OCCURRENCE OF PESTICIDE PERSISTENT IN AMVRAKIKOS GULF – N.W. GREECE

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ABSTRACT

Amvrakikos gulf is located in the North-western part of Greece. It is a wetland of high environmental importance, as it provides an ideal habitant for many species of birds. Because of its importance, the whole area is protected by the Ramsar Convention.
The major threat for the ecosystem is the agricultural activity. This activity takes place in catchments which include 200 km^2 of agricultural land. The main pathways of agricultural pollutants are three rivers (Louros, Arachthos and Vovos) and three draining canals (Salaoras, Fidokastrou and Neochoriou).
This work presents the results of an extensive monitoring survey which was carried out for a period of one year in order to evaluate the concentration levels of alachlor, metalachlor, endosulfan, dimethoate, and diazinon in the water of the rivers and draining canals of the area.
For this purpose fifteen (15) water sample stations were established and 180 water samples were collected. Analysis of water samples was performed by solid phase extraction SDB-RPS disks followed by gas chromatographic techniques (GC - ECD and GC-FTD).
Analysis of water samples indicates contamination with alachlor (up to 626 ng/l), S-metolachlor (up to 1118 ng/l), endosulfan-α (up to 182 ng/l), endosulfan-β (up to 124 ng/l) and endosulfan-sulfate (up to 46 ng/l) while organophosphorus residues were found up to 1364 ng/l for dimethoate and up to 426 ng/l for diazinon.
Finally a preliminary assessment was performed to examine the water quality and potential risk to the aquatic species, concerning the selected pesticides. Already existing, water quality criteria were used for this reason.

Keywords: wetlands, pesticides, Luros and Arachthos rivers, draining canals, Amvrakikos, Greece.

1. INTRODUCTION

Wetland areas are essentially important for the conservation of wildlife. The Amvrakikos located in the North-western part of Greece (Fig1), is one of the few areas in Europe acting as a way station for migratory birds as well as an ideal biotope for many native ones. It is noticeable that 67 species of birds have identified in the area. Agriculture, which is put into practice mainly in the north part of the gulf is the main activity in this area and results in the release into the environment of pesticides and other agricultural pollutants. The contamination of this aquatic environment with pesticides has been already mentioned in previous papers [1,2,3].

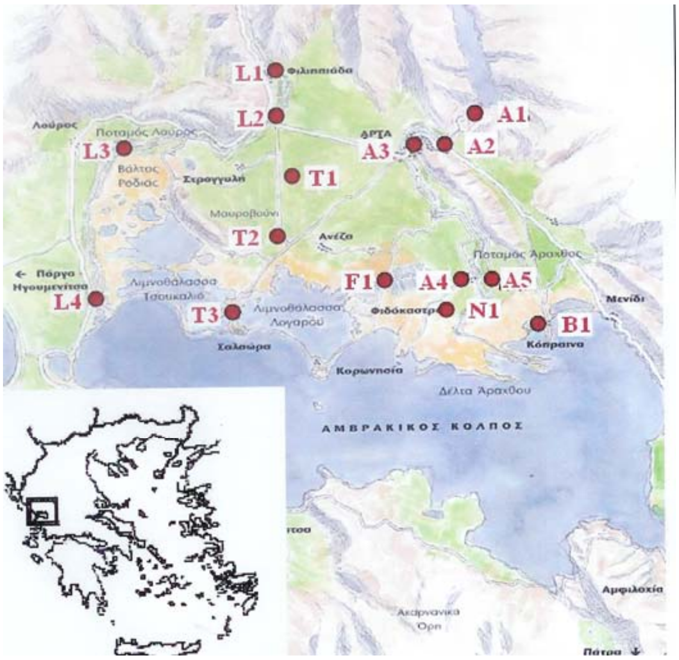

Figure 1. The Amvrakikos area and the samples stations

After a detailed research in the area, which held from May of 2004 till April of 2005 it was estimated that every year there is an input of 37.100 Kg of commercial formulations of pesticides in the agrosystem. Criteria that were used for this estimation, were the local pesticides market, the kind and the size of the farms, as well as the agricultural practice of the farmers. Among the most used pesticides are organophosphate compounds (mainly dimethoate in olive trees and diazinon almost in all crops), endosulfan which is used mainly in maize and vegetables and secondarily in alfa-alfa and alachlor and metolachlor as herbicides. The amount in active ingredients of the above pesticides which are approximately used in the area is shown in Table 1.

Table 1. Annual amounts of the selected pesticides used in agricultural catchments draining in Ambrakikos Gulf

Pesticides	Active ingredients
Dimethoate	2600 L
Diazinon	2000 L
Endosulfan	250 kg
Alachlor	1450 L
Metolachlor	1050 L

This survey aims to investigate the concentration of the above mentioned pesticides that discharge in Amvrakikos gulf through the rivers and draining canals which cross the cultivated area and to examine the potential risk to the aquatic species.

2. METHODS AND MATERIALS

2.1. Area description and sampling

In the north of Amvrakikos gulf there is the greatest agrosystem of Epirus, which include 200 Km^2 of agricultural land. The area is crossed by three rivers (Arachthos, Luros and Vovos) and three draining canals (Salaoras, Neoxoriou and Fidokastrou). Rivers and draining canals are used for irrigation as well as draining collectors. The main crops grown in the catchments, which are covered from the aqueous routs mentioned above, are shown in Table 2.

Table 2. Main crops per cathment in Ambrakikos agrosystem (Km^2).

Main Crop	Aracthos cachment	Luros cachment	Vovos cachment	Salaoras cachment	Fidokastrou cachment	Neeochoriou cachment	Total
Citrus trees	14.5	7.4	16.5	12.5	7,5	6,5	64.9
Olive trees	17.6	0	24.0	1.0	0	1,0	43.6
Maize	0.5	12.5	1.5	10.0	2,8	2,5	29.8
Alfa-alfa	1.3	11.5	3.0	23.0	3,5	3,5	45.8
Kiwi	0.5	2.1	0.5	0.5	0,3	0,5	4.4
Cotton	0	2.3	0	1.5	0	0	3.8
Other cultures	1.1	1.3	0.5	2.3	1,0	1,5	7.7
Total	35.5	37.1	46.0	50.8	15.1	15.5	200.0

According to Table 2, the main crops grown are citrus , olives, maize and alfa-alfa which cover the 92% of a 200 Km^2 agriculture area. The rest of area is cultivated with cotton, kiwi and vegetables

The majority of agricultural land is in the plain and only 18 % is located in slops. The 78% is underlain by heavy loamy soils and the rest is underlain by sandy soils.

To carry out this monitory survey 15 water sample stations were installed as follow: In Aracthos river 5 stations were established covering a field of 2.9, 8.2, 6.7, 7.8, and 9.9 Km^2 respectively. In Luros river 4 stations were established covering a field of 3.0, 18.4, 4.5 and 10,1 Km^2 respectively. In draining canal of Salaora 3 stations, covering a field of 17.5, 18.2 and 15.1 Km^2 respectively. Finally in Vovos river, draining canal of Fidokastrou and Neochoriou one sample station is established in the estuaries, covering the entire catcment.

Sampling was performed on a monthly basis from July 2005 to June 2006.

2.2. Analytical techniques

Analysis of water samples was performed by solid phase extraction using SDB-RPS disks[5].

A GC – ECD Shimadzu chromatograph equipped with capillary column ZB-5 Zebron, 5% phenyl and 95% dimethyl-polysiloxane (30m x 0,32 mm x 0,25μm) was used in the split-less mode to quantify alachlor, metolachlor end endosulfan (endosulfan-a, endosulfan-b and endosulfan sulfate)[5].

A GCC – FTD Shimadzu chromatograph 14A equipped with capillary column DB-1(J & W Scientific, Folsom, CA), used contained dimethylpolysiloxane (30 m × 0.32 mm, i.d) was used in the split-less mode to quantify dimethate and diazinon [6].

2.3. Quantification

Pesticides were identified by comparison of retention times. All samples were run in duplicate and their concentrations were determined using an internal standard (IS). In this case ethyl-bromophos was used as an IS, in both GC (GC-ECD and GC-FTD). Retention times and detection limits obtained for the selected pesticides are indicated in Table 3.

Table 3. Retention times (t_R) of selected pesticides in GC-ECD and GC-FTD, and their limits of detection (LOD, μg/l)

Pesticides	GC	t_R (min)	LOD μg/l
1.Alachlor	GC-ECD	7.900	0.002
2.S-Metolachlor		8.658	0.002
3.Ethyl Bromophos (I.S.)		10.100	0.001
4.Endosulfan-a		10.492	0.0005
5.Endosulfan-b		11.983	0.0005
6.Endosulfan sulfate		13.092	0.0006
1.Dimethoate	GC-FTD	13.935	0.005
2.Diazinon		15.383	0.002
3.Ethyl Bromophos (I.S.)		32.142	0.002

3. RESULTS AND DISCUSSION

Peak concentration of all pesticides was observed, in the estuaries sample stations (A5 for Arachthos River, L4 for Luros River, B1 for Vovos River, T3 for D.C Salaoras, N1 for D.C Neochoriou, F1 for D.C. Fidokastrou). The concentration of detected pesticides for the rivers and draining canals, in the above sample stations, are shown in Figures 2-6. The peak concentration of alachlor, metalachlor, dimethoate and diazinon corresponds to their application and to the crops distribution according to the Table 2. For endosulfan there was an unexpected high concentration in February (Fig.4). A possible explanation for this, is that there was a late insect attack to alfa-alfa in 2005, because of good whether conditions and the farmers sprayed with endosulfan as they found it in very attractive price. (There was a special offer, as this pesticide is banded in Greece in 20/6/2006).
The concentration found is similar to those reported by several studies in the area [2, 3, and 7]. There was only an exception, concerning the high concentration of dimethoate in Vovos River from August till September (Fig. 5). The explanation is given in Picture 1, as it was discovered that many growers use the rivers and draining canals not only for spray equipment washing, but as litter-bin too.

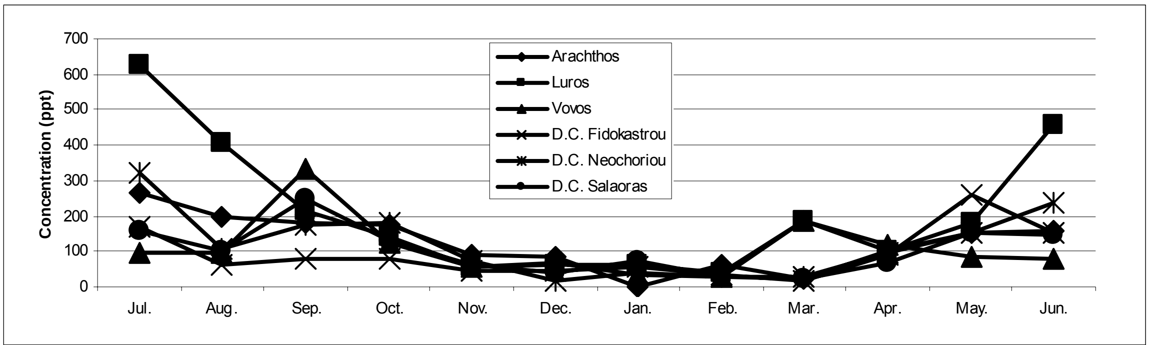

Figure 2. Monthly variation of alachlor concentration, in the estuaries of the rivers and draining canals for the period from July 2005 to June 2006.

The ecological risk assessment in water for the selected pesticides was performed applying the Risk Quotient Method for three taxonomic groups (algae, zooplankton and fish) according to directive 414/91/ European Economic Community.

Cyprinus carpio was selected as representative fish species for the draining canals, whereas *Salmon truta* was selected as representative fish species for the rivers.*Daphnia magna*, was selected of the zooplankton category and for *algae* were taken species, commonly found in water ecosystems.

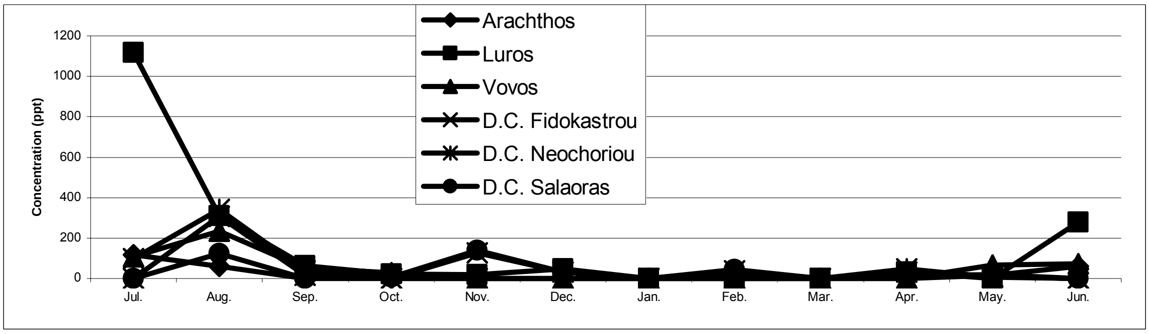

Figure 3. Monthly variation of metolachlor concentration, in the estuaries of the rivers and draining canals for the period from Jul. 2005 to Jun. 2006.

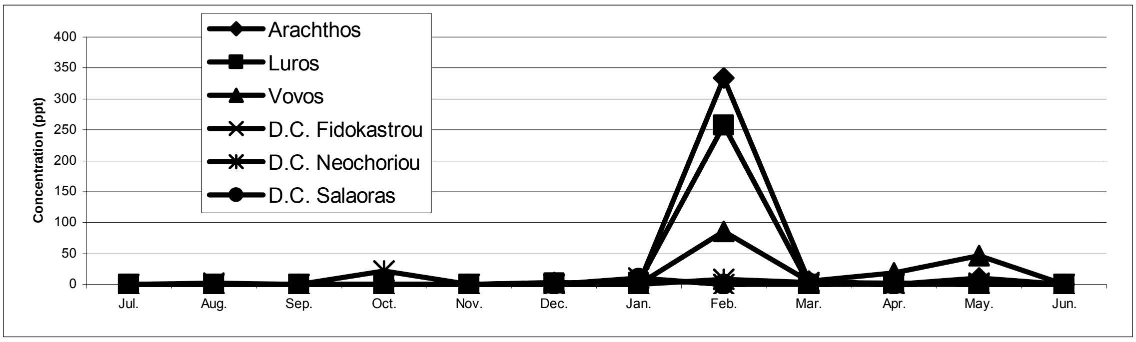

Figure 4. Monthly variation of endosulfan (endosulfan-a, endosulfan-b and endosulfan sulphate) concentration, in the estuaries of the rivers and draining canals for the period from July 2005 to June 2006.

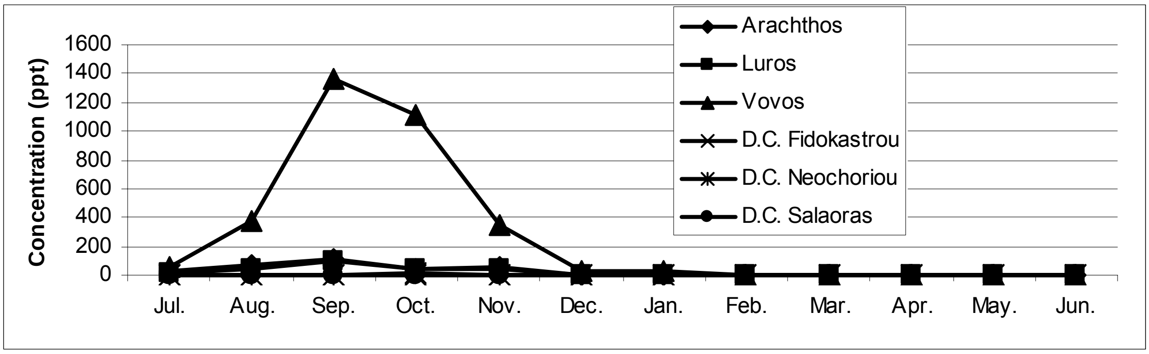

Figure 5. Monthly variation of dimethoate concentration, in the estuaries of the rivers and draining canals for the period from July 2005 to June 2006.

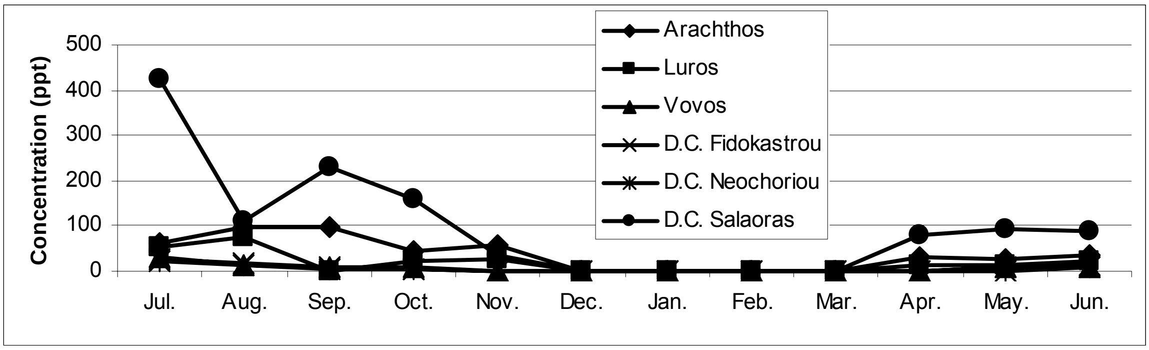

Figure 6. Monthly variation of diazinon concentration, in the estuaries of the rivers and draining canals for the period from July 2005 to June 2006.

Picture 1. Packages of pesticides formulation in Vovos river

The Risk Quotient was calculated according to equation (1)

$$Risk\ Quotient\ (RQ) = \frac{Exposure}{toxicity} = \frac{Water\ or\ Sediment\ Concentration}{LC50\ or\ EC50} \quad (1)$$

Table 3. Rate of RQ and risk levels

RQ	Levels of Risk (Acute effect level)
<0.01	Low
0.01<RQ≤0.1	Medium
0.1< RQ ≤1	High
RQ>1	Very High

For additive toxicity of pesticides and if there are no synergistic, antagonistic or other interactions, the sum of the toxic quotients of all compounds detected, gives an estimate of the total toxicity according to equation (2):

$$TU_{mix} = \sum_{i=1}^{n} TU_i \quad (2)$$

The initial approach to the risk assessment was undertaken using the “worst case” scenario (maximum detected concentrations) [8].

According to the RQ, there are four levels of risk, which are given in Table 3.

EC_{50} and LC_{50} data were obtained from the open literature containing validated toxicological data (Munn and Gilliom, 2001, Orne and Kegley, 2003)

The results shown that under high risk assessment (0.1<RQ≤1) is phytoplankton in Luros River, and in the draining canals of Neochoriou and Fidokastrou (Figures 7,8,9). Zooplankton in Arachthos and Luros Rivers is also in high risk (Figures 7,10), while in the draining canal of Salaora is under very high risk (Figure 11).

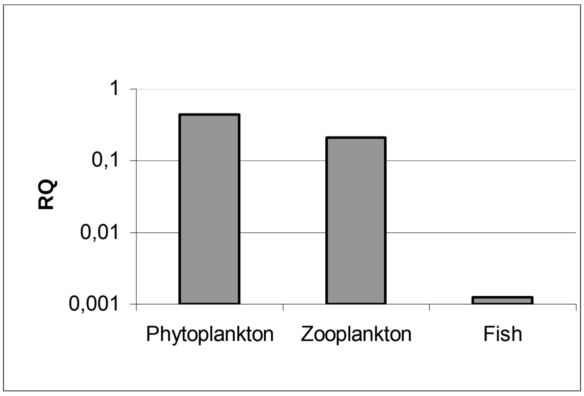

Figure 7. Combined taxonomic risks based on acute toxicity data in Luros River

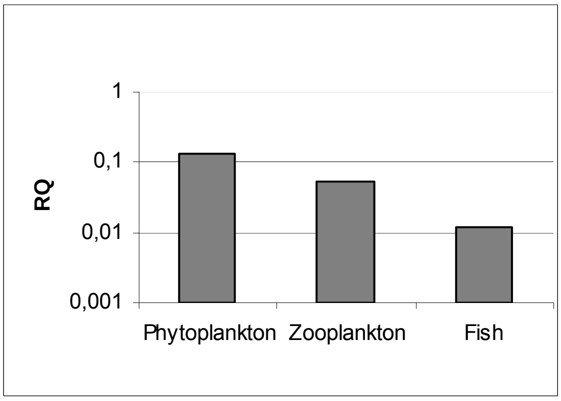

Figure 8. Combined taxonomic risks based on acute toxicity data in D.C Neochoriou

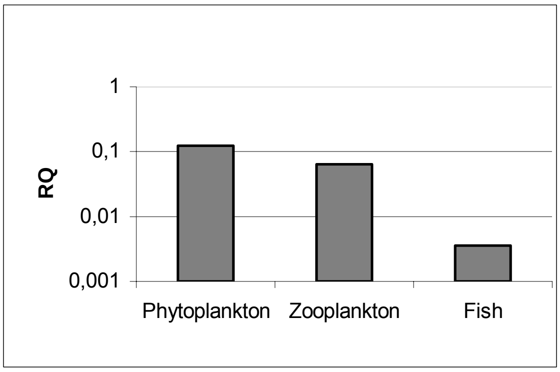

Figure 9. Combined taxonomic risks based on acute toxicity data in D.C Fidokastrou

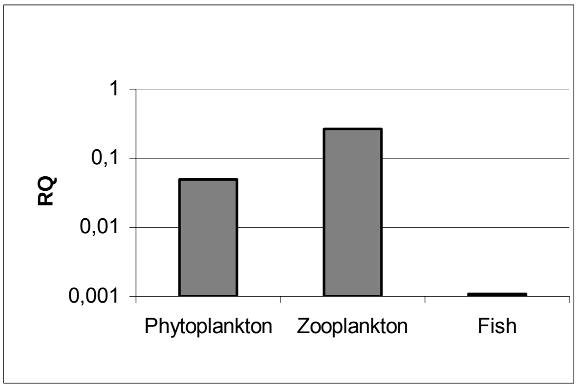

Figure 10. Combined taxonomic risks based on acute toxicity data in Arachthos River

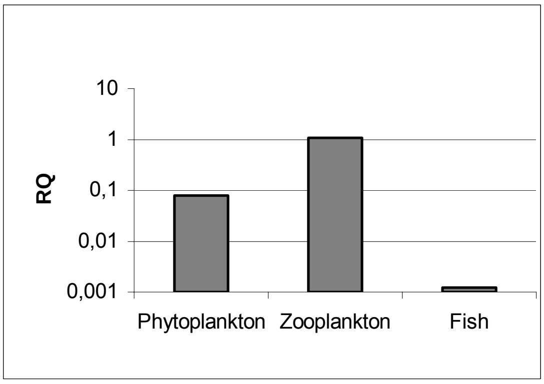

Figure 11. Combined taxonomic risks based on acute toxicity data in DC Salaoras

According to the percentage contribution of detected pesticides in total acute toxicity the responsible pesticide for high risk assessment in phytoplankton is S-metolachlor and for the zooplankton is diazinon.

4. CONCLUSIONS

Taking into account that this study concerned only the impact of five pesticides in the ecosystem, representing about the 40% of the total amount of pesticides used in the agrosystem, we can surely conclude that wetland of Amvrakikos is under environmental risk.

The major input of pesticides into the rivers and draining canals correspond to their application. The greatest concentrations of dimethoate were observed in August – November, as this pesticide is used for *Bactrocera* (dacus) control in olive trees. For the rest selected pesticides the greatest concentrations were observed in May - September. The case of endosulfan must be considered as an exception of the rule, because of special weather and market conditions at this period.

It has been shown that agricultural practices in the area have degraded the water quality, so the first step for the improvement of Amvrakikos ecosystem is the implementation of the rules of the right agriculture practice.

ACKNOWLEDGMENTS

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REFERENCES

1. Albanis, T.A., Hela, D.G., Hatzilakos, D. 1995b *Organochlorine residues in eggs of Pelecanus crispus and its prey in wetlands of Amvrakikos Gulf, north-western Greece Chemosphere* 31 (11-12), pp. 4341-4349
2. Albanis, T.A., Danis, T.G., Hela, D.G. 1995. *Transportation of pesticides in estuaries of Louros and Arachthos rivers (Amvrakikos Gulf, N.W. Greece) Science of the Total Environment* 171 (1-3), pp. 85-93
3. Hela, D; Lambropoulou, D; Sakkas, V and Albanis T. 2000. *Concentration levels of pesticide residues in the surface waters of Epirus*. Proceedings of the 1st European conference on pesticides and related organic micro pollutants in the environment.
4. Poole C.F., Gunatilleka A.D., Sethuraman A., 2000, *«Contributions of theory to method development in solid-phase extraction»*, *Journal of Chromatography* A, 885, pp 17 – 39.
5. Albanis T.A., Hela D.G., Sakellarides T.M., Konstantinou I.K., 1998, *«Monitoring of pesticide residues and their metabolites in surface and underground waters of Imathia by means of solid phase extraction disks and gas chromatography», Journal of Chromatography* A, 823, pp 59 – 71
6. Tsoutsi C., I. Konstantinou, D. Hela and T. Albanis, 2006. *Screening method for organophosphorus insecticides and their metabolites in olive oil samples based on headspace solid-phase microextraction coupled with gas chromatography. Analytica Chimica Acta* Volumes 573-574, Pages 216-222
7. Albanis T.A and D. Hela, 1998. *Pesticides concentrations in Luros River and their Fluxes into the marine environment. Inter. J. Environ. Anal. Chem*. Vol. 70(1-4)pp.105-120
8. Hela D.G., Lambropoulou D.A., Konstantinou I.K., and Albanis T.A., 2005, *«Environmental Monitoring and Ecological Risk Assessment for Pesticide Contamination and Effects In Lake Pamvotis, Northwestern Greece», Environmental Toxicology and Chemistry*, Vol. 24, No. 6, pp. 1548–1556.