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Transportation of pesticides in estuaries of Louros and Arachthos rivers (Amvrakikos Gulf, N.W. Greece)

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Abstract

Water and sediment samples from seven stations in estuaries of the Louros and Arachthos rivers as well as in the wetlands of the Amvrakikos Gulf were collected for a period from March 1992 to February 1993. The herbicides atrazine, simazine, alachlor, metolachlor, trifluralin and diuron and the organochlorine insecticides α-BHC, lindane and 4,4′-DDE were detected in riverine estuaries and wetlands. The highest concentrations of herbicides, atrazine, simazine, alachlor, metolachlor, diuron and trifluralin in water samples were detected during the period from March to August. The same herbicides and organochlorine insecticides as well as the β-BHC and 4,4′-DDT were found in significant amounts in sediments of river estuaries and wetlands of the Amvrakikos Gulf. The percentage of total amount of detected pesticides released through the rivers into Amvrakikos Gulf are estimated as 3.1% for atrazine, 1.7% for simazine, 1.9% for diuron, 0.3% for metolachlor, 0.9% for alachlor, 0.3% for lindane and 0.6% for trifluralin.

Keywords: Estuarine area; Louros and Arachthos rivers; Greece; Herbicide; Organochlorine insecticide

1. Introduction

In the past 20 years herbicide usage has increased in Greece. The persistence of herbicide residues in the soil and their movement in the water-soil system are key aspects in their environmental behaviour. Chemical reactions and physical displacements influence the persistence of chemicals in soil, but with different environmental implications. Chemicals which are sufficiently resistant to degradation and adequately soluble to be transported in water may reach the sea in significant amounts. Water runoff and river transportation are the main processes involved in transfer of chemicals [1].

The major category of pesticides used in Greece are the herbicides and especially the triazine compounds (27% of the total used herbicides). The next categories are the substituted ureas (9%), acidic herbicides (8%) and thiocarbamates (6%) [2]. Organochlorine insecticides such as DDT, endrin, dieldrin, aldrin, heptachlor, heptachlor epoxide and technical BCH were extensively used in Greece before 1972 [3].

The aim of this work is to determine the residue

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concentrations of selected pesticides in river estuaries and wetlands, as well as to estimate the transportation of pesticide residues through rivers where a very important agricultural area of Northwestern Greece is draining into the Amvrakikos Gulf. A first estimation as to the potential impact of pesticides on the estuaries and wetlands can be drawn by the balance of pesticide usage and the persistence and solubility of the compounds.

2. Area description

The rivers Louros and Aracthos meet in the wetlands of the Amvrakikos Gulf which is protected by the Convention of Ramsar (1971). The region of the Amvrakikos Gulf is an almost closed and hence protected marine area, which communicates with the adjacent lagoons via controlled accesses. The Amvrakikos Gulf is the recipient of a runoff basin, its total area is 4400 km^2. Total average annual runoff from rainfall into the Amvrakikos Gulf is estimated at 28×10^8 m^3.

The runoff basin of the Louros river has an area of 800 km^2, its length is 80 km and the average annual flow rate has been estimated at 19.4 m^3/s. The summer flow is used for the irrigation of a section of the Arta plain, which has an area of 5500 hectares. The runoff basin of the Arachthos river has an approximate area of 1900 km^2. It is 110 km long and its average annual flow rate has been estimated at 61 m^3/s. A dam, which was built by the Public Power Corporation 4.5 km N.E. of Arta, regulates the flow of the river, which is used to irrigate the largest part of the Arta plain.

The lowlands of the Arta plain, on the eastern side of Amvrakikos Gulf, consist of saline soils, and beyond them stretch the agricultural areas with a surface of 74700 hectares (30% citrus fruits, 22% olives, 9% alfalfa, 14% corn and 7.5% cotton, etc.).

The annual amounts of selected pesticides in the agricultural area of Arta plain are shown in the Table 1. The most used herbicides in agricultural areas around the Amvrakikos Gulf (Arta plain) for 1992 were alachlor, atrazine, 2,4-D, MCPA, metolachlor, prometryne, simazine and trifluralin.

Table 1
Annual amounts of the most used herbicides in agricultural areas draining in Amvarkikos Gulf (Arta plain)

Pesticides	Use in kg
Alachlor	4350
Atrazine	7432
2,4-D	2960
Diuron	820
Linuron	no data
MCPA	3800
Metolachlor	5740
Metribuzin	630
Prometryne	1930
Simazine	2470
Molinate	420
Trifluralin	4850

The use of aldrin, endrin, dieldrin, α-BCH, β-BCH, heptachlor and heptachlor epoxide has been banned in Greece since 1972. The use of lindane in the agricultural area of the Amvrakikos Gulf is estimated to have been about 680 kg in 1992 and 450 kg in 1993.

Sampling area is shown in Fig. 1. Sampling stations 1 and 7 are located in the flows of the Louros and Arachthos rivers. Stations 2 and 6 are located in the estuaries of the rivers and stations 3, 4 and 5 are located in lagoons (wetlands) Rodia, Tsoukalio and Logarou. Three multi-residue analyses, two for 15 selected herbicides and one for nine organochlorine insecticides as well as for DDT metabolites were performed.

3. Methods and materials

3.1. Sampling

Water and sediment samples from the estuaries and wetlands of the Amvrakikos Gulf were collected between March 1992 and February 1993. Three to four 2.5-l glass bottles of water were collected to allow analyses of the groups of pesticides involved in the study. After filling with water the bottles were sealed with screw caps lined with aluminum foil. Samples reached the laboratory 1 day after sampling, were stored at 4°C prior extraction, normally within 48 h. Bottom sediments were collected from the top 8-cm layer in

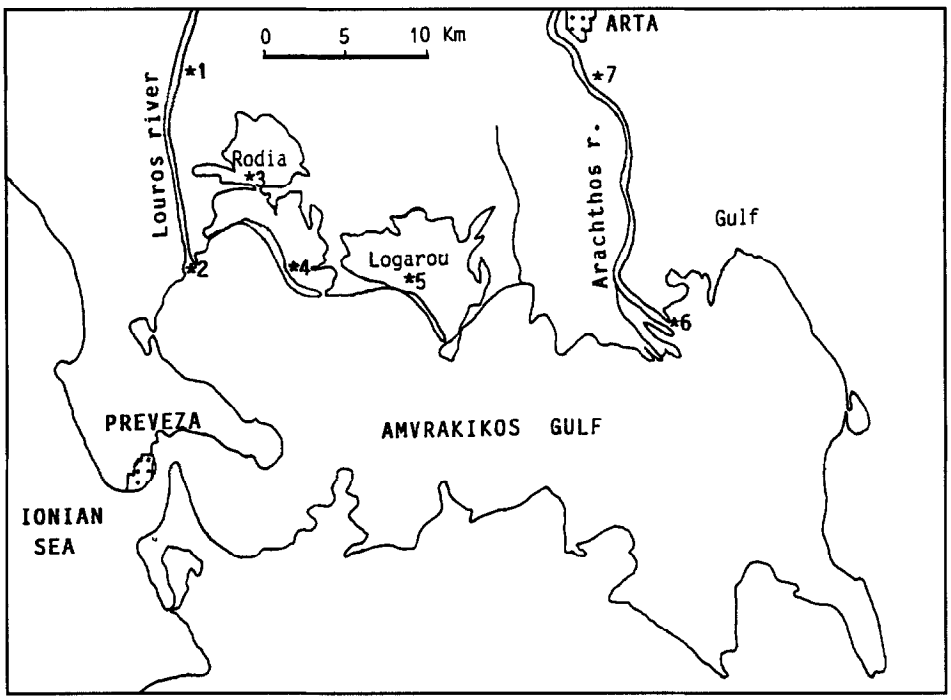

Fig. 1. The plain of Arta-Preveza and the Amvrakikos Gulf, showing the sampling stations.

the river bed and in the gulf wetlands. These samples were stored at −20°C before analyses.

3.2. Analytical procedures

Unfiltered water samples and sediments were analysed for three different groups.

- Insecticides extracted as 'organohalogen': 2,4′-DDD, 2,4′-DDT, 4,4′-DDD, 4,4′-DDT, 4,4′-DDE, dieldrin, endrin, aldrin, lindane, α-BHC, β-BHC and heptachlor.
- Pesticides extracted as 'neutral': atrazine, alachlor, linuron, metolachlor, prometryne and simazine.
- Pesticides extracted as 'acidic': 2,4-D, bentazon, diuron, isoproturon, chlorotoluron, MCPA and trifluralin.

3.3. Water liquid-liquid extraction

Chlorinated hydrocarbons. Water samples (1.5 l) were extracted twice with 50 ml dichloromethane by shaking vigorously for 60 s after addition of 50 ml saturated aqueous NaCl solution. The extracts were combined, evaporated just to dryness and redissolved in *n*-hexane for determination of oragnochlorine compounds.

Neutral compounds. Water samples (1.5 l) were adjusted to pH 9.5 with NH_4OH:H_2O (1:2) and extracted into dichloromethane as described previously [4]. The extracts are evaporated with a gentle stream of nitrogen and dissolved in 2 ml of methanol [4,5].

Acidic compound. Two litres of water are acidified with H_2SO_4 1:1 (v/v) or phosphate buffer (pH = 2.5). The samples are then extracted with dichloromethane and evaporated as the neutral compounds above [6]. The resulting phenoxy and phenyl urea compounds are hydrolysed with potassium hydroxide solution and washed with hexane. The free acids of herbicides are extracted with dichloromethane (after acidification by H_2SO_4). The extracts are evaporated to dryness and dissolved in iso-butanol. The hydrolysis products are methylated for 2,4-D, MCPA and phenyl urea herbicides. They are extracted as described previously [4] for phenoxy compounds and by the S6-A method-DFG [7] for phenyl ureas.

3.4. Sediment

Chlorinated hydrocarbons and neutral compounds. Twenty grams of sediment were ground with 100 g sodium sulphate in a mortar and Soxhlet extracted for 12 h with 250 ml of methanol. The extracts were combined, evaporated in a rotary evaporator and redissolved in *n*-hexane for the cleanup [8,9].

Acidic compounds. Sediment samples of 10 g were mixed with 85 ml of 0.1 M phosphate buffer (pH = ~ 2.5). The mixtures were twice extracted with 75 ml dichloromethane with sonication. The extracts were then isolated, evaporated and the residues were displaced into hexane, and treated as for the 'neutral' compounds [8,9].

3.5. Florisil cleanup

Sediment extracts in hexane were added to a Florisil column and eluted with a solvent mixture of *n*-hexane:ethyl ether 50:500 (v/v) [10]. The extracts were then reduced in volume and the residue redissolved in a solvent compatible with subsequent analyses. The extracts of acidic herbicides are hydrolysed, methylated and concentrated as described for the water samples.

3.6. Quantification

The gas-liquid chromatographic determinations and quantifications for organochlorine compounds and for 'acidic' herbicides were made using two packed columns (1.5% OV-17 + 1.95% QF-1 and 4% SE-20 + 6% OV-210), with an electron capture detector (ECD) [11]. Pesticides were identified by comparison of retention times on both columns with those of standards at two different column temperatures 180 and 200°C. The temperatures of the injector and detector were 220 and 300°C, respectively. Nitrogen was used as the carrier gas with a flow rate of 30 ml/min.

The analysis of 'neutral' compounds, triazines acetanilide and phenyl urea herbicides was made using a capillary column (DB-1, 30 m long, i.d. 0.32 mm) with a specific thermionic detector (FTD). The temperature program of the column was 55°C for 2 min, temperature rate 5°C/min up to 210°C and at 210°C for 30 min. The temperatures of the injector and detector were 220 and 250°C, respectively.

All samples were run in duplicate and their concentrations were determined by direct comparison with pure analytical standards and their mixtures. The minimum detection limits of pesticides in water (μg/l) and in sediments (mg/kg) are shown in Table 2.

3.7. Collective model for pesticide transportation

The annual amounts of each pesticide which were transported in the Thermaikos Gulf waters through river estuaries can be determined by the

Table 2
The detection limits of selected pesticides in water (μg/l) and in sediment (mg/kg)

Herbicides	In water	In sediment	Organochlorines	In water	In sediment
Alachlor	0.005	0.001	α-BHC	0.001	0.001
Atrazine	0.05	0.002	β-BHC	0.005	0.002
Chlortoluron	0.05	0.002	Lindane	0.001	0.001
2,4-D	0.05	0.001	Heptachlor	0.01	0.001
Diuron	0.01	0.001	Hept. epoxide	0.01	0.002
Isoproturon	0.1	0.002	2,4'DDT	0.05	0.002
Linuron	0.1	0.002	4,4'DDT	0.05	0.002
MCPA	0.05	0.001	2,4'-DDD	0.05	0.002
Metolachlor	0.1	0.002	4,4'-DDD	0.05	0.002
Metribuzin	0.1	0.001	4,4'-DDE	0.01	0.002
Molinate	0.001	0.001	Aldrin	0.005	0.001
Prometryne	0.05	0.001	Dieldrin	0.01	0.001
Propanil	0.005	0.005	Edrin	0.05	0.001
Simazine	0.05	0.001			
Trifluralin	0.005	0.001			

collective equation [12]:

$$W_{\text{total}} = \sum_{i,j=1}^{n} C_{ij}Q_{ij} = C_{11}Q_{11} + C_{12}Q_{12} + \cdots + C_{1j}Q_{1j} + C_{21} + \cdots + C_{ij}Q_{ij} \quad (1)$$

where W_{ij} is the pesticide residue mass which was transported through river point i during the time period j, C_{ij} is the pesticide mean concentration ($\mu g/l$) in the period j, Q_{ij} is the total water amount (l) which outflow in the period j.

4. Results

4.1. Water quality

The concentrations of detected pesticides in the rivers Louros and Arachthos and in lagoons (wetlands) of the Amvrakikos Gulf, for three subperiods, March–April, May–August and September–February, are shown in Tables 3–5. The sampling dates were March 15, April 28, May 17, June 19, July 13, August 17, September 27 and November 16, in 1992 and February 19, in 1993. Six herbicides, atrazine, simazine, alachlor, metolachlor, trifluralin and diuron, and three organochlorine insecticides, α-BHC, lindane and 4,4′-DDE were identified in rivers and wetlands of the Amvrakikos Gulf at the sampling stations shown in Fig. 1. Peak concentrations of herbicides were observed corresponding to their application in the season from May to August. The highest concentrations of herbicides were determined in estuaries of the river Louros: alachlor (1.65 $\mu g/l$), atrazine (4.1 $\mu g/l$), diuron (0.14 $\mu g/l$), metolachlor (1.12 $\mu g/l$), simazine (1.45 $\mu g/l$) and trifluralin (0.36 $\mu g/l$).

The concentrations found are similar to those reported by different authors in several studies [3,13–15]. Hence atrazine, one of the herbicides most widely used in the USA and in European countries over the last 30 years, and used for weed control among crops of corn, wheat, barley and sorghum and also in railroads [16] has been reported in surface and groundwaters throughout the world. It has been detected in many U.S. groundwaters at concentrations in the range of 0.17–4 $\mu g/l$ with median levels of 0.5 $\mu g/l$ and it is the most commonly detected compound in the so-called 'corn-belt areas' in the Mississippi river [17].

Lindane, α-BHC and 4,4′-DDE were the dominant chemical species of organochlorine compounds in water samples analysed. Lindane and α-BHC residues were detected in water samples of the river Louros, and 4,4′-DDE residues were detected only in the river Arachthos. The same compounds were also detected in water samples from the estuaries of the Axios, Loudias and

Table 3
The incidence and concentrations ($\mu g/l$) of pesticides at sampling stations 1 and 2 in the Louros river by season: March 1992–February 1993

Pesticides[a]	March–April		May–August		September–February	
	Mean ($n = 4$)	Range ($\mu g/L$)	Mean ($n = 8$)	Range ($\mu g/L$)	Mean ($n = 6$)	Range ($\mu g/L$)
Alachlor	0.1	n.d.–0.4	0.39	0.23–1.65	—	n.d.
Atrazine	0.1	n.d.–0.3	1.20	0.18–4.10	0.06	n.d.–0.11
Diuron	—	n.d.	0.05	n.d.–0.14	—	n.d.
Metolachlor	—	n.d.	0.03	n.d.–1.12	—	n.d.
Simazine	0.02	n.d.–0.1	0.23	0.07–1.45	—	n.d.
Trifluralin	—	n.d.	0.16	0.08–0.36	—	n.d.
α-BHC	0.012	n.d.–0.023	0.017	n.d.–0.029	—	n.d.
Lindane	0.008	n.d.–0.013	0.009	n.d.–0.016	0.003	n.d.–0.007

n.d. = not detectable.
[a] The rest of the 27 selected pesticides, listed in Table 2, were not detected in any case.

Table 4
The incidence and concentrations ($\mu g/l$) of pesticides at sampling stations 6 and 7 in the Arachthos river by season: March 1992–February 1993

Pesticides[a]	March–April		May–August		September–February	
	Mean ($n = 4$)	Range ($\mu g/l$)	Mean ($n = 8$)	Range ($\mu g/l$)	Mean ($n = 6$)	Range ($\mu g/l$)
Alachlor	—	n.d.	0.13	0.06–0.35	—	n.d.
Atrazine	0.01	n.d.–0.03	0.15	n.d.–0.24	0.02	n.d.–0.05
Diuron	—	n.d.	0.03	n.d.–0.26	—	n.d.
Metolachlor	—	n.d.	0.04	0.02–0.06	—	n.d.
Simazine	—	n.d.	0.04	n.d–0.11	—	n.d.
Trifluralin	0.01	n.d.–0.04	0.02	n.d.–0.09	—	n.d.
4,4′-DDE	0.002	n.d.–0.006	0.009	n.d.–0.011	—	n.d.

n.d. = not detectable.
[a]The rest of the 27 selected pesticides, listed in Table 2, were not detected in any case.

Aliakmon rivers, in a previous work for the same season [3].

By using the flow rates of the rivers Arachthos and Louros (Table 6) the usage and the mean concentrations of herbicides (Tables 1, 3 and 4), we can estimate the losses of detected pesticides through rivers in Amvrakikos Gulf. These results were obtained by a collective equation (Eq. (1)) for used and detected pesticides, and are shown in Table 7.

Table 5
The incidence and concentrations ($\mu g/l$) of pesticides at sampling stations 3, 4 and 5 in the wetlands of the Amvrakikos Gulf by season: March 1992–February 1993

Pesticides[a]	March–April		May–August		September–February	
	Mean ($n = 6$)	Range ($\mu g/l$)	Mean ($n = 12$)	Range ($\mu g/l$)	Mean ($n = 9$)	Range ($\mu g/l$)
Alachlor	—	n.d.	0.07	0.01–0.26	—	n.d.
Atrazine	0.01	n.d.–0.07	0.03	n.d.–0.17	—	n.d.
Metolachlor	0.02	n.d.–0.05	0.11	0.04–0.31	—	n.d.
Simazine	—	n.d.	0.01	n.d.–0.05	—	n.d.
Trifluralin	0.01	n.d.–0.03	0.07	n.d.–0.13	—	n.d.

n.d. = not detectable.
[a]The rest of the 27 selected pesticides, listed in Table 2, were not detected in any case.

Table 6
Seasonal flow rates of rivers in Amvrakikos Gulf (1992)

Period	Louros Flow rate		Arachthos Flow rate	
	m^3/s	$10^6 m^3$/period	m^3/s	$10^6 m^3$/period
March–April	16.86	89	38.77	204
May–August	11.48	119	32.60	338
September–December	18.56	192	31.44	326
Mean (1992)	5.63	486	26.40	1166

Table 7
Percent transportation of used pesticides through the Louros and Arachthos rivers into the Amvrakikos Gulf

	March–April		May–August		September–December		Total
	Mean (kg/period)	Loss/use (%)	Mean (kg/period)	Loss/use (%)	Mean (kg/period)	Loss/use (%)	Loss/use (%)
Leachers							
Atrazine	10.9	0.15	193	2.60	24.6	0.33	3.08
Simazine	1.8	0.07	40.9	1.65	—	—	1.72
Diuron	—	—	16.1	1.95	—	—	1.95
Metolachlor	—	—	17.1	0.29	—	—	0.29
Transition							
Alachor	8.9	0.20	32.2	0.75	—	—	0.95
Non-leachers							
Trifluralin	2.0	0.04	25.8	0.53	—	—	0.57
Lindane	0.7	0.11	1.0	0.15	—	—	0.33

Pesticide discharges measured at the mouth of the two rivers in the Amvrakikos Gulf for the period of 1992 (Table 7, Fig. 2), in order of decreasing amounts were: atrazine > diuron > simazine > alachlor > trifluralin > lindane > metolachlor. The determined herbicides can be divided into groups according to the classification by Gustafson [18], i.e., 'leachers', 'non-leachers' and 'transition'. According to this kind of estimation for the transportation of compounds in Table 7, the pesticides, atarzine, simazine, diuron and metolachlor, belong to the 'leachers'; the pesticides, trifluralin and lindane, belong to the 'non-leachers'; and alachlor belongs to the 'transition' group.

4.2. Sediments

The concentrations of herbicide and organochlorine residues in the bottom sediments collected from sampling stations 2–6 (Fig. 1) are shown in Table 8 and Fig. 3. The herbicides alachlor, atrazine, simazine, metolachlor and tri-

Table 8
Pesticides detected in sediments and their concentrations (μg/kg) for estuaries of the rivers Louros and Arachthos, as well as for the wetlands of the Amvrakikos Gulf, for the year 1992 (sampling stations 2–6 are shown in Fig. 1)

Pesticides[a]	Louros		Arachthos		Wetlands/Gulf	
	Mean ($n = 4$)[b]	Range (μg/kg)	Mean ($n = 4$)[b]	Range (μg/kg)	Mean ($n = 12$)	Range (μg/kg)
Alachlor	32.7	n.d.–71	9.8	n.d.–27	2.4	n.d.–13
Atrazine	31.3	n.d.–110	20.3	n.d.–76	4.2	n.d.–12
Metolachlor	11.2	n.d.–47	4.7	n.d.–20	0.5	n.d.–3
Simazine	9.5	n.d.–41	13.3	n.d.–31	4.7	n.d.–7
Trifluralin	0.3	n.d.–2	0.5	n.d–3	0.2	n.d.–1.1
α-BHC	4.3	n.d.–21	3.2	n.d.–15	1.1	n.d.–6
β-BHC	1.2	n.d.–4	—	n.d.	0.1	n.d.–0.5
Lindane	4.0	n.d.–8	—	n.d.	0.5	n.d.–3
4,4′-DDE	2.3	n.d.–11	0.2	n.d.–1.2	1.6	n.d.–5
4,4′-DDT	0.5	n.d.–	3	–n.d.	0.4	n.d.–2

n.d. = not detectable.
[a]The rest of the 27 selected pesticides, listed in Table 2, were not detected in any case.
[b]The sampling dates were April 20, July 13, August 7 and December 19, in 1992.

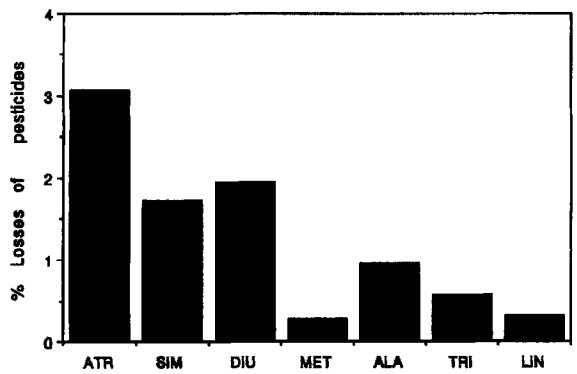

Fig. 2. The surface losses of detected pesticides from agricultural areas, through the rivers Louros and Arachthos.

fluralin, as well as the organochlorine compounds, α-BHC, β-BHC, lindane, 4,4′-DDE and 4,4′-DDT, were detected and shown to be significantly accumulated in sediments which contain 3–4.5% organic matter. Concentrations of herbicides were shown to maximise at the time of application and subsequently decline, although measurable residues were shown to persist throughout the period. Concentrations of detected organochlorine compounds were almost at the same level throughout the three subperiods (Fig. 3). The maximum concentrations of detected compounds at sampling stations were: alachlor, 71 μg/kg; atrazine, 110 μg/kg; simazine, 41 μg/kg; metolachlor, 47 μg/kg; trifluralin, 3 μg/kg; α-BHC, 21 μg/kg; β-BHC, 4 μg/kg; lindane, 8 μg/kg; 4,4′-DDE, 11 μg/kg; and 4,4′-DDT, 3 μg/kg. Diuron, which was detected in water samples from the rivers Louros and Arachthos, was not detected in sediment samples and this indicates no accumulation in sediments. β-BHC and 4,4′-DDT were not detected in water or sediment samples from the river Arachthos.

The presence of organochlorine compounds in a stable level of concentrations in sediments, shows this sedimentary reservoir of these compounds to act as a source and sustain aqueous contamination for a few years should their usage cease. The concentrations and distribution of detected herbicides in sediments from the rivers Louros and Arachthos and from wetlands of the

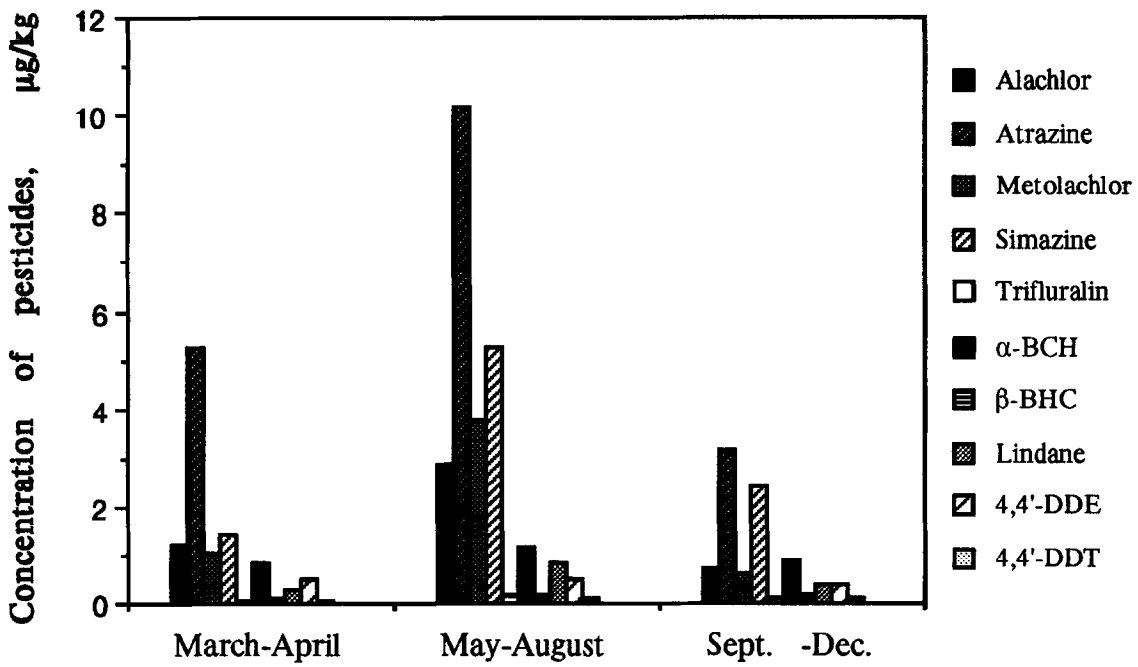

Fig. 3. Seasonal trend in concentrations of detected pesticides in sediments of the Amvrakikos wetlands and the estuaries of the rivers Louros and Arachthos (sampling stations 2–6).

Amvrakikos Gulf, reflected those in the water samples.

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References

[1] R.J. Wagenet, in T.J. Logan et al. (Eds), Effect of Conservation Tillage on Groudwater Quality: Nitrates and Pesticides. Lewis Inc., Chapter 11, 1987, p. 189.

[2] National Statistical Bureau of Greece. Ministry of Agriculture, Paper EOP-1, 1988–89.

[3] T.A. Albanis, T.G. Danis, and M.K. Kourgia, Transportation of pesticides in estuaries of Axios, Loudias and Aliakmon rivers (Thermaikos Gulf). Sci. Total Environ., 156 (1994) 11–22.

[4] HMSO, Chlorophenoxy acidic herbicides, trichlorobenzoic acid, chlorophenols, triazines and glyphosate in water. HMSO Publication Centre, London, 1985.

[5] G. Durand and D. Barcelo, Liquid chromatographic analysis of chlorotriazine herbicides and its degradation products in water samples with photodiode array detection. I. Evaluation of two liquid-liquid extraction methods. Tox. Environ. Chem., 25 (1989) 1–11.

[6] HMSO, The determination of carbamates, thiocarbamates related compounds and ureas in water. HMSO Publication Centre, London, 1985.

[7] DFG, Deutsche Forschungsgemeinschaft, in H.P. Thier and H. Zeumer (Eds), Manual of Pesticide Residue Analysis. Method S-6A, Pbs VCH, Weinheim, 1987.

[8] G. Durand, R. Forteza and D. Barcolo, Determination of chlorotriazine herbicides, their dealkylated degradation products and organophosporus pesticides in soil samples by means of two different clean-up procedures. Chromatographia, 28 (1989) 597–604.

[9] D.F. Gruka, F.L. Shore and Shu-Teh Pan, Singe-laboratory validation of EPA method 8150 for determination of chlorinated herbicides in hazardous waste. J. Assoc. Off. Anal. Chem., 69 (1986) 970–975.

[10] A.J. Cessna, R. Grover, L.A. Kerr, and M.L. Aldred, A multi residue method for analysis and verification of several herbicides in water. J. Agric. Food Chem., 33 (1985) 504–507.

[11] EPA, Method 505, Analyisis of organochlorine pesticides and commercial PCBs in water by micro-extraction and Gas Chromatography. EPA-600/4-88/039, Cincinatti, 1988.

[12] T.A. Albanis, Herbicides losses in runoff from the agricultural area of Thessaloniki in Thermaikos Gulf, N. Greece. Sci. Total Environ., 114 (1992) 59–71.

[13] R. Frank, and Ll. Logan, Pesticide and industrial chemical residues at the mouth of the Grand, Saugeen and Thames rivers, Ontario, Canada 1981–85. Arch. Environ. Contam. Toxicol., 17 (1988) 741–754.

[14] S. Galassi and V. Leoni, Atrazina e simazina nelle acque del Po e dei suo affluenti. Acqua Aria, 3 (1988) 327–331.

[15] E. Benfenati, P. Tremolada L. Chippetta R. Frassanito, G. Bassi, N. Di Toro, R. Fanelli and G. Stella, Simultaneous analysis of 50 pesticides in water samples by solid-phase extraction and GC-MS. Chemosphere, 21 (1990) 1411–1421.

[16] D. Barcelo, Occurrence, handling and chromatographic determination of pesticides in the aquatic environment. Analyst, 116 (1991) 681–689.

[17] W.E. Pereira and C.E. Rostad, Occurrence, distributions and transport of herbicides and their degradation products in the lower Mississippi river and its tributaries. Environ. Sci. Technol., 24 (1990) 1400–1406.

[18] D.I. Gustafson, Groundwater Ubiquity Score: A simple method for assessing pesticide leachability. Environ. Toxicol. Chem., 8 (1989) 339–357.