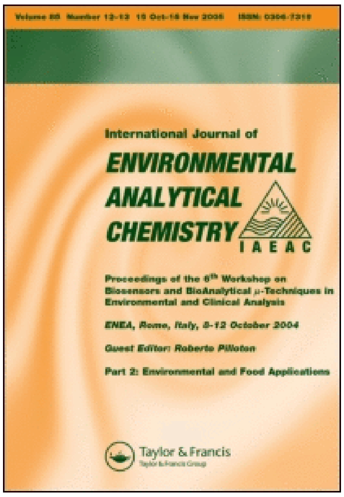

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Pesticide Concentrations in Louros River and Their Fluxes into the Marine Environment

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PESTICIDE CONCENTRATIONS IN LOUROS RIVER AND THEIR FLUXES INTO THE MARINE ENVIRONMENT

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Seasonal variations and riverine input of pesticide residues to the coastal zone were determined in Louros River for the period of 1995 and 1996. The sampling sites for the determination of fluxes were located at the main river flow and its estuary at the boundary between freshwater and the brackish zone. Solid-phase extraction (SPE) disks followed by gas chromatographic techniques (GC with MSD and FTD) were used for the monitoring of various pesticides and metabolites in river waters from the sources to the estuary. The inputs of the five major herbicides, atrazine, simazine, alachlor, metolachlor and desethyl-atrazine (DEA) to the Louros River are mainly from tributaries and the agricultural area draining to the river estuary. The highest concentrations of these pesticides occured in May and June seasons, just after their application. The seasonal variation studies showed a continuous presence of triazines, alachlor and metolachlor, which were detected in the dissolved phase throughout the year at 0.02–0.27 μg/L, whereas the other pesticides exhibited a sporadic occurence related to agricultural and irrigation practices. Atrazine and its degradation product DEA are the most abundant herbicides discharged into Amvrakikos Gulf, followed by metolachlor, simazine and alachlor. Their annual mean flux was estimated as 122.7 g/day for atrazine, 127.5g/day for DEA, 49.1 g/day for metolachlor, 43.9 g/day for simazine and 11.2 g/day for alachlor.

Keywords: Pesticides; concentration; fluxes; river; marine environment

INTRODUCTION

Diffused 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 accompaning in the area of diffused pollution of surface waters and groundwaters. This is because of the seasonality, inherent variability, and multiplicity of nonpoint-source pollution[1]. Pesticide contamination of surface waters

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

Pesticides are the main chemicals among the various pollutants supplied to the marine environment via riverine transport. To estimate the impact of the pesticides on the coastal zone, it is important to understand the quantity and modes of the riverine input. Seasonal variation in the riverine input, form of entry (e.g. dissolved or suspended form), and timing of input (e.g. continuous or pulse discharge) are key considerations for reliable prediction of behavior of the pesticides in a coastal environment. The persistence of pesticide residues in the soil and their movement in the system water-soil are key aspects in their environmental behaviour. Pesticides are primarily moved from agricultural fields to surface waters in surface runoff[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]. Mathematical models developed to simulate the behaviour of pesticides applied to agricultural fields have been used mainly to predict losses of pesticides from individual fields and small watersheds[5]. At this scale, a number of the important variables (such as soil type, rainfall, and agricultural-management practices) can be controlled or measured. It is not known whether predictions from models applied at this small scale, can be extrapolated to account for pesticide transport and fate on a regional scale.

Pesticide properties most directly affecting runoff of pesticides include the dissipation rate in soil, water solubility, and the extent of sorption to soil particles[5,7]. Values of these properties for the pesticides included in this study are shown in Table I. The interaction of these properties and their influence on the amount of specific pesticides transported in runoff water, is complex, and no single property can be used to predict even the relative amounts of various pesticides lost from fields. Recently, Goss[7] developed a relative runoff-potential rating for most pesticides with past or present agricultural use, by using computer simulations with GLEAMS model[8]. The ratings were derived by using combinations of a number of different soils and pesticides as inputs to the model, and examining the predicted runoff losses of pesticides. The pesticides were assigned a runoff-potential rating of small, medium or large, based on the results from these simulations. The runoff-potential ratings derived for the pesticdes included in this study are shown in Table I.

TABLE I Target compounds in Louros river basin, selected chemical and environmental properties, and runoff-potential rating in solution phase (see text)

Pesticides	*Annual use (kg)*[a]	*Water Solubility (mg/L)*	*Soil half-life (days)*[b]	*Soil sorption (Koc)*[c]	*Runoff- potential rate*[d]
Alachlor	4,350	240	18	120	S
Atrazine	7,432	35	64	160	L
Desethyl-Atrazine	-	3200[e]		48	
Carbofuran	800	351	40	28	L
Methyl parathion	1,200	50	15	5100	M
Metolachlor	5,740	530	42	200	L
Molinate	420	800	60	415	
Prometryne	1,930	40	60	610	
Propanil	2,960	200	6	150	M
Simazine	2,470	5	75	130	L
Trifluralin	4,850	0.05	132	8000	M

[a] Regional agricultural use of pesticides estimated from cultivation distribution and agricultural.

[b] $T_{1/2soil}$, data of half-life in soi from Jury et al., 1987[10] and Wauchop et al., 1992[11].

[c] Koc, sorption coefficient normalized to organic carbon content from Jury et al., 1987[10] and Wauchop et al., 1992[11].

[d] Runoff-potential rating, according simulation with GLEAMS model[7]: L-large, M-medium, S-small.

[e] Mills and Thurman, 1994[12].

This paper is a study of the seasonal variations, distributions and fluxes of pesticides in the Louros River basin during January 1995 to August 1996. The fluxes of pesticides from the river into the marine area are estimated by using an averaging based on a collective equation[9]. The selection of the studied pesticides was based firstly on their presence in riverine water as detected by the applied analytical and chromatographical techniques and secondly on their use in the river basin.

METHODS AND MATERIALS

Area description and sampling

Louros river meets the Amvrakikos Gulf (Ionian Sea) which is protected by the Convention of Ramsar (1971). The region of the Amvrakikos Gulf is an almost closed marine area, which communicates with the adjacent lagoons via controlled accesses with narrow channels. The watershed of Louros River includes an area of 800 km^2. The river length is 80 km and the average annual water discharge has been estimated at 19.4 m^3/sec. The agricultural areas at the river watershed have a surface of 74,700 hectars and are cultivated with citrus fruits (30%), olives (22%), alfa-alfa (9%), corn (14%) and cotton (7.5%) etc. The annual amounts of selected pesticides applied in the agricultural area of the river basin as well as their chemical and environmental properties, are shown in Table I. The most used pesticides in 1995 and 1996 were alachlor, atrazine, MCPA, metolachlor, molinate, prometryne, propanil, simazine, terbutylazine and trifluralin .

Water samples for pesticide analyses were collected monthly from January 1995 to August 1996 from five points in the main stream that include one site at the river sources, two sites at the discharge of the main tributaries into the Louros River and two sites at the estuary in the boundary between the freshwater and the brakish zone (Figure 1). Samples were collected by equal-discharge-increment procedure.

The sampling schedule was based on fixed time intervals, rather than the timing of the individual runoff events. Three to five liters of water were collected in glass bottles sealed with aluminum foil lined screw caps. The bottles were transported in the same day to the laboratory, stored at 4°C and extraction carried out normally within 48 h.

Analytical techniques

Solid-phase extraction procedure and chromatographic techniques were applied to quantify the pesticides. The water samples, were pre-filtered over 0.45μm PTFE filters (Millipore Bedford, MA, USA) to eliminate particulate matter and acidified with sulfuric acid (1:1, v/v) to pH 2.5. Methanol modifier (10 ml) was added to 2 L water samples to improve the extraction[13,14]. Prior to the extraction, the C18-bonded phase (J.T. Baker) and SDB disks of 47 mm diameter and 0.5 mm thickness which contained 500 mg of the bonded phase, were washed with 10 ml of acetone followed by 10 ml of methanol under vacuum. The disk was not allowed to become dry, as recommended[15,16]. The water samples were mixed well and allowed to percolate through the disks with a flow rate of

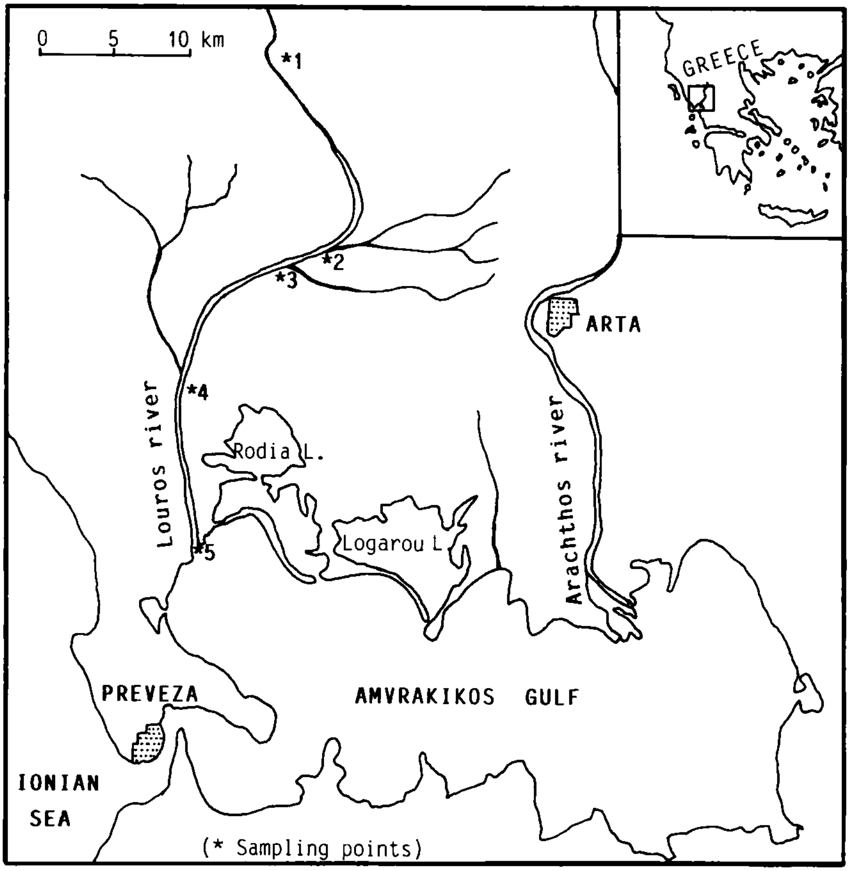

FIGURE 1 Sampling sites at Louros river basin

50 ml/min under vacuum. 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 eluted fractions were evaporated to 0.5 ml in a gentle stream of nitrogen for GC injections.

Gas chromatographic Conditions

GC-MSD

A GC-MSD, QP 5000 Shimadzu equipped with capillary column 007 Quatrex-Methyl 5% phenylsilicone (30m × 0.32 mm × 0.5 μm) was used in the splitless mode at the following chromatographic conditions: injector temperature 220°C, column temperatures from 55°C (2min), to 210 °C (20 min) at 5°C/min and to 270°C (4 min) at 20°C/min. Helium was used as the carrier gas. The ion source and transfer were kept at 200°C and 300°C respectively. The spectra are obtained at 70 eV. Two ions for each pesticide were chosen for screening analysis in selected ion monitoring (SIM). 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.

GC-FTD

A Shimadzu 14A capillary gas chromatograph equipped with flame thermionic detector (FTD) at 250°C was equipped with a methylsilicone DB-1 column, (30m × 0.32mm i.d.) (J & W Scientific, Folsom, CA). 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 gas and nitrogen as make-up gas.

TABLE II Retention times (t_R, min) of 11 selected pesticides in GC-FTD and GC-MS systems, their limits of detection (LOD, ng/L), recoveries with C_{18} extraction phase and standard deviations (SD, ±%)

Peak No/ Pesticides	*FTD/DB-1*				*GC-MS-SIM/Q-007*	
	t_R (min)	*LOD (ng/L)*	*Recovery (%)*	*SD (%)*	*t_R (min)*	*Selected ions (m/z)*
1. Molinate	27.77	5	78.1	18.3	25.79	187,189
2. Desethyl-Atrazine	30.84	10	56.7	6.4	26.35	187,172
3. Trifluralin	31.61	5	78.3	10.5	32.54	335,337
4. Carbofuran	32.32	5	93.6	16.7	33.59	221,223
5. Simazine	32.44	5	88.6	17.4	30.73	201,186
6. Atrazine	32.75	5	92.8	5.6	30.96	200,215
7. Propanil	35.96	2	110.2	15.6	33.72	217,161
8. Methyl parathion	36.80	5	87.3	11.6	34.27	263,265
9. Alachlor	37.84	2	97.5	6.2	34.71	269,188
10. Prometryne	37.55	5	79.3	13.8	35.41	241,226
11. Metolachlor	40.75	2	80.6	8.1	39.15	173,127

Quantification

Quantification was performed with the GC-FTD system after GC-MS-SIM confirmation of the pesticides.Two ions for each pesticide were chosen for screening analysis in selected ion monitoring (SIM) (Table II). Vinclozolin and diazinon were used as "external" and "internal" standards, respectively. Sample analyses were run in either duplicate or triplicate. Riverine water samples (n=3) of 2 L each were spiked with a mixture of 11 selected pesticides to the final concentrations of 0.05, 0.1, 0.25, 0.5 and 1.0 .μg/L for recovery tests. Retention times, recoveries and detection limits obtained for the pesticides are indicated in Table II. Recoveries of "spiked" pesticides from water generally varied between 78.1 to 110.2% with relative standard deviations of approximately 5.6 to 18.3%, except desethyl-atrazine that gave lower recovery at 56.7% (SD=6.4). Appropriate corrections were made for recoveries. GC detectors used, FTD and MSD, afforded detection limits typically between 2 to 10 ng/L for a 2 L water sample (Table II).

RESULTS AND DISCUSSION

Seasonal variations and concentration distributions

The monitoring seasons were devided in three subperiods from January to April, from May to August and from September to December, representing respectively the periods before, during and after pesticide application in agricultural fields. Atrazine, desethyl-atrazine (DEA), simazine, alachlor and metolachlor were detected throughout the whole subperiods while carbofuran, methyl parathion, molinate, propanil and trifluralin were detected only during the period of May to August, at the five sampling stations of Louros River (Table III). The mean concentrations measured in the subperiod from May to August, 1995, were up to 11.9 ng/L for alachlor, 50.5 ng/L for atrazine, 12.4 ng/L for desethyl-atrazine, 1 ng/L for carbofuran, 0.8 ng/L for methyl parathion, 11.8 ng/L for metolachlor, 6 ng/L for molinate, 12.5 ng/L for propanil, 23.7 ng/L for simazine and 69.6 for trifluralin following the application season May to June and diminished significantly in fall and winter. Water pollution by triazine and chloroacetanilides is the highest at the estuarine area, sampling points 4 and 5, (Figures 2d-e) showing that many of these compounds are transported to significant distances from their application sites, but decreased at sampling points 1, 2 and 3 (Figure 2a-c) in a way similar to that reported in a previous survey[9, 17]. Concentration of these herbicides in the dissolved phase are shown in Figure 2. The major inputs of atrazine, alachlor, simazine and metolachlor occured in May and June just after their application. Desethyl-atrazine (DEA) was also detected at high concentrations in the same period but no de-isopropyl-atrazine (DIA). This is not surprising since continued dealkylation of DIA is fast as compared to DEA. The removal of an ethyl chain is preferential over an isopropyl chain, so DEA is more stable[18] and additionaly DIA has poor recovery efficiency with C_{18} and SDB phase extraction[19,20].

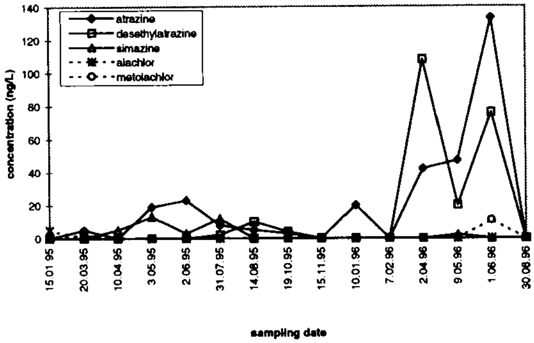

FIGURE 2A Herbicides concentration in Louros river, sampling point 1 for the period Jan. 1995-Aug. 1996

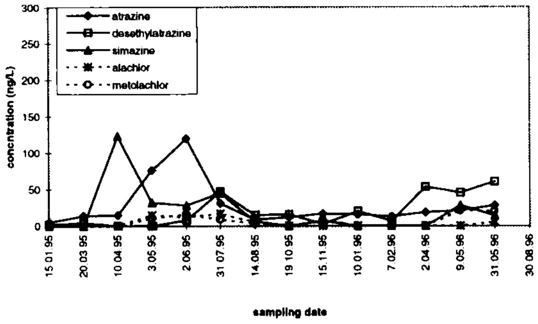

FIGURE 2B Seasonal variation of herbicides concentration in Louros river, sampling point 3 for the period from Jan. 1995 to Aug.1996

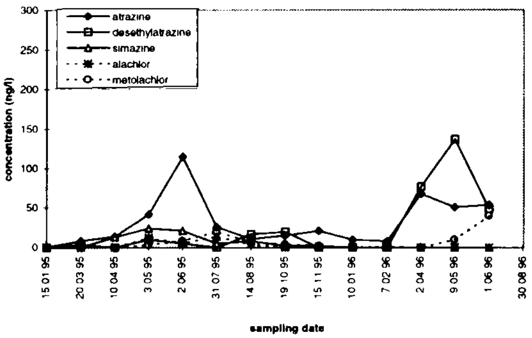

FIGURE 2C Seasonal variation of herbicides concentration in Louros river, sampling point 2 for the period from Jan. 1995 to Aug. 1996

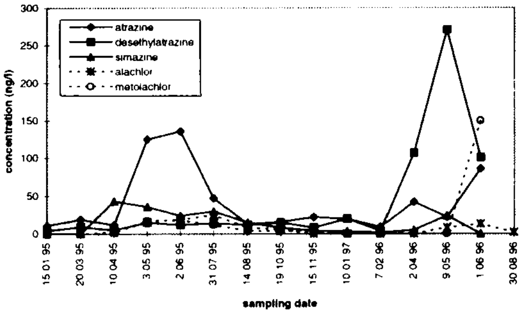

FIGURE 2D Seasonal variation of herbicides concentration in Louros river, sampling point 4 for the period from Jan. 1995 to Aug. 1996

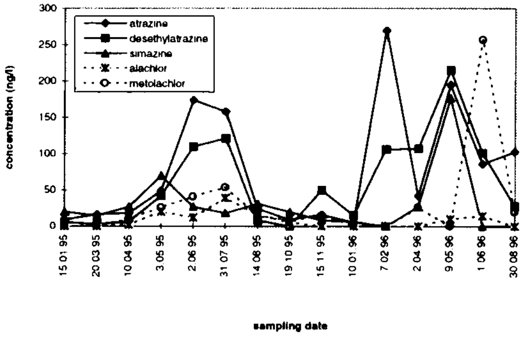

FIGURE 2E Seasonal variation of herbicides concentration in Louros river, sampling point 5 (estuary) for the period from Jan. 1995 to Aug. 1996

TABLE III Mean and range of pesticide concentrations (ng/L) at five sampling stations of Louros river, for the Period from Januarv 1995 to August 1996

Pesticides 1995	*January-April*		*May-August*		*September-December*	
	Mean (N=15)	*Range (ng/L)*	*Mean (N=20)*	*Range (ng/L)*	*Mean (N=10)*	*Range (ng/L)*
Alachlor	0.62	nd-2	11.9	nd-39	1.10	nd-5
Atrazine	9.72	5–18	63.8	9–174	13.1	9–16
Desethyl-Atrazine	2.74	nd-6	25.7	nd-121	11.4	nd-50
Carbofuran	-	nd	1.0	nd-4	-	nd
Methyl parathion	-	nd	0.8	nd-5	-	nd
Metolachlor	0.94	nd-10	13.8	3–54	4.26	nd-14
Molinate	-	nd	6.0	nd-24	-	nd
Propanil	8.6	nd-37	12.5	nd-50	-	nd
Simazine	16.3	nd-27	23.7	6–70	5. 1	nd-20
Trifluralin	-	nd	69.6	nd-206	-	nd
1996	*(N=10)*		*(N=15)*			
Alachlor	0.14	nd-1	1.44	nd-14		
Atrazine	41.7	nd-270	79.8	21–195		
Desethyl-Atrazine	41.4	nd-107	128.9	20–215		
Carbofuran	-	nd	1.71	nd-15		
Methyl parathion	-	nd	0.5	nd-2		
Metolachlor	5.8	nd-26	102	nd-257		
Molinate			3.6	nd-36		
Propanil	-	nd	-	nd-		
Simazine	2.9	nd-27	32.8	nd-177		
Trifluralin	-	nd	29.4	nd-89		

nd = not detected, Prometryne was not detected in any water sample.

The observed low concentrations of carbofuran and molinate may be due firstly to the small amounts used in the agricultural area and secondly to photodegradation, which was reported to be a major route of dissipation of these compounds in water and it occurs quickly in summer[11]. Methyl parathion and trifluralin were also detected in riverine waters only during the application season. These compounds show high Koc values and small leaching potential and consequently their residues are adsorbed strongly enough in soil systems. Finally, propanil concentrations decreased very rapidly along the summer in a way similar to molinate and carbofuran. Propanil, the least hazardous compound in the surface water, was reported to be present in ditch water at concentration levels up to 1 μg/L but only immediately after treatment[21].

The concentrations of the pesticides measured in this study can be compared to those reported by different authors in several studies[21–25]. Residues of 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 have been reported in surface and groundwaters. U.S. reports on surface waters indicate concentrations in the range of 0.05–4.7 μg/L for atrazine, 0.01–0.26 μg/L for simazine, 0.08–0.55μg/L for alachlor and 0.03–1.5 μg/L for metolachlor. These are also the compounds most commonly detected in the so called "corn-belt area" of the Mississippi river[26].

Flux of Pesticides

The Louros River integrates the pesticide loading from the plains of Arta and Preveza and discharges these agrochemicals into the Amvrakikos Gulf. The flux of a pesticide is the mass transported in the river past the sampling point during a specified time period. The following equation was used for averaging estimation of pesticide flux in Louros River and Estuary:

$$L = [\sum_{i=1}^{n}(C_i Q_i) / \sum_{i=1}^{n} Q_i] Q_{an} \qquad \text{(Equation1)}$$

where L is the annual mass of pesticide residues which was transported through a riverine or estuarine sampling point, C_i is the pesticide mean concentration (μg/L) in the period between sampling dates, Qi is the water volume (L) which flows in the same period and Qan is the annual water flow (L).

Monthly mean river discharge values were available for all sampling points for the entire twenty month period. The mean water flow and the monthly and annual fluxes of the most frequently detected pesticides at the estuary (point 5), are shown in the Table IV. Atrazine and its degradation product DEA are the most abundant herbicides discharged into the Amvrakikos Gulf, followed by metolachlor, simazine and alachlor. The annual mean fluxes were estimated at 122.7 g/day for atrazine, 127.5g/day for DEA, 49.1 g/day for metolachlor, 43.9 g/day for simazine and 11.2 g/day for alachlor (Table IV). Annual mean fluxes of atrazine, DEA and metolachlor for the 1996 period were about twice higher than those of 1995, while simazine flux was at the same level for both periods and that of alachlor was about 25% lower in 1996. The mean monthly flux of each pesticide was higher in the periods from May to August, for both years, 1995 and 1996, when pesticides presented the maximum concentrations in the river water and diminished significantly in fall and winter when the higher water flows appeared.

TABLE IV Fluxes of the five pesticides most frequently detected at Louros estuary (sampling point 5), during the period from January 1995 to August 1996

Sampling Date	*Water flow (m^3/s)*	*Atrazine*		*DEA*		*Simazine*		*Alachlor*		*Metolachlor*	
		concn. (ng/L)	*flux (g/day)*	*concn. (ng/L)*	*flux (g/day)*	*concn. (ng/L)*	*flux (g/day)*	*concn. (ng/L)*	*flux (g/day)*	*concn. (ng/L)*	*flux (g/day)*
1995											
Jan.	23	9	17.9	5	9.9	20	39.7	-	-	-	-
Mar.	13	16	17.9	3	3.4	14	15.7	-	-	-	-
Apr.	23	18	35.8	6	11.9	27	53.7	2	3.9	10	19.9
May	17	49	71.9	42	61.7	70	103	20	29.4	26	38.2
Jun.	13	174	195.4	110	123.5	27	30.3	12	13.5	41	46.0
Jul.	18	158	245.7	121	118.2	18	27.9	39	60.7	54	21.8
Aug.	27	24	55.9	8	18.7	31	72.3	16	37.2	14	32.7
Oct.	10	9	7.8	-	-	20	17.3	5	4.3	8	6.9
Nov.	20	16	27.7	50	86.4	8	13.8	-	-	14	24.2
1995 mean :	18.2	52.5	84.3	38.3	48.2	26.1	41.5	10.4	16.5	18.5	21.1
1996											
Jan.	35	5	15.1	15	45.4	6	18.4	-	-	-	-
Feb.	40	270	34.6	106	-	-	-	-	-	-	-
Apr.	29	42	105	107	518	27	-	-	-	26	65.1
May	17	195	580	215	462	177	260	10	14.7	-	-
Jun.	17	86	126	101	148	-	-	14	20.6	257	377
Aug.	12	103	106.8	28	67.7	-	-	-	-	20	20.7
1996 mean:	25	116.8	161.2	95.3	206.8	25	46.4	4	5.9	50.5	77.1
Annual mean:	21.6	84.6	122.7	66.8	127.5	25.5	43.9	7.2	11.2	34.5	49.1

- = not detected.

TABLE V Agricultural use and estuarine flux given in percentage of use of pesticides at Louros river basin, during the periods of 1995 and 1996

Pesticides	*Annual use in basin (kg)*	*1995 Flux as % of use*	*1996 Flux as % of use*
	Pesticides with large runoff potential		
Atrazine	7,430	0.37	0.89
Desethyl-Atrazine	7,430*	0.24*	1.02*
Metolachlor	5,740	0.18	0.33
Molinate	420	0.27	0.22
Simazine	2,470	0.61	0.46
Trifluralin	4,850	0.27	n.d.
	Pesticides with medium runoff potential		
Alachlor	4,350	0.14	0.03
Propanil	2,960	0.13	n.d.
	Pesticides with small runoff potential		
Carbofuran	800	0.02	0.05
Methyl parathion	1,200	0.04	0.01
Prometryne	1,930	n.d.	n.d.

* The annual use of atrazine was used for DEA flux computations.

A comparison between the river flux and the data on the agricultural use of each pesticide in the drainage basin (Table I) is given in Table V as percentage of the amount applied. For the most often detected pesticides, i.e. atrazine, simazine, DEA, alachlor and metolachlor, all concentrations below the detection limit were assigned a value of zero in the calculation of the flux. Thus the total flux and percentages reported in Tables IV and V may be conservative estimates for some compounds, since the actual concentrations of pesticides reported as less than detection limit may have ranged up to the detection limit without being observed[3]. For most of the detected pesticides, however, substitution of either zero or the detection limit for "less-than" values had little effect on the reported flux, relative to the differences in the flux observed for different pesticides. When both the detection frequency and the agricultural use of a pesticide were low, there is considerable uncertainty in the calculated flux. For low-use pesticides, relatively small fluxes produced by concentrations below the detection limit could represent a significant percentage flux of the amount applied in the basin. Several factors contribute to the uncertainty of the flux estimates shown in Table IV. The error associated with the discharge mesasurements is approximately ± 10%[27]. The errors associated with the analytical method discussed earlier imply that concentrations of most of the analytes are underestimated. Errors in the concentrations estimated for non-sampling days are as likely to be positive as negative, and may largely cancel out[3]. Despite this uncertainty, valid comparisons can still be made between the fluxes of the pesticides in this study, since fluxes for the different compounds range over several orders of magnitude when expressed as a percentage of the amount of the pesticides applied in drainage basin of Louros River.

Mass transport of pesticides into the Gulf of Amvrakikos

The annual flux of herbicides (atrazine, desethylatrazine simazine, alachlor, metolachlor, molinate, propanil, trifluralin) calculated using the concentrations measured in the dissolved phase was much greater than the annual flux of insecticides (methyl parathion and carbofuran) at Louros Estuary (Table IV and V). The annual flux of all pesticides through Louros Estuary into the marine environment of the Amvrakikos Gulf was estimated at 95.5 kg for 1995 and 149.3 kg for 1996. The pesticide discharges estimated by the collective equation (eq.1) at Louros Estuary for the period 1995 and 1996, in order of decreasing amounts were: atrazine > DEA > simazine > metolachlor > molinate > trifluralin > alachlor > propanil > carbofuran > methyl parathion > prometryne. The determined compounds can be divided into groups according to the classification by Larson and co-workers (1995)[3], i.e., pesticides with "large, medium and small runoff potential". According to this kind of estimation for the transportation of compounds in Table IV, the pesticides, atrazine, DEA, simazine, metolachlor, molinate and trifluarlin belong to the "pesticides with large runoff potential"; alachlor and propanil to the "pesticides with medium runoff potential", and carbofuran, methyl parathion and prometryne to the "pesticides with small runoff potential". This classification is in accordance with the study published by Larson and co-workers (1995)[3] for the most of the studied compounds. Methyl parathion and carbofuran showed a smaller flux level in our study which may be due to their small use rate in the Louros River basin.

The fluxes as percentage of the applied amount of the most frequently detected pesticides seem to increase from the river source (point 1) to the estuary (point 5) (figure 3). The loads of the five major pesticides (atrazine, DEA, simazine, alachlor, metolachlor) at sampling site 1 are low and remain at the same level after the contribution of the river tributaries (sampling sites 2 and 3), except for simazine for the period of 1995. The tributary at sampling point 4 as well as the agricultural area draining in the river estuary are the major contibutors of atrazine and simazine followed by metolachlor. In effect, the tributaries at sampling points 2 and 4 have a point-source impact on the Louros River, which acts as an intergrator of water quality. Therefore, the water quality of the Louros River is directly related to the farming practices in the plains of Arta and Preveza.

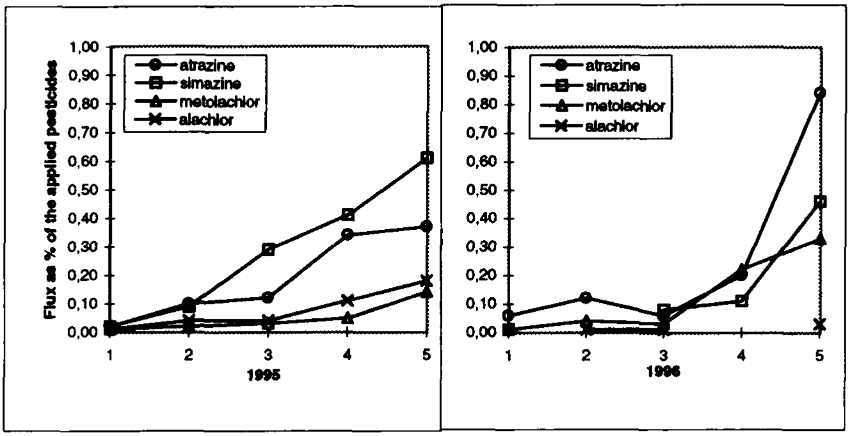

FIGURE 3 Riverine flux, at sampling points of Louros river, as a percentage of the amount applied in the river basin, for atrazine, simazine, alachlor and metolachlor. Sampling sites are arranged in order from river sources to the estuary (points 1 to 5 of the figure 1)

CONCLUSIONS

This work clearly demonstrates that agricultural practices in the Louros River basin have degraded the water quality of the river. It has been shown that the Louros River serves as drainage channel for pesticide-contaminated surface water. Atrazine, DEA, simazine, metolachlor and alachlor were the most frequently detected compounds in river water and the major inputs of the compounds into the river occured in May and June, just after their application in agricultural fields. The tributaries have a point-source impact on the Louros River, which acts as an integrator of water contamination. These compounds and also molinate and trifluralin are transported to significant distances from their sites of application. Based on measurements in river water and mass flow computations it is concluded that less than 1% of herbicides and insecticides applied in the watershed enters the river via surface runoff discharges. Little is known about the fate of the other 99% of land-applied compounds. A small part of the land-applied herbicides is probably lost by volatilization whereas the major portion probably remains bound to soil. More studies are needed to understand whether the bound residues are irreversibly bound to the organic soil, not only losing their pesticidal activity but remaining protected against biodegradation[1].

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