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Organochlorine and Organophosphorus Pesticide Residues in the Water of the Pinios River, Greece

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The Pinios River is one of the main rivers in central Greece. The river originates on the mountain chain of Pindos and discharges into Thermaikos bay, in the Aegean Sea. Its total length is 205 km, but its depth and width are varying from one season to another. The river often floods after heavy rainfalls. Pinios runs across the plain of Thessaly, the biggest in Greece, where pesticides are extensively used in wheat, beet, cotton, corn and other cultivations. The water of the river is mainly used for irrigation, but for very limited time periods it is mixed with groundwater to supply Larissa, the biggest city in Thessaly, with potable water.

The possibility of potable water pollution with pesticides from agricultural activities is of great concern within the European Union. The maximum allowable concentration (MAC) is only 0.1 μg/L for any individual pesticide and 0.5 μg/L for total pesticides (EC Council Directive 1980). Measurement at that low levels is considered prone to errors and positive identification requires evidence from more than one chromatographic procedure.

The importance of weather conditions on pesticide residues in natural waters is clear. In a recent similar study, the influence of key environmental factors on pesticide concentrations in surface waters was demonstrated (Miliadis 1994). The aim of the present study was to determine the levels of organochlorine and organophosphorus pesticides' residues in the water of the Pinios river, as well as in the groundwater of the Larissa area, and record the influence of environmental factors on them.

MATERIALS AND METHODS

Water samples were collected from the river entering the water plant of the city of Larissa. Samples were also taken from the groundwater that supplies Larissa with potable water. Sampling was usually performed on a monthly basis over a period of 2 years, from October 1991 to July 1993. River samples were collected from the surface water, in 2.5-L glass bottles and transferred to the laboratory for analysis, that was normally conducted within 24 hr of collection.

Water samples were extracted with CH_2Cl_2 and cleaned through a celite-activated charcoal column, according to a method previously described (Miliadis 1993). The

method is a multiresidue procedure suitable for the determination of approximately 150 pesticides, mainly organophosphorus and organochlorine.

The extracts were analyzed with a Varian 3700 gas chromatograph equipped with a glass column containing 1:1 mixture of 10% OV-101 and 15% OV-210 on Chromosorb WHP (80-100 mesh) connected to a Ni-63 electron capture detector (ECD), and a glass column containing 10% OV-101 on WAW (80-100 mesh) connected to a nitrogen-phosphorus detector (NPD). 1-μL of the sample extract was injected for analysis in both ECD and NPD. Identification of the unknown peaks found in the samples' chromatograms was made by comparing the relative retention time (RRT) of the unknown peak to the RRTs given in various RRT data tables (U.S. Dept. of Health 1982), and accomplished using reference pesticide solutions. Further positive identification was performed by changing, by each other, the two glass columns and comparing again the RRTs of the unknown peaks to those given in the RRT data tables. Quantification was performed using reference solutions. Duplicates were carried out for all samples. Minimum detection limit for organochlorine compounds was at the 0.001-0.01 μg/L levels and for organophosphorus compounds at the 0.01-0.1 μg/L levels. Blank determinations were performed with each set of samples.

RESULTS AND DISCUSSION

Table 1 presents the concentration levels of organochlorine or organophosphorus pesticides found in the water samples of the Pinios river, over the 2-year period. As seen from the Table, no pesticides were detected in all the groundwater samples of the Larissa area.

On the contrary lindane, alachlor, parathion methyl and parathion ethyl were detected periodically in the water of the Pinios river. The agricultural origin of the river's pollution is indicated from the presence of these substances during the spring, a period of increased agricultural activity. Lindane and alachlor were broadly used in the 1992 spring cultivations of corn, cotton and beet in the Zarkos-Piniada area, by the river. After heavy rainfalls and consequent flood events that occurred during the spring of 1992 the two pesticides, as seen from Table 1, were detected in the water of the Pinios river from March to June of this year, at concentrations ranging from 0.002 to 0.012 μg/L for lindane and 0.05 μg/L for alachlor. Lindane was also used from November to December 1992 in the winder cultivation of wheat and makes its appearance in the river's water after the rains of February 1993. Thereafter lindane concentration in the river's water decreases until April when an increase is observed, attributed again to lindane uses in the 1993 spring cultivations of corn, cotton and beet. Lindane has also been detected in the water of another river in N. Greece (Kilikidis 1992). The contact insecticides parathion ethyl and methyl were also detected in two samples of the Pinios river water, at concentrations slightly higher than the EEC MAC of 0.1 μg/L. However taking into account the fact that the MAC was exceeded for a certain limited time period, during which the river water was not used as potable, we may accept that there was no risk to human health.

The data obtained in this study indicate that the groundwaters in Larissa serving as drinking water supplies are not contaminated with pesticides from agricultural

Table 1. Levels of organochlorine and organophosphorus pesticides (μg/L) in groundwater used as potable in the city of Larissa and in the water of the Pinios river, related to the level of the river water and the monthly precipitation. (N.D. = not detected)

Month	Groundwater	Pinios river water	Water level(m)	Precipitation of month (mm)
10/91	N.D.	N.D.	3.1	25
11/91	N.D.	N.D.	3.2	48
12/91	N.D.	N.D.	3.3	3
2/92	N.D.	N.D.	3.3	15
3/92	N.D.	lindane 0.006 alachlor 0.05	3.5	10
4/92	N.D.	lindane 0.012 alachlor 0.05	4.4	88
5/92	N.D.	lindane 0.002 m.parathion 0.2	3.4	51
6/92	N.D.	lindane 0.002	3.2	74
7/92	N.D.	N.D.	3.1	13
8/92	N.D.	N.D.	3.0	0
9/92	N.D.	N.D.	3.1	0
10/92	N.D.	N.D.	3.2	39
11/92	N.D.	N.D.	3.3	62
12/92	N.D.	N.D.	3.7	25
1/93	N.D.	N.D.	3.9	16
2/93	N.D.	lindane 0.025 alachlor 0.03 e.parathion 0.15	4.3	29
3/93	N.D.	lindane 0.004	4.1	25
4/93	N.D.	lindane 0.02	3.6	12
6/93	N.D.	lindane 0.007	3.5	80
7/93	N.D.	N.D.	3.1	1

uses. However some mobile pesticides, with broad agricultural use, rapidly migrate via the fissures into surface drains following heavy rains and cause sudden peaks in the Pinios river water. The presence of these pesticides in the water of the river was found to be seasonal, during the spring of each survey year.

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