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## Monitoring of *N*-methylcarbamate pesticides in the Pinios River (central Greece) by HPLC

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Seasonal variations of *N*-methylcarbamate pesticides in Pinios River waters of central Greece were determined for a period of one year (January to December 2003). The water samples were collected every month from four sampling sites. Liquid–liquid extraction followed by HPLC was used for the determination of 10 carbamate pesticides. The ranges of the most commonly encountered pesticides in the surface river water were for carbofuran 25–206 ng L<sup>-1</sup>, aldicarb nd–69 ng L<sup>-1</sup>, aldicarb sulphoxide 5–107 ng L<sup>-1</sup>, methomyl nd–86 ng L<sup>-1</sup>, 3-hydroxycarbofuran nd–117 ng L<sup>-1</sup>, propoxour nd–91 ng L<sup>-1</sup>, carbaryl 10–100 ng L<sup>-1</sup>, and methiocarb 7–117 ng L<sup>-1</sup>. The higher concentrations in river water were measured during the period of May to October, following seasonal application, and diminished significantly during the autumn and winter. The highest concentrations of the carbamate pesticides were detected in sampling site 2 (Piniada), near an area with intense agricultural activity. This work clearly demonstrates that agricultural practices in the agricultural area of Thessaly have degraded the quality of surface waters. *N*-methylcarbamate pesticides data obtained in this study were statistically analysed by two-way analysis of variance (ANOVA). It was proved that both seasonal and spatial variations are significant sources for the total variance, the latter making a greater contribution than the former.

*Keywords:* Carbamate pesticides; Pinios River; Monitoring

### 1. Introduction

The worldwide increase in the use of pesticides during the last decades has led to the presence of residues of these pesticides not only on the crops to which they are applied but also, owing to leaching into and runoff from the soil, in ground water and surface waters, respectively. Pesticides and other organic compounds also can be transported into the atmosphere by various processes. Once in the atmosphere, these compounds can be dispersed by air currents and redeposited on water and land surfaces, often at considerable distances from their origin. More than 20 agricultural pesticides have

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been reported in fog and rainfall in the USA, Canada, and Europe. Because of the proven or suspected toxicity of many of these pesticides, their monitoring is needed from both regulatory and the consumer points of view [1, 2].

Carbamates are an important class of pesticides and have come into increasing use as substitutes for organochlorine pesticides because of their biodegradability and low phytotoxicity. They are widely used as insecticides or fungicides. The *N*-methylcarbamates (NMCs) have the highest insecticide activity of this group.

Carbamates are effective insecticides by virtue of their ability to inhibit the enzyme acetylcholinesterase like the organophosphorus compounds, but with the carbamates the inhibition is reversible, so they are less toxic to mammals. They can also inhibit other esterases. The carbamate pesticides carbofuran, carbonyl and aldicarb are highly toxic to cold and warm water fish, freshwater, invertebrates and to birds [3].

Numerous studies have shown that carbamates can be flushed from croplands and transported to receiving waters as pulses during spring and early summer rainfall, and climatic and hydrological conditions seem to be the principal means of control regarding the concentrations of carbamates in surface water [4].

The recent discovery of aldicarb in the groundwater of agricultural regions prompted many countries to regulate pesticide use and require routine monitoring of drinking water and raw source water, since the maximum allowable concentration (MAC) for drinking water established by the EEC is  $0.1 \mu\text{g L}^{-1}$  for individual pesticides and  $0.5 \text{mg L}^{-1}$  for total pesticides [4].

Carbaryl is known for its wide application as an insecticide and low mammalian toxicity ( $\text{LD}_{50}$  for the rat by ingestion =  $850 \text{mg kg}^{-1}$ ). Carbaryl and carbofuran are known for their toxicity to honeybees, and some others are suspected carcinogens and mutagens.

Deterioration of surface water and especially river water quality has recently been observed in many aquatories [5]. The potential causes of such a situation are various point and non-point sources. The impact of point-source pollution (domestic and industrial effluents) can be localized and well established, whereas the influence of non-point pollution (runoff from intensively cultivated areas and urban centres) is less obvious because of the inadequately defined direction and frequently of non-point source loading. Most of those activities lead to the pollution of rivers [6, 7]. In Greece, both point and non-point pollution sources contribute to the deterioration of river water quality. Until recently, few domestic waste-water treatment plants were in operation in Greece, and consequently, in many cases, urban effluents are still being discharged untreated to the neighbouring water sources. On the other hand, because agriculture represents a major activity in Greece (with extensive use of fertilizers and pesticides), agricultural land runoff also plays a very important role in the degradation of the surface water quality, especially in the region of Thessalia, which is the largest plain with the highest agricultural production in Greece. To prevent the adverse environmental effects of development onto a river system and its catchment area, the implication of an integrated environmental management plan is considered as the most effective approach to ensure sustainable use of water resources and protection of river water quality.

The major categories of pesticides used in Greece are insecticides (3520 tonnes/year) herbicides (3440 tonnes/year) and fungicides (2800 tonnes/year). Triazines (27% of the total used herbicides) and organophosphorus compounds (23% of the total used insecticides) are the main chemical groups used [8]. Organochlorine insecticides

such as DDT, endrin, dieldrin, aldrin, heptachlor, heptachlor epoxide, and technical benzene hexachloride (BHC) were extensively used in Greece before 1972.

The concentrations of carbamate pesticides in rivers and lakes of northern Greece range from not detectable to  $38 \text{ ng L}^{-1}$ . The annual application of these pesticides is for 60 tonnes/year for carbaryl, 150 tonnes/year for carbofuran and 50–60 tonnes/year for thiram; and for central Greece (Thessalia), the annual application of carbamate pesticides was more than 80 tonnes. These compounds are rarely detected in freshwater systems, as their stability decreases quite markedly in aquatic environments, where they can persist for only 4–12 weeks, depending on temperature, pH, etc. [9–11].

It is of considerable interest that, although carbamate pesticides such as carbofuran, aldicarb sulphoxide and methiocarb are commonly applied to fields of corn, cotton, wheat, and some fruit in the region, no study searching for carbamates has been reported in this area.

Most carbamates are thermally unstable. Hence, it is necessary to analyse them by liquid chromatography rather than by gas chromatography. A large number of methods for the determination of *N*-methyl carbamates and some of their degradation products use post-column fluorescence derivatization with *o*-phtalaldehyde (OPA), which allows direct injection of samples for trace determination [12].

The objective of this article was to study the seasonal variations and distribution of *N*-methylcarbamate pesticides in the river Pinios in the main plain of central Greece (Thessalia) in a predominantly agricultural region during a period of one year (from January to December 2003). The water samples were collected every month from four sampling sites.

## 2. Experimental

The Pinios river catchment basin (ca.  $4 \times 10^3 \text{ km}^2$ ) with the sampling sites is shown in figure 1. The area, with a population of about 500 000 inhabitants, is mainly agricultural with little industrial activity. The drinking-water and irrigation needs of this area are covered by groundwater extracted from numerous boreholes. In parallel, a significant percentage of the water needs are covered by surface water from the Pinios and its tributaries, distributed via a dense network of earthed irrigation canals. The natural environment is still relatively unspoilt in the greater part of the basin, but environmental destruction and degradation problems have become more important in recent years as a result of poor management of environmental matters [13].

Pinios, together with its tributaries, is the unique receiver of the largest hydrological basin in Greece. The mean water discharge is about  $108 \text{ m}^3 \text{ s}^{-1}$ . Apart from agricultural and industrial activities, the river is largely influenced by the domestic sewage of the city of Larissa (150 000 inhabitants). Daily, about  $25\,000 \text{ m}^3$  of treated sewage water from the city of Larissa and about  $12\,000 \text{ m}^3$  of treated industrial effluents are discharged directly into the river.

Four sampling sites were established along the river Pinios. Surface-water samples (ca. 0.5 m under the surface and the middle of the river) were taken (punctual sampling) in a monthly rate. In most cases, turbulent conditions prevail. Sampling Site 1 (Karavoporo, upstream of the catchment basin) was located south of the city of Trikala, after its confluence with the tributary Lithos and after the discharge of the

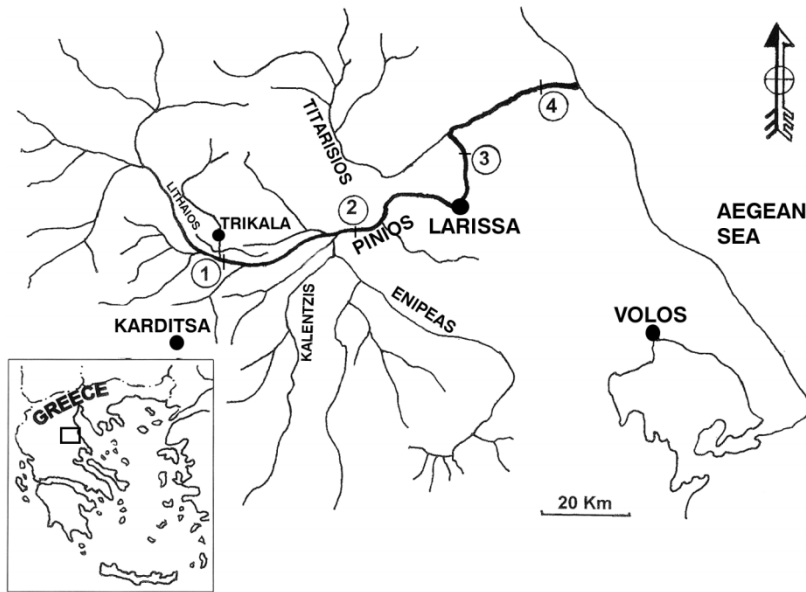


Figure 1. Map of the area studied with sampling sites.

municipal sewage of the city of Trikala. Sampling site 2 (Piniada) was located after the confluence of Pinios with its tributaries Enipeas and Kalentzis. Sampling site 3 (Koulouri) was located near the village Koulouri, after an area where the treated municipal sewage from the city of Larissa and wastewaters from the industrial zone are discharged. Sampling Site 4 (Palaiopyrgos, downstream of the catchment basin) was located after the exit of the river from the narrow pass of Tembi. In this area, more than 20 springs, which are unpolluted, are discharged into Pinios' river flow. From this site, up to the estuaries of the Pinios in Aegean Sea, the river is polluted only from agricultural runoff.

The environmental problems met in the Pinios river basin may be considered typical of many other areas in Greece and include: (1) pollution from the discharge of municipal sewage, industrial waste and agricultural runoff to the river, (2) uncontrolled disposal of municipal refuse, (3) overuse of water resources, (4) uncontrolled use of pesticides and air-spraying practices.

Its water quality is very important because it is used for water supply, irrigation, and industrial needs. The agricultural cultivations in this area are: cereals, cotton, sugar beets, tobacco, vegetables, tree plantations, etc. The increased used of N- and P-fertilizers created unfavourable conditions for the environment. In some cases, the  $\text{NO}_3$  concentrations increased significantly in groundwater because of leaching. In addition, eutrophication processes have already been observed at the river estuary.

The basin of the Pinios River estuary, which has an area extent of  $62 \text{ km}^2$  and a very smooth topographic relief with negligible altitude profile, is formed of fluviolacustrine alluvial deposits and is characterized by significant lateral and vertical variation of lithology and thickness.

Currently, 27% of the land is used for agriculture, 37% is occupied by forests, 25% is rangeland, 2% is wetlands, while the rest, 9%, is used up by other activities. The mean annual rainfall at this region is around 800 mm.

## 2.1. Chemicals

HPLC-grade methanol, dichloromethane, and water were obtained from Merck (Germany). Analytical reagent grade standards for aldicarb, aldicarb sulphoxide, carbaryl, methomyl, propoxour, methiocarb, 3-hydroxy-carbofouran, carbo-fouran-oxamyl, and aldicarb sulphone were purchased from Merck (Germany) with  $\geq 98\%$  purity. Chromatographic-grade *o*-phthalaldehyde (OPA) and carbamate analysis hydrolysis reagent were purchased from Pickering Laboratories (USA). The OPA reagent solution and the HPLC mobile-phase solvents were degassed under vacuum prior to use.

## 2.2. Chromatography

Separation of pesticides was performed by high-performance liquid chromatography (HPLC) with a Shimadzu LC-10 system workstation consisting of a solvent delivery system and the RF-10A fluorescence detector. The analytical column was  $250 \times 4.6$  mm i.d. prepacked with a sum octadecylsilica and was connected to a valve with a  $20 \mu\text{L}$  loop. Post-column fluorescence derivatization was performed with a Pickering Laboratories PCX 5100 derivatization unit. The chromatographic separation was made with the following methanol–water gradient elution programmes using the LC-post-column fluorescence detector system: at  $42^\circ\text{C}$ , 20% of methanol at time 0 for 1 min, 75% up to 44 min, and 100% up to 49 min, with a reagent flow rate of  $0.3 \text{ mL min}^{-1}$  [12].

## 2.3. Water-sample preparation

River-water samples were collected from four sampling sites in 1 L glass bottles. The vials were carefully filled just to overflowing, to prevent any air entrapment. To prevent degradation of some of the more labile carbamates, the water samples have been conserved by adding glacial acetic acid to yield a pH of 3. Samples were filtered through fibreglass filters to remove sand and debris and stored in a refrigerator ( $4^\circ\text{C}$ ).

## 2.4. Analytical procedure

An 800 mL sample of surface water was extracted with four separate 100 mL portions of dichloromethane using a separating funnel and shaking vigorously. The organic phases were combined and concentrated in a rotary evaporator under vacuum. The residues of carbamates were collected with 5 mL of  $\text{CH}_2\text{Cl}_2$  and then transferred into a centrifuge tube. The extract was evaporated to dryness with a gentle stream of nitrogen, and the residue was taken up in 0.5 mL of methanol. From the final extract,  $20 \mu\text{L}$  was injected into the HPLC system. The carbamate concentrations were calculated via the internal standard BDMC (4-bromo-3,5-dimethylphenyl-N-methylcarbamate) for both sample extracts and standard mixtures, each containing the same absolute amount of internal standard ( $100 \mu\text{L}$ ) [14–16]. Sample analysis was run in either duplicate or triplicate, and relative standard deviations of less than 15% were generally achieved. Recoveries of spiked pesticides from samples generally varied between 75% and 113%, with relative standard deviations of approximately 4–12%. Appropriate corrections were made for recoveries. The detection limits were  $2\text{--}5 \text{ ng L}^{-1}$  according to compound response for a 100 mL water sample.

Table 1. Average percentage recovery, retention time, detection limits, and range of concentrations of the analysed pesticides.

No.	Pesticides	Retention time (min)	Recovery (%)	Limit of detection (LOD ng/L)	SD (%)	Range of concentrations (ng/L)
1	Aldicarb sulphoxide	6.90	75	4	6	5–107
2	Aldicarb sulphone	7.91	110	5	5	nd <sup>a</sup>
3	Oxamyl	8.93	108	5	4	nd
4	Methomyl	10.84	113	3	7	nd–86
5	3-Hydroxycarbofuran	18.81	108	2	6	nd–117
6	Aldicarb	24.75	80	4	12	nd–69
7	Propoxour	30.33	77	4	11	nd–91
8	Carbofuran	30.88	107	3	4	25–206
9	Carbaryl	32.84	108	2	6	10–100
10	Methiocarb	42.32	102	3	5	7–117

<sup>a</sup>nd: not detected.

Analysed *N*-methylcarbamate pesticides, and their retention time, mean recoveries and detection limits are shown in table 1.

### 3. Results and discussion

The results of the analyses of the samples have shown the presence of a number of *N*-methylcarbamate pesticides in the river Pinios water samples. The compounds detected were aldicarb sulphoxide, aldicarb, carbaryl, methomyl, propoxour, methiocarb, 3-hydroxy-carbofouran, and carbofouran. No detection of oxamyl and aldicarb sulphone could be observed in any sample. Aldicarb sulphone has not been allowed for use in agriculture for many years, while oxamyl is mainly used for greenhouse vegetables, which are not cultivated in this area. Additionally, aldicarb sulphone is hydrolysed very rapidly in water media, which could explain the lack of detection.

The results (mean values) of water-sample analyses are presented in figure 2. Sampling was carried out every month from January 2003 to December 2003. The highest concentrations of the carbamate pesticides were detected in station 2 (Piniada) because of the confluence with the tributaries Kalentzis and Enipeas in that area. These tributaries transfer the pesticide residues from an area (Trikala and Karditsa) with intense agricultural activity. In this area, large quantities of many types of pesticides have been applied each year.

At sampling site 4 (Palaiopyrgos), which is located after the exit of the river from the narrow pass of Tempi and before the estuaries of the Pinios in Aegean Sea, water pollution by carbamate pesticides was the lowest, probably due to (1) physical dilution of Pinios from more than 20 spring waters, which are unpolluted, and (2) the small amounts of pesticides in this agricultural area, and (3) the possible transfer of these compounds from their application sites.

The concentrations of carbamate pesticides show little variation (figure 3) between the sampling stations 1 (Karavoporo) and 3 (Koulouri). Methomyl, 3-hydroxy-carbofouran, aldicarb, and propoxour were detected in the river waters of sampling stations 1, 3, and 4 only during the application season, while at sampling site 2, they were detected all year round, indicating that this area is the most polluted.

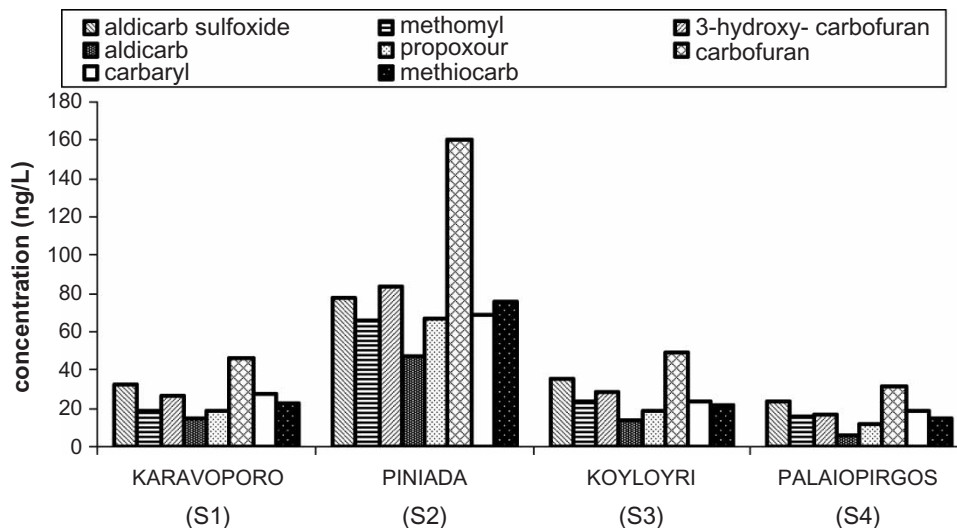


Figure 2. Mean concentrations of *N*-methylcarbamate pesticides examined in Pinios river water from four sampling sites.

The highest concentrations of pesticides detected in river waters were  $107 \text{ ng L}^{-1}$  for aldicarb sulphoxide,  $86 \text{ ng L}^{-1}$  for methomyl,  $117 \text{ ng L}^{-1}$  for 3-hydroxycarbofouran,  $69 \text{ ng L}^{-1}$  for aldicarb,  $91 \text{ ng L}^{-1}$  for propoxour,  $206 \text{ ng L}^{-1}$  for carbofuran,  $100 \text{ ng L}^{-1}$  for carbaryl, and  $117 \text{ ng L}^{-1}$  for methiocarb, and occurred in October for almost all compounds. Carbofuran is detected in higher concentrations in all the other *N*-methylcarbamate pesticides and at all sampling sites. Its concentration showed considerable temporal and spatial variation:  $35\text{--}62 \text{ ng L}^{-1}$  at sampling site 1,  $120\text{--}206 \text{ ng L}^{-1}$  at sampling site 2,  $38\text{--}64 \text{ ng L}^{-1}$  at sampling site 3, and  $25\text{--}42 \text{ ng L}^{-1}$  at sampling site 4.

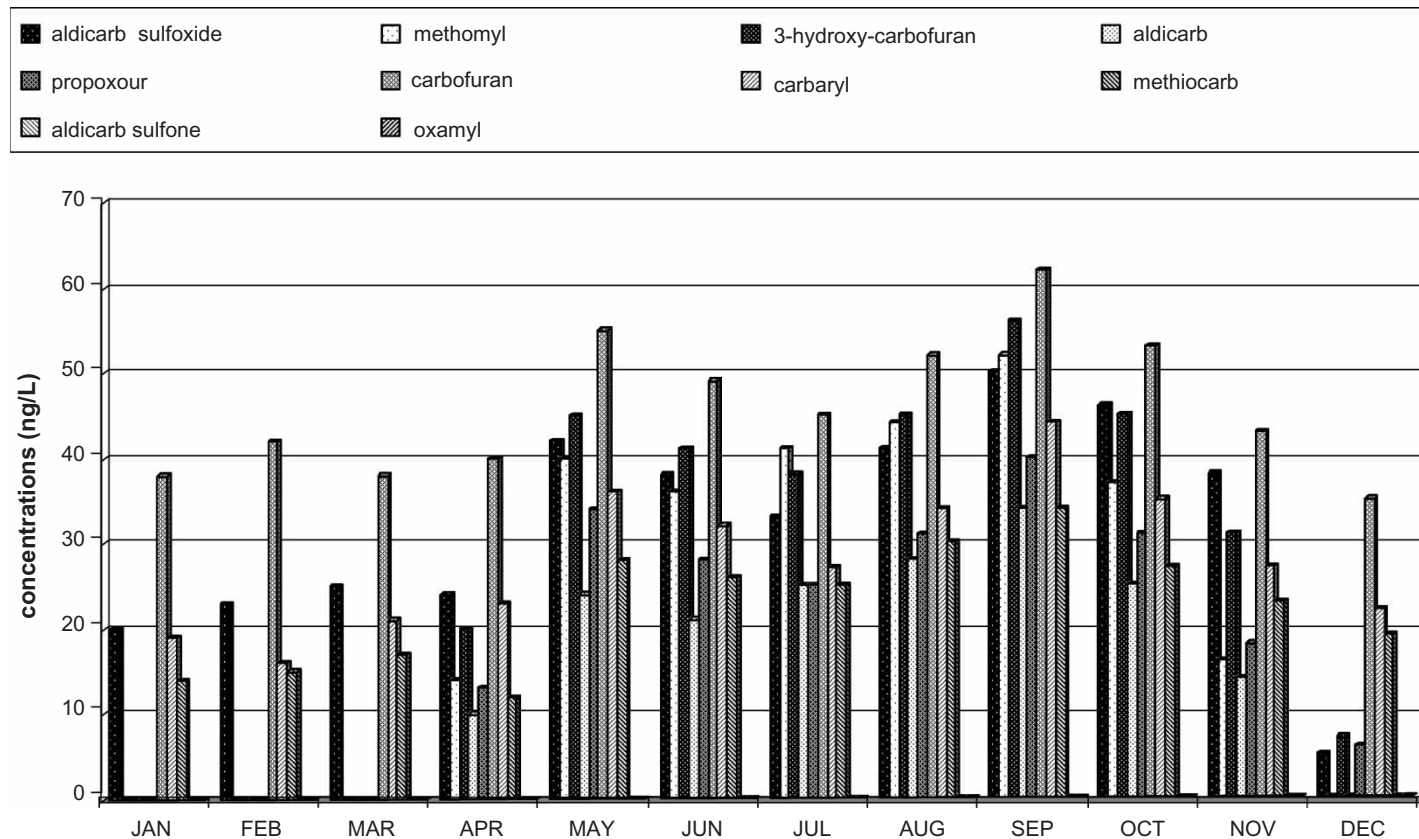
Generally, high concentrations were detected from May to October, the period of major inputs of these compounds, just after their application. This result was in accordance with the field application of pesticides in that area, where the application period of pesticides generally lists about 16 weeks, starting in the last week of April and lasting until the first week of September. Autumn and winter applications are minima, and this is reflected in the small concentrations and low detection frequency during the autumn and winter months.

A correlation analysis between the various analytes taking into consideration all the sampling periods and all the sampling stations revealed that all the analytes are strongly correlated ( $r > 0.85$ ; level of significance  $\alpha = 0.05$ ). This fact proves that the behaviour of the analytes follows a well-defined model during the whole year and reflects the simultaneous usage of these compounds in the whole examined area (table 2).

In order to assess the overall variation of the concentration levels and the contribution of the seasonal changes as compared with the spatial changes, a two-way analysis of variance was applied to the results of all the sampling sites. The results are shown in table 3. It was shown that both seasonal and spatial variations are significant sources for the total variance at the 95% probability level. However, a more detailed comparison between these two sources of variance shows that the spatial variation is a stronger contributor than the seasonal variation (table 3).



## Site 1: Karavoporo

Figure 3. Temporal and spatial distribution of the examined *N*-methylcarbamate pesticides at four sampling sites on the Pinios River.

Site 2: Piniada

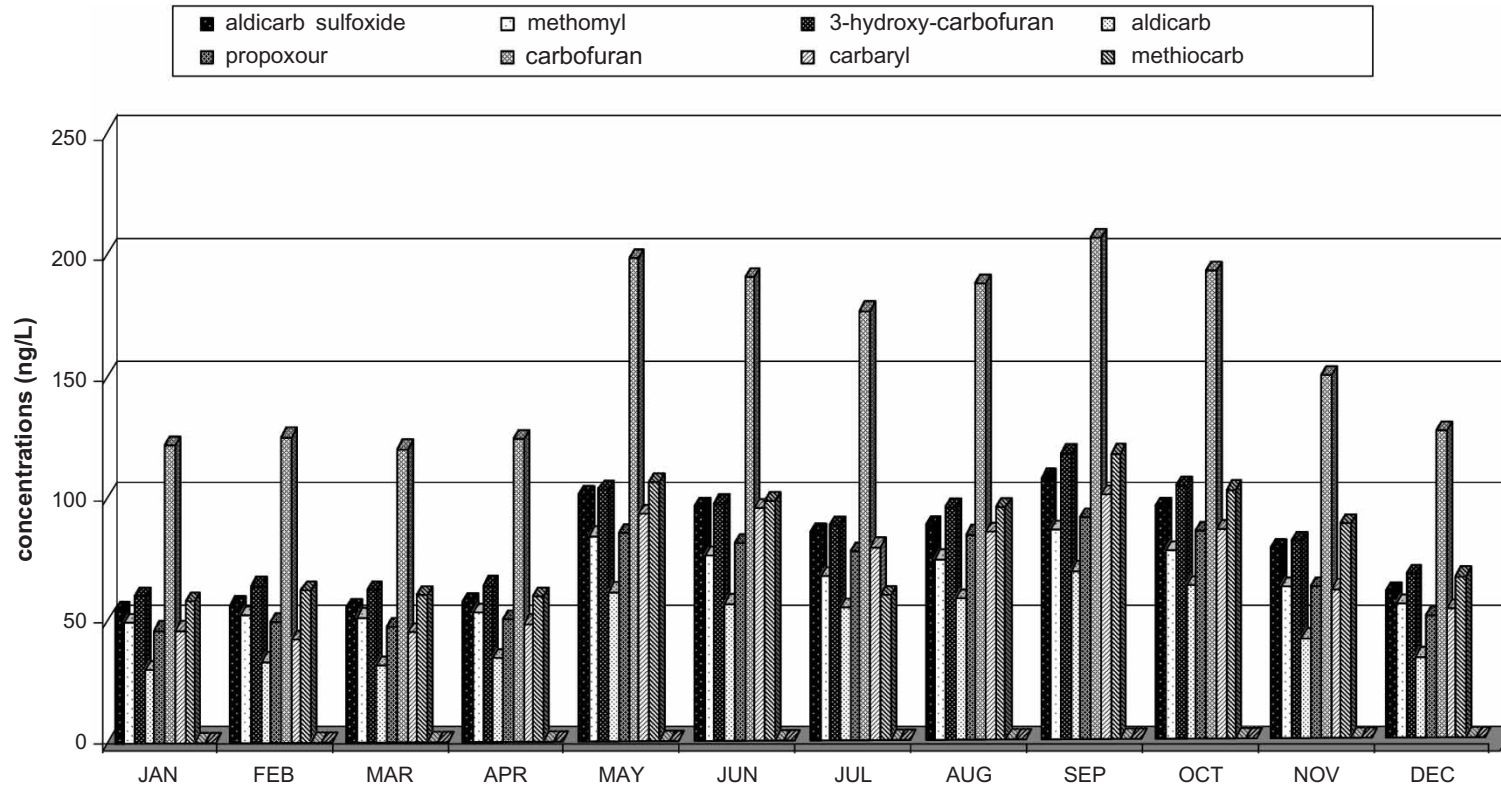


Figure 3. Continued.

## Site 3: Koulouri

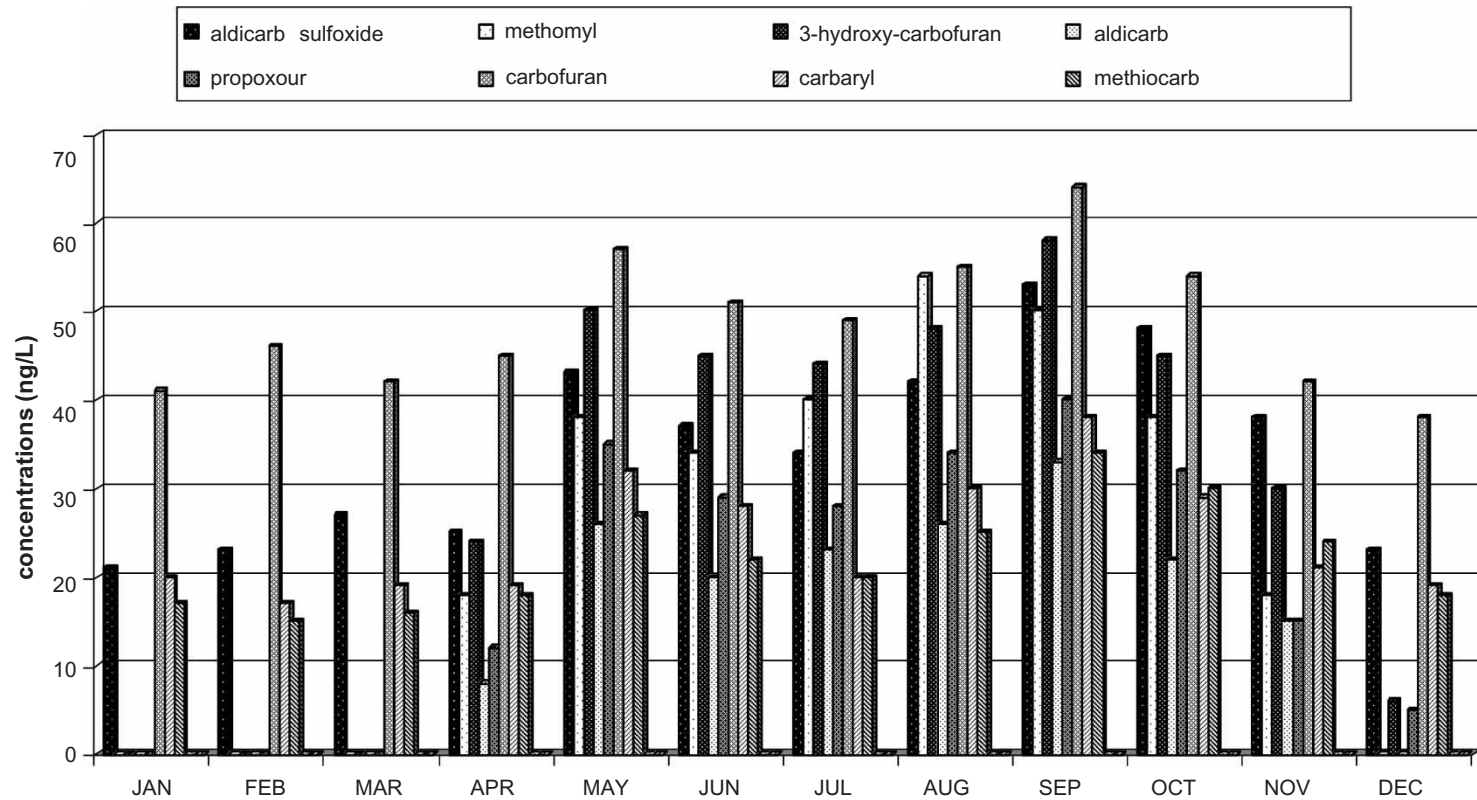


Figure 3. Continued.

Site 4: Palaiopyrgos

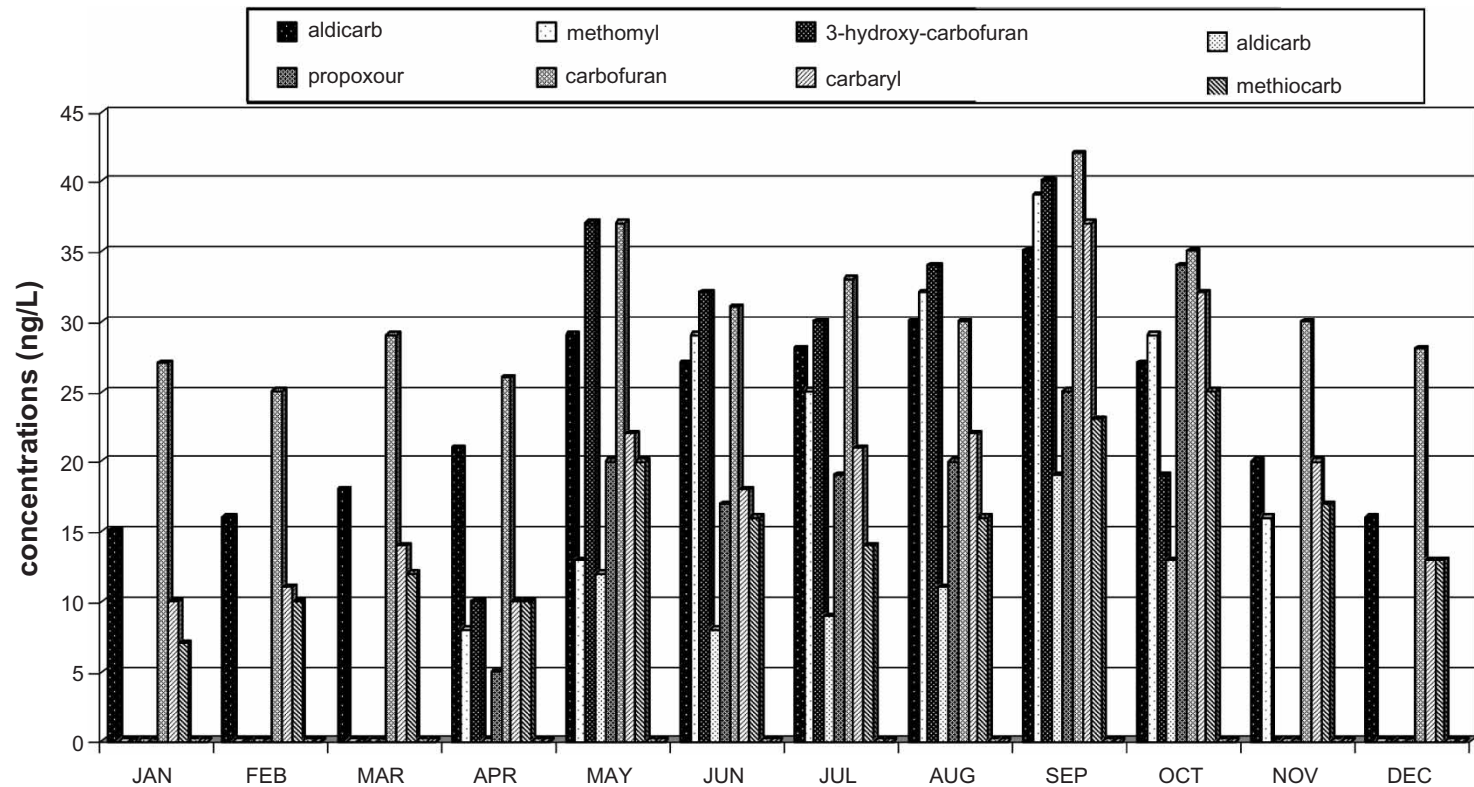


Figure 3. Continued.

Table 2. Correlation matrix between all the analytes.

	Aldicarb sulphoxide	Methomyl	3-Hydroxy-carbofuran	Aldicarb	Propoxour	Carbofuran	Carbaryl	Methiocarb
Aldicarb sulphoxide	1.0000							
Methomyl	0.9242	1.0000						
3-Hydroxy-carbofuran	0.9582	0.9746	1.0000					
Aldicarb	0.9715	0.9691	0.9848	1.0000				
Propoxour	0.9694	0.9647	0.9832	0.9868	1.0000			
Carbofuran	0.9553	0.8480	0.8959	0.9140	0.9315	1.0000		
Carbaryl	0.9709	0.8921	0.9240	0.9503	0.9593	0.9626	1.0000	
Methiocarb	0.9557	0.8639	0.9056	0.9175	0.9339	0.9781	0.9610	1.0000

Table 3. Results of a two-way analysis of variance.

Analyte	Source	df <sup>a</sup>	MS <sup>b</sup>	F <sub>exp</sub>	F <sub>crit</sub>
Aldicarb sulphoxide	Seasonal	11	593.2	12.6	2.1
	Spatial	3	7075.7	150.8	2.9
	Error	33	46.9		
Methomyl	Seasonal	11	1126.7	32.8	2.1
	Spatial	3	6068.7	176.5	2.9
	Error	33	34.4		
3-Hydroxy carbofuran	Seasonal	11	1509.4	47.2	2.1
	Spatial	3	10817.0	338.0	2.9
	Error	33	32.0		
Aldicarb	Seasonal	11	520.2	32.0	2.1
	Spatial	3	3897.6	240.0	2.9
	Error	33	16.2		
Propoxour	Seasonal	11	873.7	51.1	2.1
	Spatial	3	7853.4	459.5	2.9
	Error	33	17.1		
Carbofuran	Seasonal	11	731.9	3.5	2.1
	Spatial	3	42254.7	201.2	2.9
	Error	33	210.0		
Carbaryl	Seasonal	11	485.8	7.4	2.1
	Spatial	3	6391.1	97.2	2.9
	Error	33	65.7		
Methiocarb	Seasonal	11	383.7	5.2	2.1
	Spatial	3	11246.2	151.4	2.9
	Error	33	74.3		

<sup>a</sup>df: degrees of freedom. <sup>b</sup>MS: mean square.

Even after elimination of the Piniada station, which is the most polluted site, a two-way ANOVA for the rest three stations applied at the 95% probability level proved that the above conclusion still applies. The reason for this difference is based on the fact that the bulk usage of the analytes is almost simultaneous at all sites during the 'high period', partially masking the effect of the spatial distribution of the examined pesticides. As can be seen from the time-series bar charts, at all sampling stations, the highest concentrations were observed during the semester May–October for almost all the analytes (figure 4).

According to the comparative diagrams for all eight analytes (except aldicarb sulphoxide and oxamyl, which were not detected at all samples and sites), the sampling site at Piniada appears to be more contaminated than the other three. The estimated levels for all analytes at this station are two- to threefold higher than the others. Furthermore, it is clear that the seasonal profile of the analytes is similar at all four stations, with the higher values observed during the period May–October and lower or zero values during the period December–March. A moderate situation is observed for November and April at all stations (figure 4).

#### 4. Conclusions

This work clearly demonstrates that agricultural practices in the agricultural area of Thessaly have degraded the quality of surface waters. The concentrations of pesticides detected are similar to those reported by different authors in several studies [9, 16, 17].

The major inputs of the carbamate pesticides occurred from May to October just after their application. The utilization of surface water containing considerable

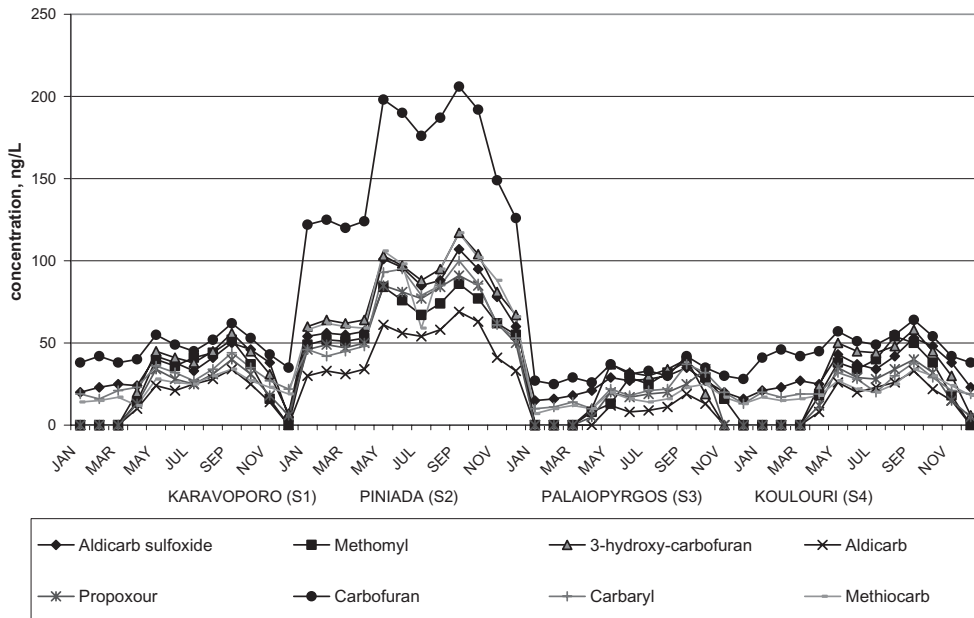


Figure 4. Concentration profiles of the eight analytes in the four sampling sites.

amounts of several pesticides for irrigation purposes can result in an almost uniform distribution of pesticide residues to the whole studied area. It is also possible that agricultural practices that are considered common by local farmers might have effects on the quality of groundwater systems [18, 19].

Rationalization of pesticide application to cultivations would also improve water quality, safeguard the environment, and indirectly increase farmers' incomes. Optimized use of water resources and prevention of pollution of agricultural origin are the key targets of the compiled Code of Good Agricultural Practice for the wider region of Thessaly, which follows the systematic monitoring of water resources in accordance with the current European Union Water Directive (EU Council, 2000).

This article provides a summary of water quality of Pinios River concerning the distribution of carbamate pesticides. Nonetheless, further work is required in relation to flux estimation to provide a detailed assessment of the errors associated with analytical measurements, sampling frequency, and aptness of the record in relation to climate and hydrological variability.

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