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Monitoring of pesticide residues and their metabolites in surface and underground waters of Imathia (N. Greece) by means of solid-phase extraction disks and gas chromatography

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Abstract

Seasonal variations of pesticide residues in surface waters and ground waters of the Imathia area of Central Macedonia (N. Greece) were determined for the period from May 1996 to April 1997. The sampling cruises included eight sites in rivers Aliakmon, Loudias, Tripotamos, Arapitsa and Canal-66, seven water springs in the mountain Vermion, seven rainfall water collection stations and one hundred underground points. Solid-phase extraction disks followed by gas chromatographic techniques with flame thermionic detection, electron capture detection and mass-selective detection were used for the monitoring of various pesticides their transformation products in environmental waters. The most commonly encountered pesticides in underground waters, were alachlor, atrazine, desethylatrazine (DEA), metolachlor, molinate, propanil, simazine, carbofuran, diazinon and parathion methyl. The above compounds including propazine, trifluralin, malathion, parathion ethyl, lindane, α -benzene hexachloride (α -BHC), β -BHC, 4,4'-DDE and heptachlor were determined in river waters. The higher concentrations in underground waters were measured during the period from May to August, 1996, following seasonal application and diminished significantly during the autumn and winter. Water pollution by triazine and chloroacetanilides was highest in the estuarine areas, showing that many of these compounds are transported significant distances from their application sites. The major inputs of atrazine, alachlor, simazine and metolachlor occurred in May and June just after their application. Atrazine, DEA, diazinon and metolachlor were also detected in spring waters at concentration levels below 0.006 $\mu\text{g}/\text{l}$. Finally, atrazine, DEA, carbofuran, simazine, diazinon, parathion ethyl and parathion methyl were detected in rainfall water samples collected in the agricultural area of Imathia (central part of the plain). © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nonpoint-source contamination of surface water and groundwater has emerged as an important environmental problem in the last decade. Although significant advances have been made in controlling point-source pollution, little progress has been accomplished in the area of nonpoint-source pollution

of surface waters and groundwaters. This is because of the seasonality, inherent variability, and multiplicity of origins of nonpoint-source pollution [1]. Pesticide contamination of surface waters and groundwaters from agricultural use has been well documented around the world. Pesticide residues in surface waters have been a concern since the 1940s [2,3]. Before 1970 attention was primarily focused on contamination by organochlorine insecticides. Since that time, a broad array of modern, medium to

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polar pesticides is used in agriculture, with less persistence, partly to reduce the potential for residue contamination of surface waters. Several hundreds of compounds are being employed [4].

The persistence of pesticide residues in the soil and their movement in the water–soil system are key aspects in their environmental behaviour. Pesticides are primarily moved from agricultural fields to surface waters in surface run-off [2]. The amount lost from fields and transported to surface waters depends on several factors, including soil characteristics, topography, weather, agricultural practices, and chemical and environmental properties of individual pesticides [5,6]. The combined effect of these factors on the temporal and spatial magnitude of pesticide concentrations and fluxes in large integrating river systems is largely unknown [3]. Chemical reactions and physical displacements, influence the persistence of the chemicals in the soil, but with different environment implications. Chemicals which are sufficiently resistant to degradation and are adequately soluble to be transported in water may reach the sea in significant amounts. Water run-off and river transport are the main processes involved in the land–sea transfer of the chemicals [6,7].

Freshwater is considered the most precious of all natural resources. In rural areas, groundwater is often the only source of water with acceptable quality for human consumption without treating the water. But groundwater can be contaminated by domestic, industrial and agricultural wastes, including fertilizers and pesticides. Several studies have demonstrated a positive correlation between concentrations of pesticides and nitrates, suggesting that these contaminants are linked through land use practice [8,9]. Monitoring studies have been the most widely used method for assessing groundwater contamination with pesticides. Pesticides detected during monitoring of ground water in the USA and Europe have included atrazine, cyanazine, simazine, alachlor and metolachlor [10–12]. Compiled information on the occurrence of pesticides in groundwater tested across the USA indicates 17 pesticides have been detected across 17 states at levels exceeding the lifetime health advisory level (LHAL) [13]. Carbofuran, methiocarb, methomyl and their metabolites were reported to be the major pollutants in ground waters in Spain at contamination levels from 10 ng/l to 3.0

µg/l [11] and simazine, atrazine, methyl parathion and ethyl parathion were found in raw and finished drinking water in four Spanish cities [11].

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 [14]. More than 20 agricultural pesticides have been reported in fog and rainfall in the USA [15–17], Canada [18] and Europe [19,20].

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

This paper is a study of the seasonal variations, distributions of pesticides in surface water and groundwaters in the main plain of central Macedonia (Imathia) for a period of 1 year (from May 1996 to April 1997). In order to learn more about pesticides in rainfall on a regional scale this study was conducted to investigate the occurrence and depositions of selected pesticides in precipitation water. The selection of the pesticides studied was based firstly on their presence in river and groundwaters as detected by the applied analytical and chromatographical techniques and secondly on their use in agricultural practices in Imathia area. Solid-phase extraction (SPE) disks followed by gas chromatographic techniques with flame thermionic detection (FTD), electron capture detection (ECD) and mass selective detection (MS) were used for the monitoring of various pesticides and their transformation products in environmental waters.

2. Methods and materials

2.1. Area description

Imathia is a Greek province located in the central

Macedonia in the north of Thermaikos Gulf. With 52 760 hectares of cultivated fields (mainly fruit trees), this region has become one of the major suppliers of fruits to most of the EU countries. The major crops cultivated include peach trees 23 640 hectares (44.7%), cotton 8300 hectares (15.7%), corn 7540 hectares (14.1%), sugar beets 1540 hectares (8.6%), apple trees 2770 hectares (5.3%), rice 2500 hectares (4.8%) and others (tobacco, vegetables etc.) during the 1995–1996 season. The agricultural area of Imathia is draining through the rivers Loudias and Aliakmon into the Thermaikos Gulf (Fig. 1). The delta of Loudias and Aliakmon river consist of a large wetland on the Thermaikos Gulf coast, which is protected by the Convention of Ramsar (1971).

Aliakmon river and the small rivers Tripotamos and Arapitsa comprise the main irrigation sources for the plain of Imathia (Fig. 1). The mean annual water flow of Loudias is $15 \text{ m}^3/\text{s}$ and of Aliakmon $28 \text{ m}^3/\text{s}$ with large differences from year to year [21].

The annual usage of the studied pesticides in the agricultural area of Imathia and their physicochemical properties are shown in Table 1. The most used pesticides in the agricultural area of Imathia for 1995 and 1996 were alachlor, atrazine, metolachlor, propanil, prometryne, simazine, molinate, trifluralin, methyl parthion, diazinon and carbofuran. The total amount of pesticides used in Imathia plain was estimated to 4.5% of the total amount used in Greece.

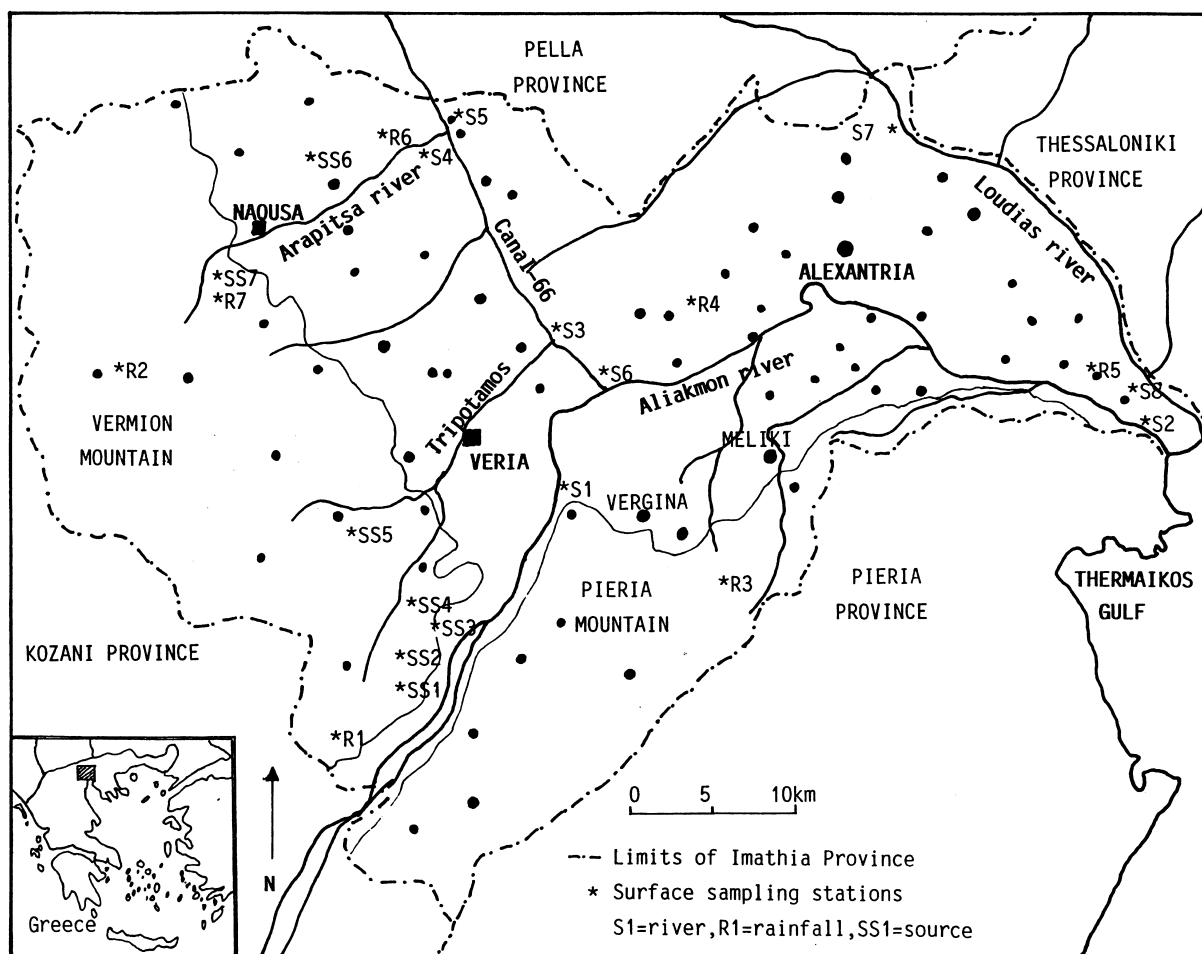


Fig. 1. Studied area of Imathia province and the sampling stations of surface (S), rainfall (R) and sources (SS) waters.

Table 1
Target compounds in Imathia plain, their annual usage (1996) and selected physicochemical and environmental properties

Pesticides	Annual use (kg) ^a	Water Solubility (mg/l)	Soil half-life (days) ^b	Soil sorption (K_{oc}) ^c	GUS score ^d	Leacher
<i>Herbicides</i>						
Alachlor	9400	240	18	120	2.1	Marginal
Atrazine	10 100	35	64	160	4.1	Yes
Metolachlor	5740	530	42	200	2.9	Yes
Molinate	2500	800	60	415	2.5	Marginal
Prometryne	2600	40	60	610	2.4	Marginal
Propanil	2900	200	6	150	1.4	No
Propazine	1100	4.8	25	160	2.5	Marginal
Simazine	4700	5	75	130	3.9	Yes
Trifluralin	7800	0.05	132	8000	0.7	No
<i>Insecticides</i>						
Diazinon	3200	40	32	83	3.0	Yes
Dimethoate	1500	20 000	14			
Carbofuran	3400	351	40	28	3.5	Yes
Ethion	1000	1	20	4350	0.5	No
Fenamiphos	1100	700	10	170	1.8	Marginal
Fenitrothion	1700	30	15	11 500	0.1	No
Fenthion	900	55	15	8900	0.1	No
Malathion	1400	145	4	1800	0.6	No
Monocrotophos	1600	1 (kg/l)		—		
Parathion ethyl	2300	24	18	10 950	0.1	No
Parathion methyl	4900	50	15	5100	0.4	No

^a Regional agricultural use of pesticides estimated from cultivation distribution. The use of aldrin, endrin, dieldrin, α -BHC, β -BHC, DDT, heptachlor and heptachlor epoxide has been banned in Greece since 1972. The use of lindane in agricultural areas of Thessaloniki is estimated to be about 1600 kg in 1995 and 1200 kg in 1996.

^b $t_{1/2soil}$, data of half-life in soil from Jury et al. [22] and Wauchop et al. [23].

^c K_{oc} , sorption coefficient normalized to organic carbon content from Jury et al. [22] and Wauchop et al. [23].

^d The GUS index provides a comparison of soil leaching potential of pesticides based solely on measurements of K_{oc} and soil degradation half-life for each pesticide using the formula: $GUS\ score = \log(t_{1/2}) \cdot [p - \log K_{oc}]$, where $p=4$ [24].

2.2. Sampling

Eight sampling points for surface waters were selected in the main flows and estuaries of rivers Aliakmon, Loudias, Tripotamos, Arapitsa and canal-66. Seven sampling stations were established for rainfall water collection, (three in Vermion mountain, one in Pieria mountain and three in the plain of Imathia). Seven water springs from Vermion mountain and one hundred wells were also involved in this study (Fig. 1).

Water samples were collected monthly for surface waters between May 1996 and April 1997. Water samples from wells were collected in June 1996, September 1996, January 1997 and March 1997. Water depth of wells ranges from 25 to 70 m. Two 2.5-l volumes of water were collected in glass bottles

from each sampling site. After filling with water, the bottles were sealed with screw caps lined with aluminium foil. Samples were acidified to pH 2.5 with sulfuric acid to inhibit biological activity and were filtered through fiber glass filters to remove sand and debris. Samples reached the laboratory 1 day after sampling, stored at 4°C prior to extraction, normally within 48 h.

2.3. Analytical techniques

SPE and chromatographic techniques were applied to quantify pesticides. The collected samples from rivers, were prefiltered on 0.45- μ m HVLP filters (Millipore Bedford, MA, USA) to eliminate particulate matter and were acidified with sulfuric acid (1:1, v/v) to pH 2.5. Methanol modifier (10 ml) was

added to 2-l water samples to allow better extraction [25,26]. Prior to the extraction, the C₁₈ bonded phase (J.T. Baker) and poly(styrene–divinylbenzene) disks of 47 mm diameter and 0.5 mm thickness which contain 500 mg of the bonded phase, were washed with 10 ml of acetone under vacuum followed by 10 ml of methanol. The disk was not allowed to dry, as recommended [27,28]. The sample was mixed well and allowed to percolate through the disks at a flow-rate of 50 ml/min under vacuum. After sample extraction, the pesticides trapped in the disk were collected by using 2×10 ml of dichloromethane–ethyl acetate (1:1, v/v) as eluting solvent. The fractions were evaporated to 0.5 ml in a gentle stream of nitrogen for GC injections.

2.4. Gas chromatographic conditions

2.4.1. GC–MS

A GC–MS, QP 5000 Shimadzu instrument equipped with capillary column 007 Quatrex-Methyl 5% phenylsilicone 30×0.32 mm×0.5 μm was used under the following chromatographic conditions: injector temperature 220°C, column programme of temperatures 55°C (2 min), 55–210°C (5°C/min), 210°C (20 min), 210–270°C (20°C/min), 270°C (4 min). Helium was used as the carrier gas at 14 p.s.i. (1 p.s.i.=6894.76 Pa). The ion source and transfer were kept at 200°C and 300°C, respectively. The spectra were obtained at 70 eV. Two ions for each pesticide were chosen for screening analysis in selected ion monitoring (SIM) mode. The ions traces were divided into five groups that were recorded sequentially during the injection, on the basis of the retention times of the single substances.

2.4.2. GC–FTD

A Shimadzu 14A capillary gas chromatograph equipped with FTD at 250°C, was used. The DB-1 column, 30 m×0.32 mm I.D., used contained methylsilicone (J&W Scientific, Folsom, CA, USA). The column was programmed from 55°C (2 min) to 210°C (20 min) at 5°C/min and to 270°C (4 min) at 20°C/min. The injection temperature was 220°C. Helium was used as the carrier at 25 cm/s and nitrogen was used as make-up gas at 25 ml/min. The detector gases were hydrogen and air, and their flow-rates were regulated according to results given

through the simplex optimization of the analytical variables, in this instance air and hydrogen flow-rates in the detector. The FTD ion source was an alkali metallic salt (Rb₂SO₄) bonded to a 0.2 mm spiral of platinum wire.

2.4.3. GC–ECD

A Shimadzu 14A capillary gas chromatograph equipped with ECD at 250°C, was used. The DB-5 column, 30 m×0.32 mm I.D., used contained 5% methylsilicone (J&W). The column was programmed from 55°C (2 min) to 210°C (20 min) at 5°C/min and to 270°C (4 min) at 20°C/min. The injection temperature was 220°C. Helium was used as the carrier at 25 cm/s and nitrogen was used as make-up gas at 25 ml/min.

2.5. Quantification

Quantification was performed by external and internal calibration using authentic standards. Sample analyses were run in either duplicate or triplicate and relative standard deviations (R.S.D.s) of less than 15% were generally achieved. Recoveries of spiked pesticides from water generally varied between 85 and 110% with R.S.D.s of approximately 5–15%. Appropriate corrections were made for recoveries. GC detectors using FTD, ECD and MS afforded detection limits typically between 1 and 5 ng/l according to compound response for a 2-l water sample.

3. Results and discussion

3.1. Surface water

Table 2 contains a summary of the occurrence and concentrations of pesticides detected in samples collected during the 12-month study period at eight river sampling points. Nine herbicides, atrazine, desethylatrazine (DEA), alachlor, metolachlor, molinate, propanil, propazine, simazine and trifluaralin, four insecticides, diazinon, malathion, parathion ethyl and parathion methyl and six organochlorine insecticides, lindane, α-BHC, β-BHC, 4,4'-DDE and heptachlor were detected in the river water samples throughout the whole subperiod of April 1996 to

Table 2

Summary of pesticides concentrations detected in river water samples from eight sampling sites in Imathia area during May 1996–April 1997^a

Pesticides	Detection (%)	Number of water samples ($\mu\text{g/l}$)	Limits of detection ($\mu\text{g/l}$)	Maximum concentration ($\mu\text{g/l}$)
<i>Herbicides</i>				
Alachlor	15.6	15	0.002	0.265
Atrazine	71.9	69	0.002	0.310
DEA	66.7	64	0.005	0.526
Metolachlor	11.5	11	0.002	0.558
Molinate	19.8	19	0.003	0.320
Propanil	12.5	12	0.005	0.340
Simazine	24.0	23	0.003	0.317
Trifluralin	7.3	7	0.001	0.021
<i>Insecticides</i>				
Diazinon	18.8	18	0.001	0.032
Malathion	2.1	2	0.001	0.018
Parathion ethyl	6.3	6	0.0005	0.090
Parathion methyl	17.7	17	0.0005	0.183
<i>Organochlorine Insecticides</i>				
Lindane	45.8	44	0.0001	0.022
α -BHC	18.8	18	0.0001	0.013
β -BHC	10.4	10	0.0001	0.018
4,4'-DDE	4.2	4	0.0002	0.015
Heptachlor	1.1	1	0.0002	0.008

^a The total number of samples analysed was 96.

April 1997 in the area of Imathia (Tables 2 and 3 and Figs. 1–3). The seasonal variation of herbicides and insecticides detected with high frequency at higher concentrations in Aliakmon and Loudias river are shown in Figs. 2 and 3. The higher concentrations of pesticides detected in river waters were 0.243 $\mu\text{g/l}$ for alachlor, 0.300 $\mu\text{g/l}$ for atrazine, 0.121 $\mu\text{g/l}$ for desethylatrazine, 0.423 $\mu\text{g/l}$ for metolachlor, 0.320 $\mu\text{g/l}$ for molinate, 0.038 $\mu\text{g/l}$ for propanil, 0.317 $\mu\text{g/l}$ for simazine, 0.021 $\mu\text{g/l}$ for trifluralin, 0.022 $\mu\text{g/l}$ for diazinon, 0.018 $\mu\text{g/l}$ for malathion, 0.090 $\mu\text{g/l}$ for parathion ethyl, 0.183 $\mu\text{g/l}$ for parathion methyl, 0.022 $\mu\text{g/l}$ for lindane, 0.013 $\mu\text{g/l}$ for α -BHC, 0.07 $\mu\text{g/l}$ for β -BHC, 0.015 $\mu\text{g/l}$ for 4,4'-DDE and 0.008 $\mu\text{g/l}$ for heptachlor. Water pollution by triazine and chloroacetanilides was the highest in the estuarine areas, showing that many of these compounds are transported significant distances from their application sites. The major inputs of

atrazine, alachlor, simazine and metolachlor occurred in May and June just after their application. DEA was also detected at high concentrations in the same period but no deisopropylatrazine (DIA). The removal of an ethyl chain is preferential over an isopropyl chain, so DEA is more stable [29].

The low observed concentrations of molinate, below 0.1 $\mu\text{g/l}$ (Figs. 2 and 3), may be due firstly to the small amounts used in the agricultural area and secondly to the photodegradation which was reported to be a major route of its dissipation in water [1] and which probably takes place in the fields rather than in the river itself and occurs quickly in summer. Methyl parathion, ethyl parathion and trifluralin were also detected in river waters only during the application season. These compounds show high K_{oc} values and small leaching potential and consequently their residues are adsorbed strongly enough in soil systems. Finally, propanil is the least hazardous com-

Table 3

Mean and range of pesticide concentrations determined in water samples from 8 sampling sites in Aliakmon river, canal 66 and Loudias river during May 1996–April 1997 ($N=24$)

Pesticides	Concentrations ($\mu\text{g/l}$)					
	Aliakmon river (S2, S3)		Canal 66 (S5, S6)		Loudias river (S7, S8)	
	Mean	Range	Mean	Range	Mean	Range
<i>Herbicides</i>						
Alachlor	0.005	Bdl–0.023	0.002	Bdl–0.037	0.020	Bdl–0.265
Atrazine	0.015	Bdl–0.048	0.036	Bdl–0.301	0.022	Bdl–0.310
DEA	0.032	Bdl–0.235	0.062	Bdl–0.526	0.055	Bdl–0.407
Metolachlor	–	Bdl	0.039	Bdl–0.265	0.080	Bdl–0.558
Molinate	0.021	Bdl–0.112	0.001	Bdl–0.010	0.027	Bdl–0.320
Propanil	–	Bdl	0.008	Bdl–0.026	0.050	Bdl–0.340
Simazine	0.002	Bdl–0.027	0.005	Bdl–0.027	0.009	Bdl–0.125
Trifluralin	–	Bdl	–	Bdl	0.002	Bdl–0.016
<i>Insecticides</i>						
Diazinon	–	Bdl	0.005	Bdl–0.032	0.003	Bdl–0.028
Malathion	–	Bdl	0.001	Bdl–0.006	0.004	Bdl–0.018
Parathion ethyl	–	Bdl	–	Bdl	–	Bdl
Parathion methyl	–	Bdl	0.015	Bdl–0.120	0.023	Bdl–0.183
<i>Organochlorine insecticides</i>						
Lindane	–	Bdl	0.009	Bdl–0.16	0.006	Bdl–0.022
α -BHC	–	Bdl	–	Bdl	0.004	Bdl–0.013
β -BHC	–	Bdl	–	Bdl	0.002	Bdl–0.018
4,4'-DDE	–	Bdl	–	Bdl	0.002	Bdl–0.015
Heptachlor	–	Bdl	0.001	Bdl–0.014	0.001	Bdl–0.008

Bdl=below detection limit, $N=24$ (number of analysed samples).

pound in the surface water and it has been reported that ditches are remarkably polluted only immediately after treatment, at concentration levels up to $1 \mu\text{g/l}$ [11].

The concentrations of pesticides detected are similar to those reported by different authors in several studies [29–32]. Hence atrazine, simazine, alachlor and metolachlor, four of the herbicides most widely used in the USA and European countries over the last 30 years for weed control among crops of corn, wheat, barley and sorghum as well as on railroads [33] have been reported in surface and groundwaters throughout the world. They have been detected in many US surface waters at concentrations in the range of 0.05 – $4.7 \mu\text{g/l}$ for atrazine, 0.01 – $0.26 \mu\text{g/l}$ for simazine, 0.08 – $0.55 \mu\text{g/l}$ for alachlor and 0.03 – $1.5 \mu\text{g/l}$ for metolachlor and they are the most commonly detected compounds in the so called 'corn-belt areas' in the Mississippi river [34]. Similar

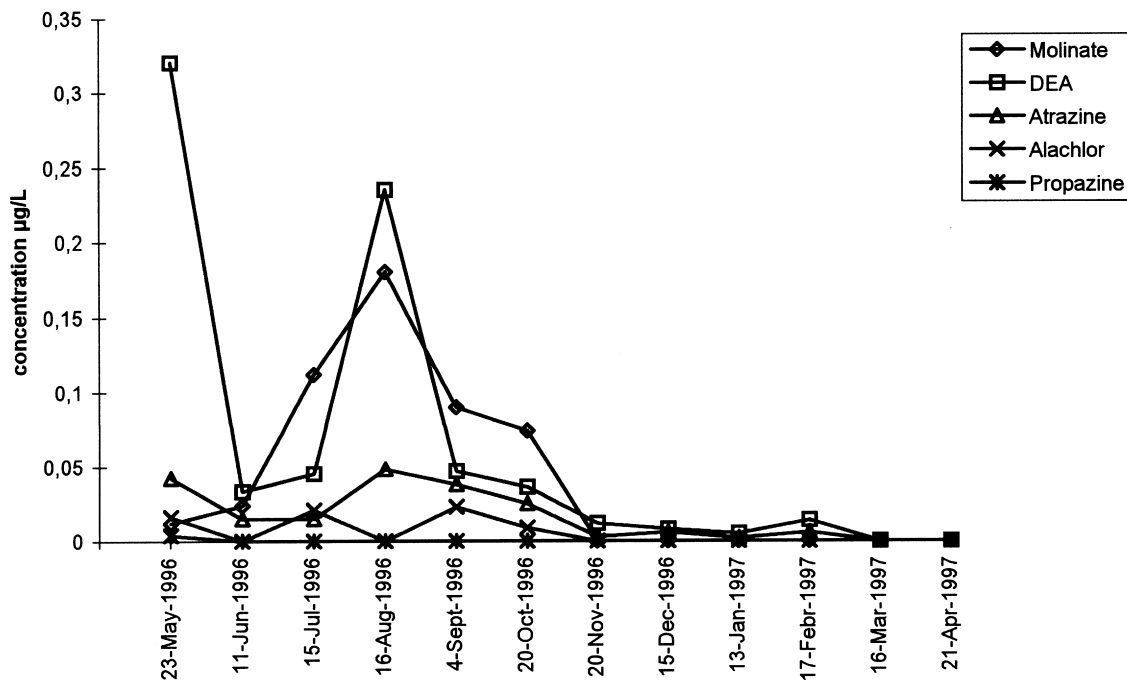
levels of contamination for atrazine, DEA, metolachlor and alachlor, were reported in the surface waters of Spain and Greece reaching 0.3 – $0.5 \mu\text{g/l}$ following spring application. [11,30,35,36]

3.2. Ground water

3.2.1. Water springs

Seven water spring in the mountain Vermion (sampling points SS in Fig. 1) were studied during the 12-month study period. Atrazine, diazinon and DEA residues were detected at Mavroneri spring (SS4) and atrazine, DEA and metolachlor were detected at Aristoteles spring (SS6). Their concentrations levels were below $0.060 \mu\text{g/l}$. The seasonal variation of pesticides detected at water springs of Imathia are shown in Fig. 4.

S-2



S-2

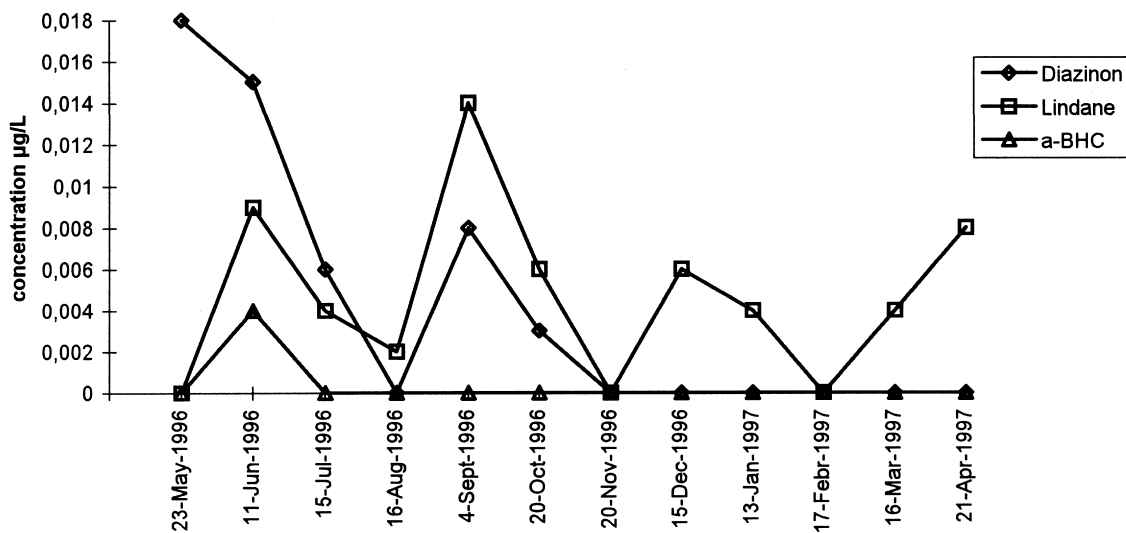


Fig. 2. Seasonal variation of herbicides and insecticides detected at sampling point S2 of Aliakmon river, during May 1996–April 1997.

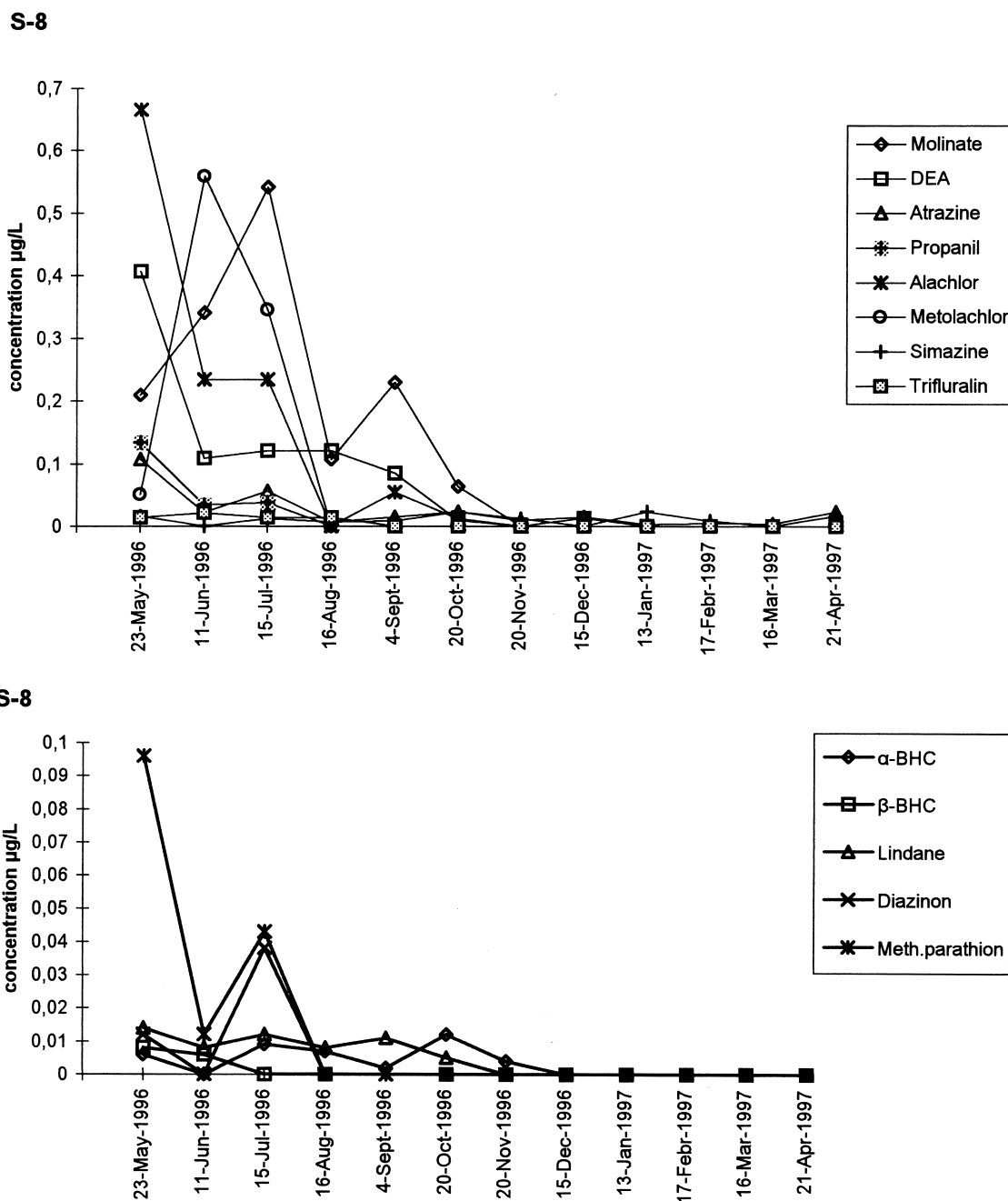


Fig. 3. Seasonal variation of herbicides and insecticides detected at sampling point S8 of Loudias river, during May 1996–April 1997.

3.2.2. Wells

Table 4 contains a summary of the occurrence and concentrations of pesticides detected in samples collected during the 12-month study period at 100

wells of Imathia province. Seven herbicides, atrazine, DEA, alachlor, metolachlor, molinate, propanil and simazine and three insecticides, carbofuran, diazinon and parathion methyl were detected at least

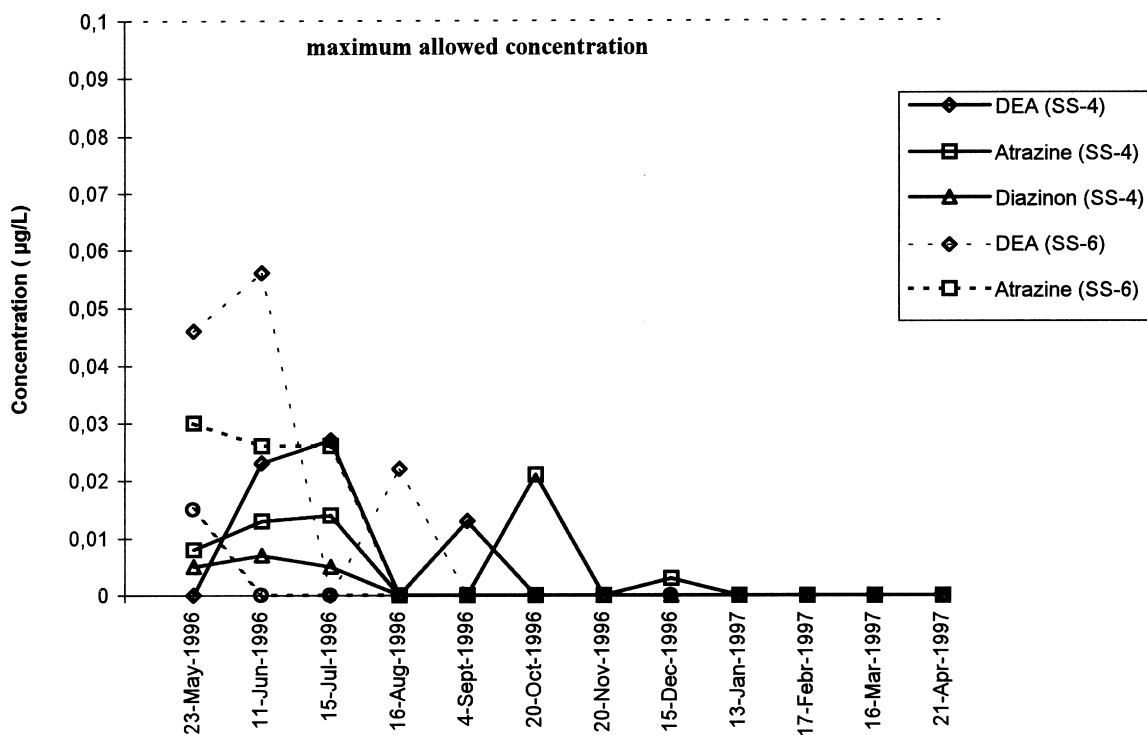


Fig. 4. Seasonal variation of pesticides detected at Mavroneri (SS4) Aristoteles (SS6) water springs during May 1996–April 1997.

once in wells of Imathia throughout the whole subperiod of April 1996 to April 1997. The seasonal variation of herbicides and insecticides detected with

high frequency at higher concentrations in four of the more polluted wells (W-39, W-56, W-64 and W-66) are shown in Fig. 5. The higher concentrations in

Table 4

Summary of pesticides concentrations determined in wells from 100 sampling sites (W) in the Imathia area during May 1996–April 1997

Pesticides	10–14 June 1996		2–5 September 1996		12–16 January 1997		16–20 March 1997	
	Number detection	Max. conc.	Number detection	Max. conc.	Number detection	Max. conc.	Number detection	Max. conc.
<i>Herbicides</i>								
Alachlor	15	0.089	5	0.086	–	–	–	–
Atrazine	42	0.098	33	0.045	28	0.041	20	0.008
DEA	49	0.113	50	0.205	28	0.016	23	0.012
Metolachlor	4	0.041	–	–	1	Bdl-	–	–
Molinate	8	0.013	19	0.077	9	Bdl	–	–
Propanil	4	0.008	3	0.018	2	Bdl	–	–
Simazine	4	0.012	7	0.037	9	0.021	3	Bdl
<i>Insecticides</i>								
Carbofuran	2	0.020	4	0.090	3	Bdl	3	Bdl
Diazinon	6	0.023	9	0.022	5	0.005	2	Bdl
Parathion methyl	1	0.007	2	Bdl*	–	–	–	–

* Bdl=below detection limit.

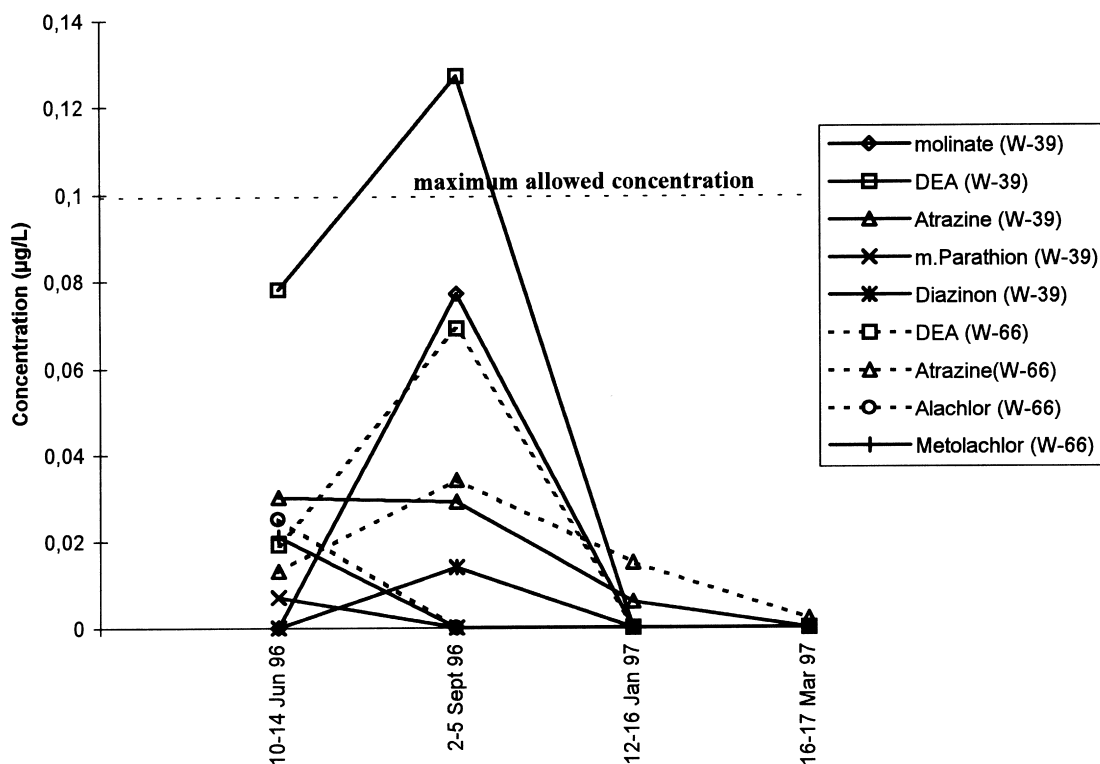


Fig. 5. Seasonal variation of pesticides detected at wells W-39 and W-66, during May 1996–April 1997.

underground waters were measured during the period June 1996, following seasonal application and diminished significantly in the fall and winter. The higher concentrations of pesticides detected in underground waters were 0.089 $\mu\text{g}/\text{l}$ for alachlor, 0.098 $\mu\text{g}/\text{l}$ for atrazine, 0.205 $\mu\text{g}/\text{l}$ for desethylatrazine, 0.090 $\mu\text{g}/\text{l}$ for carbofuran, 0.041 $\mu\text{g}/\text{l}$ for metolachlor, 0.077 $\mu\text{g}/\text{l}$ for molinate, 0.018 $\mu\text{g}/\text{l}$ for propanil, 0.007 $\mu\text{g}/\text{l}$ for parathion methyl and 0.037 $\mu\text{g}/\text{l}$ for simazine.

Atrazine and its transformation product deethylatrazine were the most frequently detected compounds in this study (Table 4). Because DEA is structurally and toxicologically similar to atrazine [37] total atrazine residue (atrazine+DEA) concentrations may also be an important consideration for their environmental occurrence. The median detectable atrazine concentration (0.026 $\mu\text{g}/\text{l}$, 123 samples) was almost half that of the atrazine residue (atrazine+DEA) concentration (0.062 $\mu\text{g}/\text{l}$, 27 samples).

These data on pesticide concentrations (Table 4) in ground waters of the Imathia area are in accordance with the available data of Table 1, which summarizes the relative leaching potential of selected compounds. GUS scores range well above 2.8, indicating a high propensity for leaching of atrazine, metolachlor, simazine, diazinon and carbofuran. A GUS score of 1.8 to 2.8 is associated with the pesticides alachlor and molinate that have been less consistently found to impact ground water as well as with the pesticides prometryne and fenamiphos which were not detected at all in the studied area. Propanil and methyl parathion are the only compounds belonging in the group of 'nonleachers' which were detected at low concentrations in wells, due in their relatively high rate of application in Imathia area (Table 1).

3.3. Rainfall water

Seven sampling stations were established for

rainfall water collection, three in Vermion mountain, one in Pieria mountain and three in the plain of Imathia (Fig. 1, sampling points R). The higher concentrations of pesticides were measured during the period September–October 1996 in the central part of Imathia plain (rainfall collectors R4, R5 and R6). The higher concentrations of pesticides detected in rainfall waters were 0.007 $\mu\text{g}/\text{l}$ for atrazine, 0.028 $\mu\text{g}/\text{l}$ for DEA, 0.005 $\mu\text{g}/\text{l}$ for simazine, 0.004 $\mu\text{g}/\text{l}$ for carbofuran, 0.017 $\mu\text{g}/\text{l}$ for diazinon, 0.004 $\mu\text{g}/\text{l}$ for parathion ethyl and 0.006 $\mu\text{g}/\text{l}$ for parathion methyl. The triazine metabolite (DEA) and diazinon were present more frequently in rainfall waters than the other present compounds. Trace concentrations of DEA were detected in five samples that contained no detectable atrazine. The ratio of DEA to atrazine concentrations, called the DAR, has been used to investigate surface water–ground water interaction [38]. Median DAR values were estimated to be 0.1–0.5 in surface waters during September–November 1996. The median DAR value calculated for rainfall samples that contained both atrazine and DEA was 1.5 for the same period. Thus, considerably more DEA is present in rainfall relative to atrazine than in rivers and streams of the Imathia agricultural plain. There are several possible explanations for this observation. One hypothesis is that DEA evaporates from the soil into the atmosphere faster than atrazine, resulting in a higher DAR value in rainfall. This hypothesis cannot be fully explored and it seems unlikely that DEA would volatilize from soil at a faster rate than atrazine, since the Henry's law constant for DEA should be similar or smaller than that for atrazine [14]. A second hypothesis discussed by Goolsby et al. [14] for the high DAR value in rainfall is that atrazine may be transformed to deethylatrazine in the atmosphere by photochemical processes. They presume that there is about 25–30% conversion of atrazine to deethylatrazine during its residence time in the atmosphere. More research is needed to better understand the processes and pathways for atmospheric degradation of atrazine and other detected pesticides.

4. Conclusions

This work clearly demonstrates that agricultural practices in the agricultural area of Imathia have

degraded the quality of surface waters, rainfalls and ground waters. The paper also provides a clear example that SPE-diks followed by GC techniques can be used in a routine way for the determination of pesticide pollution in environmental waters from Greece. The pesticides analysed in environmental waters belong in different chemical or/and active groups. Nine herbicides, atrazine, DEA, alachlor, metolachlor, molinate, propanil, propazine, simazine and trifluarlin, four insecticides, diazinon, malathion, parathion ethyl and parathion methyl and six organochlorine insecticides, lindane, α -BHC, β -BHC, 4,4'-DDE and heptachlor were detected in river water samples throughout the whole subperiod of April 1996 to April 1997 in the area of Imathia. Water pollution by triazine and chloroacetanilides was the highest in the estuarine areas, showing that many of these compounds are transported significant distances from their application sites. The major inputs of atrazine, alachlor, simazine and metolachlor occurred in May and June just after their application.

Seven herbicides, atrazine, DEA, alachlor, metolachlor, molinate, propanil and simazine and three insecticides, carbofuran, diazinon and parathion methyl were detected at least once wells of Imathia throughout the whole subperiod of April 1996 to April 1997. Seven pesticides detected in rainfall waters, atrazine, DEA, simazine, carbofuran, diazinon, parathion ethyl and parathion methyl. More DEA was present in rainfall relative to atrazine than in rivers and streams of Imathia agricultural plain. A possible hypothesis for this event is that atrazine may be transformed to deethylatrazine in the atmosphere by photochemical processes but more research is needed to better understand the processes and pathways for atmospheric degradation of pesticides.

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