundwater is the main source for irrigation water which is exploited trough the private boreholes located on the cultivated land. Dropping irrigation system is the main type of irrigation is and the main type of pesticide application is spraying.

Pesticide identification was based on the mass spectrum, retention time, relative retention time, and peak shape. To remove the effect of the matrix and to improve the limit of detection a SIM method was created. In order to reduce the impact of external factors and the loss that occurs in the process of extraction and concentration of pesticides, the calibration was made by extraction of pesticides from a real water sample into which a certain amount of pesticide is added.

Two out of twelve investigated pesticides were identified in the groundwater samples from the Region of Strumica. A pyrimidine fungicide pyrimethanil was found in concentrations of 0,0299 ± 0,00026 µg/l. Other detected pesticide was an organophosporus insecticide chlorpyrifos found in concentration of 0,0133 ± 0,00929 µg/l.

Conclusions

Even though the investigated region was considered to be vulnerable regarding pesticide application, only 5% of the investigated 78 samples showed the presence of pyrimethanil and chlorpyrifos at concentrations of 0,0299 ± 0,00026 µg/l and 0,0133 ± 0,00929 µg/l, respectively. The main reason for this is considered to be the way of pesticide application and the method of irrigation. Foliar spraying of pesticides and dropping irrigation as well as cultivation of plants in greenhouses doesn't allow enough quantity of water to leak from the soil surface in to the groundwater. Thus, it could be concluded that foliar pesticides applied by spraying in greenhouse conditions where precipitation is not available are not potential pollutants of groundwater.

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