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Organochlorine Pesticides and Triazines in the Drinking Water of Athens

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Pesticides and their metabolites are one of the most important classes of environmental pollutants. Because of their intensive use in agriculture, they can be transported via soil to the water (surface, ground, drinking water). Their control is oriented towards specific substances, according to the proposed priority pollutant lists (Telliard 1990).

Multiresidue analytical techniques are preferably developed for the determination of some groups of compounds, e.g., organochlorine pesticides, organophosphorus pesticides, triazines etc. (Bacaloni et al. 1980; Barcelo 1991; Brooks et al. 1989; Saner et al. 1979).

In this study, a procedure for the simultaneous quantitative determination of 16 organochlorine pesticides and 3 triazines in drinking water is described. Samples were taken from the major sources of drinking water of Athens. Multiresidue method, using solid phase extraction for the pre-concentration and separation steps and gas chromatography with ECD and NPD, was applied. Two capillary chromatographic columns were used for confirmation of peak identity. The mean recoveries were also estimated at various concentration levels and found very efficient. Until now there are not enough data for drinking water of Athens to access the level of contamination due to pesticides. The existing data refer mainly to natural water of Greece (Miliadis 1993).

MATERIALS AND METHODS

Forty water samples were collected from December 1992 to February 1993, at the treatment plants of the Water Company that supplies drinking water to Athens. These samples originated from Iliki lake, Marathonas lake and Mornos river which are the major sources of Athens drinking water and provide with water the treatment plants. Sampling was

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performed on a monthly basis as follows: Fifteen samples from Iliki, fifteen samples from Marathonas and ten samples from Mornos. Water samples were collected in 1 L glass bottles by filling the sample bottle to overflow from drinking water. The samples were transported to the laboratory and kept in a cool place until analysis which was conducted within 24 h of sampling.

The solvents used (acetonitrile, methanol, acetone and n-hexane) were pesticide residue free (pestiscan), Lab Scan, Dublin (Ireland). Atrazine, simazine and terbutylazine were products of Ciba-Geigy, Bazel (Switzerland) with a purity of 99%. A-HCH and endrin were obtained as solid materials from Reidel-de Haen, Seelze (Germany), with a purity of 98-99%. Lindane and aldrin were obtained as solid materials from Alltech, Chicago, IL (USA), with a purity of 99%. The other pesticides were obtained from Polyscience, Niles, IL (USA), as solutions in methanol. The mixture of 16 organochlorine pesticides was product of Alltech, Chicago, IL (USA), (2000 μg/mL in toluene). 1,2,3 Trichlorobenzene, was product of the Pesticide Analytical Standard Institute of Organic Industrial Chemistry, Warsaw (Poland). Solid phase extraction was carried out using bonded-phase silica Cl8 0.85 ml/filled cartridges, containing 360 mg of Cl8 octadecyl sorbent, Sep-Pak "classic", product of Waters, Mass. (USA). Stock solutions of each triazine were prepared in methanol at 1000 μg/mL. A stock solution of 16 organo-chlorine pesticides was made up in n-hexane containing 0.2 μg/mL of each. 1,2,3 Trichlorobenzene was used as an internal standard and was added to each sample after elution from the columns, in order to correct the deviations of injection volumes and variations in detector response.

Water samples were fortified with organochlorine pesticides at levels of 0.01, 0.02 and 0.1 μg/L and with triazines at levels of 0.2 and 10 μg/L. The samples were stirred and equilibrated 30 min before extraction.

The samples were prepared for analysis by the addition of concentrated hydrochloric acid to pH 2. Then 1 L of the water samples were filtered through a suitable glass fiber filter. A Cl8 column fitted to a glass column (25 cm x 1 cm), which was connected with an 1 L flask reservoir, was conditioned with 10 mL methanol at 10 mL/min. Then, the water sample was passed through the treated column at 10 mL/min. After the sample volume had passed through the column, nitrogen was applied, for at least 15 min, to dry the column. Organochlorine pesticides where then eluted from the column by passing 10 mL of n-hexane. The extract was collected and concentrated to 5 mL, in order to be analysed by GC-ECD. Then the column was dried again for 1 min and triazines were eluted by passing 20 mL acetonitrile. The extract was evaporated on a rotation evaporator. The solvent was replaced by methanol and it was brought to total volume of 2 mL. Then, GC-NPD analysis was performed.

The analysis of the 16 organochlorine pesticides was carried out by gas capillary chromatography using the following instruments: (1) Varian Model 3400 gas chromatograph equipped with ECD, split/splitless injection port, a DB-1 fused silica capillary column by J&W Scientific Inc. (30 m x 0.32 mm I.D., 0.25 pm film thickness) and autosampler Model 8200 cx, with program for the evaluation of GC runs (DAPA Scientific Pty.ltd, Kalamunda, Australia) and (2) Carlo Erba Model Mega 2 gas chromatograph equipped with ECD, split/splitless injection port, a DB-5 fused silica capillary column by J&W Scientific Inc. (30 m x 0.25 mm I.D., 0.25 µm film thickness) and autosampler Model A200S, with program for the evaluation of GC runs (Chrom-Card, Fisons Instruments, Rodano, Milan). The temperature program applied was as follows: 80°C for 1 min, 80°C-218°C at 8°C/min, 218°C for 18 min, 218°C-250°C at 4°C/min and 250°C for 10 min. The injection was carried out splitless at 250°C and the injection volume was 1 µl.

The analysis of the 3 triazines was carried out in a Hewlett-Packard Model 5890 II gas chromatograph equipped with NPD, split/splitless injection port, a CP-Sil 13 CB fused silica capillary column by Chrompack (50 m x 0.32 mm I.D., 0.4 µm film thickness), autosampler Model 7673 and HP 3396A integrator. The temperature program applied was as follows: 80°C for 1 min, 80°C-270°C at 20°C/min and 270°C for 10 min. The injection was carried out splitless at 250°C and the injection volume was 2 µ1.

RESULTS AND DISCUSSION

To meet the objectives for the surveillance and monitoring of pesticides in drinking water samples, we have developed a new sensitive routine method for organochlorine pesticides and triazines, which is described here. We have applied that method to evaluate the levels of the above pesticides in the drinking water of Athens. As a first step solid phase extraction of the samples, employing Sep-Pak cartridges was used for the pre-concentration and separation of the target compounds. This system afforded an enrichment factor from 200- to 2000- fold and allowed the gas chromatographic analysis of 16 organochlorine pesticides and 3 triazines at ppt level.

The gas chromatographic determination was performed using capillary columns and specific detectors; ECD for organo-chlorine pesticides and NPD for triazines.

The retention times (RT) of 16 organochlorine pesticides and internal standard were determined individually on DB-1 and DB-5 columns and are given in Table 1. The gas chromatograms of an extracted drinking water sample, spiked to 0.1 µg/L for each organochlorine pesticide on DB-5 is presented in Figure 1. It can be seen that all 16 organochlorine pesticides could

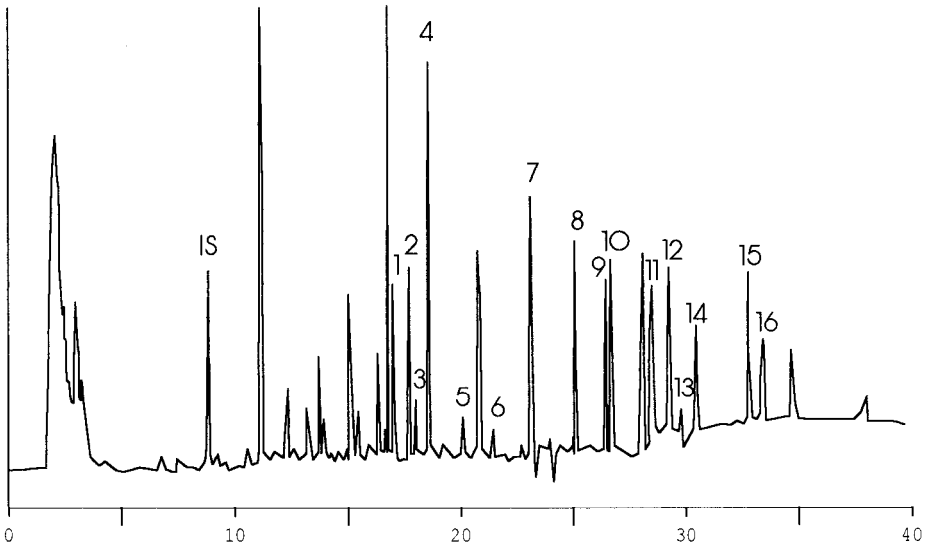

Figure 1. Gas chromatogram of a drinking water sample extract on DB-5 column (Fortification level 0.1 µg/L for each organochlorine pesticide). The numbers refer to pesticides, according to Table 1. IS = Internal Standard.

Table 1. Retention times (min) of 16 organochlorine pesticides on two different columns.

No	Organochlorine	RT (min)	RT (min)
IS	1,2,3,TCB*	6.86	8.83
1	a-HCH	14.26	17.05
2	b-HCH	14.63	17.73
3	Lindane	15.12	17.97
4	D-HCH	15.26	18.57
5	Heptachlor	17.46	20.30
6	Aldrin	18.51	21.58
7	Heptachlor Epoxide	19.61	23.25
8	a-Endosulfan	20.94	25.28
9	4,4 DDE	21.88	26.63
10	Dieldrin	22.01	26.87
11	Endrin	22.86	28.45
12	b-Endosulfan	22.98	29.13
13	4,4 DDD	23.63	29.82
14	Endrin Aldehyde	23.74	30.72
15	Endosulfan Sulfate	25.16	32.98
16	4,4 DDT	26.10	33.58

*1,2,3 Trichlorobenzene (1,2,3 TCB) was used as internal (IS).

Table 2. Retention Times (min) of 3 triazines on CP-SIL 13CB column.

No	Triazines	RT (min)\CP-SIL 13 CB
1	Atrazine	11.38
2	Simazine	11.40
3	Terbutylazine	11.53

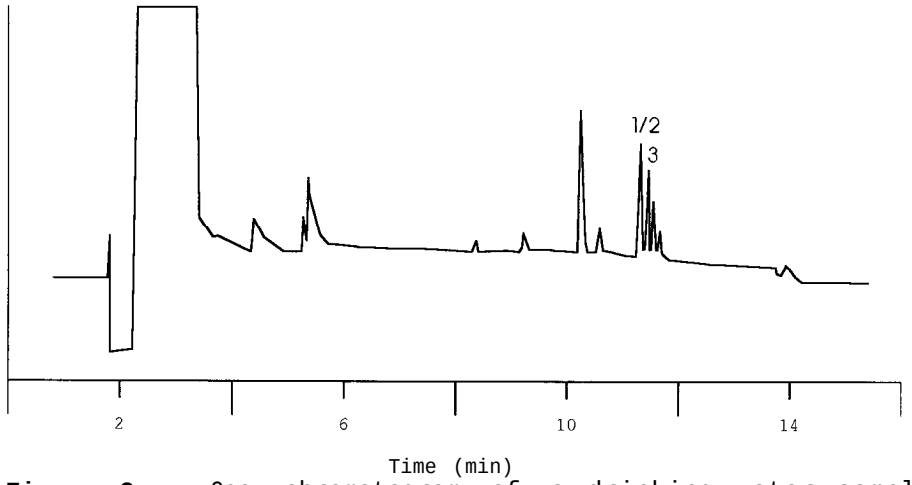

Figure 2. Gas chromatogram of a drinking water sample extract on CP-SIL 13 CB column (Fortification level 0.2 µg/L for each triazine). The numbers refer to triazines, according to Table 2.

be successfully resolved. The resolution was quite good, also, on the DB-1 column, but when compared, it seems that the DB-5 column gives better resolution of the pesticides.

The retention times (RT) of triazines on CP-SIL 13 CB column are given in Table 2. When a mixture of three triazines was used, atrazine and simazine were not separated. Results concerning RTs of triazines on different columns are reported elsewhere (Lee and Stokker 1986). The gas chromatogram of an extracted drinking water sample spiked to 0.2 µg/L for each triazine is given in Figure 2.

The recovery of the 16 organochlorine pesticides was determined with samples of 1 L of drinking water fortified with each pesticide at three concentration levels of 0.01, 0.02 and 0.1 µg/L. The results of a series of threefold experiments for each concentration level are presented in Table 3. Mean recoveries of all organochlorine pesticides at the 0.1 µg/L level of fortification were between 66-108%, except for a-HCH (35%) and endosulfan sulfate (117%). Recoveries of the same 16 organochlorine pesticides, at the same level of fortification, in reagent water, were slightly better, ranging from 65% to 105% in the mixture (Table 4). Individual analysis of some of them gave better results as in the case of a-HCH (Table 4). Recoveries were better at 0.02 µg/L level of fortification. At the lowest level of fortification (0.01 µg/L), recoveries were higher (85%-125%), except for a-HCH (40%). Mean recoveries (n=3) of atrazine, simazine and terbutylazine from drinking water samples are given in Table 5, at two concentration levels of 0.2 and 10 µg/L. The mean recoveries at the 0.2 µg/L level of fortification were between 87% and 110% and at the 100 µg/L level between 92% and 94%.

Table 3. Mean % recovery and relative standard deviation (in parentheses) of organochlorine pesticides in drinking water samples at 0.01, 0.02 and 0.10 µg/L fortification level, (n=3).

Organochlorine Pesticides	Fortification Level (µg/L) 0.01	0.02	0.10
a-HCH	40* (5)	58 (4)	35 (5)
b-HCH	103* (3)	98* (6)	93* (6)
Lindane	86* (6)	92* (5)	67* (6)
D-HCH	125* (6)	93* (2)	84* (5)
Heptachlor	85 (6)	77 (5)	66 (5)
Aldrin	123 (6)	71 (7)	68* (5)
Heptachlor Epoxide	110 (6)	80 (5)	91 (7)
a-Endosulfan	104* (1)	97* (3)	88* (6)
4,4 DDE	92* (1)	88* (5)	93* (6)
Dieldrin	120* (3)	90* (3)	98 (6
b-Endosulfan	110* (5)	87* (4)	95 (5)
Endrin	120 (6)	90* (5)	108* (6)
4,4 DDD	118* (6)	95 (5)	101 (6)
Endrin Aldehyde	l10* (6)	14 (4)	101 (6)
Endosulfan Sulfate	92 (5)	88* (5)	117* (6)
4,4 DDT	113 (4)	95 (5)	91 (4)

* Results corrected for blanks.

Table 4. Mean % recovery and relative standard deviation (in parentheses) of 16 organochlorine pesticides in reagent water samples at 0.1 µg/L fortification level, (n=3).

Organochlorine Pesticides	Measurements of pesticide mixture	Individual measurements of each pest.
a-HCH	66 (5)	77 (4)
b-HCH	98 (6)	
Lindane	92 (6)	
D-HCH	88 (1)	
Heptachlor	66 (4)	
Aldrin	65 (4)	70 (3)
Heptachlor Epoxide	88 (1)	
a-Endosulfan	90 (1)	
4,4 DDE	88 (6)	
Dieldrin	98 (3)	
b-Endosulfan	80 (6)	
Endrin	98 (3)	79 (4)
4,4 DDD	96 (6)	
Endrin Aldehyde	95 (1)	
Endosulfan Sulfate	105 (5)	
4,4 DDT	105 (5)	

Table 5. Mean % recovery and relative standard deviation (in parentheses) of 3 triazines in drinking water samples at 0.2 and 10 µg/L fortification level, (n=3).

Triazines	Fortification level (µg/L) 10	0.2
Atrazine	92 (2)	110 (3)
Simazine	90 (1)	98 (2)
Terbutylazine	94 (4)	87 (2)

Forty samples of drinking water of Athens, originated from Iliki, Mornos and Marathonas and collected at the treatment plants of the City Water Company, were analysed using the method described above. Detectable levels of organochlorine pesticides and triazines were found (Table 6).

Table 6. Levels of organochlorine pesticides and triazines (μg/L) in drinking water of Athens, for winter 1992-93, according to samples' origin. Relative standard deviations are given in parentheses, (n=15 for Iliki and Marathonas, n=10 for Mornos). N.D. = not detected.

	Mean concentration, (μg/L)		
Pesticides	Iliki	Mornos	Marathonas
a-HCH	0.001 (20)	N.D.	N.D.
b-HCH	N.D.	N.D.	0.003 (17)
Lindane	0.005 (12)	0.005 (6)	0.005 (8)
D-HCH	N.D.	N.D.	0.001 (21)
Heptachlor	N.D.	N.D.	N.D.
Aldrin	0.001 (23)	0.001 (18)	0.001 (26)
Heptachlor Epoxide	N.D.	N.D.	N.D.
a-Endosulfan	0.006 (7)	0.001 (15)	0.003 (18)
4,4 DDE	0.003 (12)	0.001 (18)	0.002 (15)
Dieldrin	0.004 (10)	0.002 (12)	0.003 (9)
b-Endosulfan	0.004 (9)	0.002 (15)	N.D.
Endrin	0.001 (18)	N.D.	N.D.
4,4 DDD	0.002 (8)	N.D.	N.D.
Endrin Aldehyde	0.002 (15)	N.D.	N.D.
Endosulfan Sulfate	N.D.	0.004 (15)	N.D.
4,4 DDT	N.D.	N.D.	N.D.
Atrazine & Simazine	N.D.	0.045 (2)	0.040 (6)
Terbutylazine	N.D.	N.D.	0.015 (7)

Especially for lindane, the mean concentration in drinking water oriented from Iliki lake, for winter 1992-93 was found to be 0.005 μg/L. This value was similar to those observed by Miliadis (1994) for the same time period; from 0.014 μg/L on December 1992 to 0.005 μg/L on March 1993. It should be noticed that Miliadis study concerns surface water of Iliki at a certain point of the lake. The level of atrazine and simazine was higher than those of organochlorine pesticides. Both atrazine and simazine as herbicides are not used only in agriculture. They are mainly applied for total weed control on railways, roads, industrial areas, paths etc. (Commission of the European Communities 1992). Such uses can involve application to areas where possible routes to ground water exist.

However the concentration levels found are much lower than the EEC maximum acceptable concentration of 0.1 μg/L (E.C. Council Directive 1980) for both organochlorine pesticides and triazines.

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