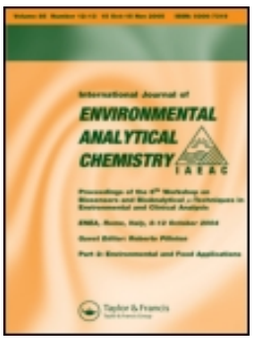

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Distribution of organochlorine pesticides in surface water and sediments in Lake Volvi (northern Greece)

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The objective of the study was to monitor the occurrence of a wide range of OCPs and sediments of the Lake Volvi in northern Greece and to determine their temporal and spatial variations. The samples have been collected seasonally for a period of one year. Solid-phase extraction followed by gas-chromatographic techniques with electron-capture detection was used for the determination of the compounds. The compounds detected were HCB, lindane, β-HCH, heptachlor, methoxychlor, α-endosulphan, and 2,4-DDT, while α-HCH, aldrin, heptachlorperoxide, 4,4-DDE, dieldrin, endrin, 4,4-DDD, β-endosulphan, and 4,4-DDT could not be observed (detection limits $\geq 1\ \mathrm{ng\,L^{-1}}$). The frequencies of the compounds detected in the samples varied between 10 and 83% and between 6 and 88% in the water and sediment samples, respectively. Among the 16 OCPs pesticides monitored, only 2,4-DDT and methoxychlor were found in detectable concentrations in sediments throughout the whole sampling period. The water–sediment distribution pattern of the detected compounds reflects the great capacity of the lake sediments to adsorb and accumulate such compounds.

Keywords: Distribution; Monitoring; Organochlorine pesticides; Water and sediments; Lake

1. Introduction

Organochlorine pesticides (OCPs) are considered dangerous not only to the environment but also to man. OCPs are very persistent substances, and it has been reported, for example, that the degradation of DDT in soil reaches about 75–100% in 4–30 years [1]. Other chlorinated pesticides such as aldrin, dieldrin, endrin, and isodrin remain persistent in the aquatic environment for many years after their application. Because of their persistence in the environment, there is great interest in examining

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the pollution which originates from these compounds. Their usage today is prohibited in Greece as well as in other countries, after evidence of their toxicity, persistence, and bioaccumulation in the environment became available [2, 3].

Generally, OCPs are hydrophobic substances, with a low water solubility, frequently found in environmental matrices at the μg or ng L^{-1} level. Most of the OCPs have octanol–water partition coefficients (K_{ow}), with log K_{ow} values between 3.5 and 6 and, thus, are very soluble in lipids. As a consequence, these pesticides accumulate in living organisms, and the OC pesticide concentration becomes bio-magnified along the food chain [4–6]. Once released into the aquatic environment, these substances can be either immediately ingested by organisms or adsorbed onto suspended particles, because of their high affinity for organic matter, and finally will end up accumulated in sediments, which may act as a secondary contamination source. These contaminants also accumulate in sediment-dwelling organisms, which then may be carried over to higher trophic levels through the food chain (again, bio-magnification). Pesticide residues may reach the aquatic environment through direct runoff, leaching, careless disposal of empty containers, equipment washing, etc. [7, 8]. Because of their large use, residues of OCPs are detectable in various environmental matrices, such as soil, water, sediments, and air. OC pesticides are known to resist biodegradation, and therefore they can be accumulated through food chains and bio-magnify.

The objective of the study was to monitor the occurrence of a wide range of OCPs and to determine their temporal and spatial variations in water and sediments of Lake Volvi. This lake is located in the northern part of Greece, about 11.5 km north-east of the city of Thessaloniki (figure 1). The whole area is protected by the Ramsar Convention as a site of international importance for the value of the wetland habitat. The area provides an ideal habitat for a variety of flora and fauna species.

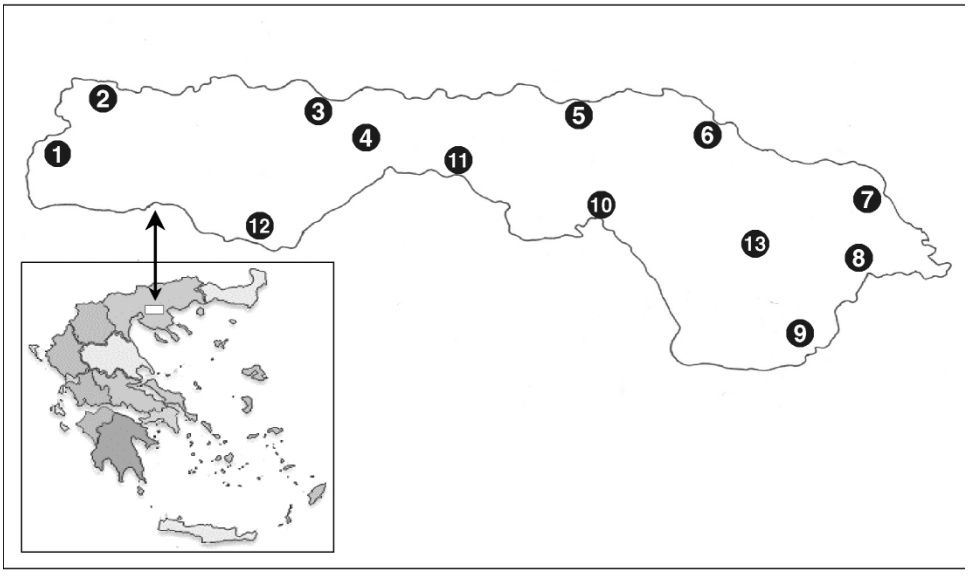

Figure 1. Outline of Lake Volvi, showing the selected sampling sites (numbers in black circles) used for surface water and sediment sampling, and map of Greece showing the position of the lake (inset).

2. Experimental

This monitoring study was carried out in water and sediment samples from the meso- to-eutrophic Lake Volvi. The water and sediment samples were collected every 3 months, from April 2003 to June 2004. Twelve sampling sites for water (sampling sites 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 13) and nine for sediments (sampling sites 1, 2, 3, 7, 8, 9, 10, 11, 12) were selected in the Volvi Lake area. For water sampling, 1 L glass bottles were used. The bottles were carefully filled just to overflowing, without passing air bubbles through the sample or trapping air bubbles in sealed bottles.

Pyrogenous copper for sulphur elimination [9] from sediment samples was prepared by mixing a slurry of 25 mL of water and 15 g of zinc powder to a solution of 25 g of copper sulphate dissolved by 20 mL of an aqueous hydrochloric acid solution ($2\,mol\,L^{-1}$). The solution was stirred in a magnetic stirrer until the colour of the solution turned reddish, and the formation of hydrogen gas stopped. Then, the solution was allowed to rest until sedimentation of the pyrogenous copper was completed. The water was decanted, and the pyrogenous copper first was washed three times with 250 mL of acetone in a glass beaker to remove residual water and then washed once with 250 mL of hexane. Thereafter, the pyrogenous copper/hexane slurry was transferred into an Erlenmeyer flask topped with more hexane and closed with a stopper.

3. Analytical procedures

3.1. *Sample preparation*

To determine the content of pesticides dissolved in water, the collected water samples were filtered through a 0.45 μm glass fibre filter (Whatman) to eliminate particulate matter, prior to acidification with hydrochloric acid to reach a pH of 2.5. Methanol (for pesticide residue analysis, 10 mL) was added as a modifier to 1 L water samples to allow better extraction. Solid-phase extraction (SPE) using pre-packed reverse-phase octadecyl bonded silica (RP-C_{18}) cartridges was used for sample pre-concentration. Prior to extraction, the SPE cartridges containing 500 mg of RP-C_{18} material were activated by subsequent washing, applying 20 mL of methanol and 10 mL of ultra pure water. The cartridges were not allowed to dry. The water samples were mixed well before they were percolated through the cartridges with a flow rate of 10–15 mL/min under vacuum. After sample extraction, the column was washed with one cartridge volume of ultrapure water. The SPE material was dried in a gentle stream of nitrogen before the pesticides were eluted by rinsing the cartridges with 10 mL of hexane (for pesticide–residue analysis). The eluates were evaporated to 1 mL in a gentle stream of nitrogen (concentration factor: 1000) before analysis [10].

Surface-sediment samples (0–10 cm) were collected using an Eckman sampling device. The samples were put into glass bottles, which were kept cool in the field (4°C). After transportation to the laboratory, the samples were then frozen and lyophilized, before being ground using a ball mill. The grinding stock was passed through a 75 μm and stainless steel sieve. Homogenized sediment samples (5 g) were extracted using a pressurized solvent extraction (PSE), using a Dionex ASE 200 Accelerated Solvent Extractor (ASE) (Dionex, Sunnyvale, CA) in combination with a solvent

controller (Dionex). The ASE 200 conditions were: oven temperature 100°C, oven heat-up time 5 min, static time 5 min, flush volume 60% of the extraction cell volume (11 mL), and extraction pressure 10 MPa. A mixture of hexane/acetone (1 : 1, v/v) was used as extraction solvent. The obtained extracts were concentrated under reduced pressure to a volume of 5.0 mL hexane.

The high sulphur content of the sediments disturbed ECD analyses, so the removal of sulphur was essential. This could be achieved by adding 100 mg of fresh prepared pyrogenous copper to an aliquot of 1.0 mL of the hexane extract and treating the mixture for 30 min in a ultrasonic bath. The pyrogenous copper pre-treated aliquot was purified by a column clean-up using 4 g of Florisil (60–100 mesh, Merck) activated at 300°C for 12 h. The Florisil was topped with 1 g of anhydrous sodium sulphate. Before the sample was transferred onto the column, 20 mL of hexane was allowed to percolate through the column. The sample was eluted from the column first with 20 mL of hexane followed by 20 mL of an acetone/hexane mixture (1 + 99, v/v). The eluents were combined and concentrated to 1.0 mL using a rotary evaporator.

3.2. Calibration and quantification

Calibration curves were prepared from a stock solution containing 10.0 mg L^{-1} of OCPs (table 1) dissolved in hexane by serial dilution to reach calibration concentrations of 5, 10, 20, 40, and 50 μg L^{-1}. Each calibration solution was analysed in triplicate by GC-ECD. The peak areas of the corresponding analytes were plotted against the calibration concentrations, and the regression coefficients were calculated as presented in table 1. Recovery experiments of OCPs were performed by spiking quartz sand with the OCP standard followed by ASE extraction, clean-up with pyrogeneous copper, florisil column clean-up, and analysis by GC-ECD. Blank samples of quartz sand were also generated and analysed.

Table 1. Pesticides and their retention time (RT) analysed in GC separation prior to electron capture detection (ECD), regression coefficients (r^2) and relative standard deviation of recovery rate (SD_R).

Compound no.	Compound	*RT* (min)	r^2	SD_R (%)
1	α-HCH	10.31	0.9995	2.8
2	HCB	10.48	0.9998	2.1
3	Lindane	11.04	0.9988	3.8
4	β-HCH	11.67	0.9993	3.6
5	Heptachlor	12.30	0.9996	4.3
6	Aldrin	12.96	0.9993	2.6
7	Heptachlor epoxide	13.99	0.9980	6.9
8	α-Endosulphan	14.84	0.9998	1.9
9	4,4′-DDE	15.20	0.9991	4.4
10	Dieldrin	15.55	0.9995	5.2
11	Endrin	16.23	0.9995	5.3
12	4,4′-DDD	16.39	0.9993	4.4
13	β-Endosulphan	16.79	0.9988	5.9
14	4,4′-DDT	17.15	0.9997	2.9
15	2,4-DDT	17.93	0.9993	5.6
16	Methoxychlor	20.11	0.9989	4.3

3.3. *GC-ECD determination of OCP in extracts of water and sediment samples*

A Perkin Elmer Autosystem gas chromatograph equipped with a ^{63}Ni ECD was used for GC-ECD analyses. GC separations were performed on a fused silica capillary column (DB-XLB; film thickness 0.50 μm; 30 m × 0.32 mm i.d. (J&W, Folsom, USA). The GC operating conditions were: injector temperature 300°C, detector temperature 320°C and carrier gas (nitrogen) flow rate 2 mL min^{-1}. The GC temperature programme conditions for the analysis of OCPs were: initial oven temperature 110°C, initial time 0.5 min, heated to 150°C by a temperature ramp of 25°C/min followed by a second temperature ramp of 12°C/min to a temperature of 260°C and a third temperature ramp of 15°C/min to an end temperature of 320°C, which was held for 2 min at 320°C. The hexane extracts of water and sediment samples were used for OCP analysis by gas chromatography in combination with an electron capture detector (GC-ECD) using aliquots of 2 μL. Injections were split (1 : 10) without and after column clean-up, respectively. Each sample was analysed twice (min) by GC-ECD. Qualification and quantification was performed using chromatographic software. The time window used for recognition of compounds was 0.1 min (RT tolerance). Typical chromatograms of standard and real surface water or sediment sample extracts, respectively, are presented in figure 2.

4. Results and discussion

The analysis of organochlorine pesticides (OCPs) present in μg or ng concentrations in environmental samples is not very easy because often the analysis is disturbed by other matrix compounds also present in the sample extracts. While the analysis of water sample extracts could be performed without any prior clean-up, the determination of OCPs in sediment extracts made the complete removal of elemental sulphur essential. This could be achieved by sample treatment, applying freshly prepared pyrogenous copper prior to ECD analyses.

The calibration curves were constructed by plotting the peak area against the concentration of the analytes. The calibration curves obtained were linear over the concentration range of 5.0–40.0 μg L^{-1} for all OCPs. The detection limits (LOD) were calculated by a signal-to-noise ratio of 3 (S/N 3 : 1) taking into account the sample amount. The calculated LODs for pesticides and water samples were about 1.0 ng L^{-1}, while the LODs for sediment samples were 1.0 μg kg^{-1} dry wt for each OCP. The limits of quantitation were about 3.3 times (S/N 10 : 1). The concentrations of analytes could be determined by using the linear regression curve (unweighted) of the calibration standards.

The results of the analysis of the samples showed the presence of a number of organochlorine pesticides in several water and sediment samples. The results of the sample analysis are summarized in table 2.

Of the compounds examined, HCB, lindane, β-HCH, heptachlor, methoxychlor, α-endosulphan, and 2,4-DDT were detected, while the compounds α-HCH, aldrin, heptachlorperoxide, 4,4-DDE, dieldrin, endrin, 4,4-DDD, β-endosulphan, and 4,4-DDT could not be observed (LOD $\geq$ 1 ng L^{-1}). The recoveries of the tested OCPs from the water and sediment samples of Lake Volvi ranged from 89 to 106% with a relative SD_R as shown in table 1.

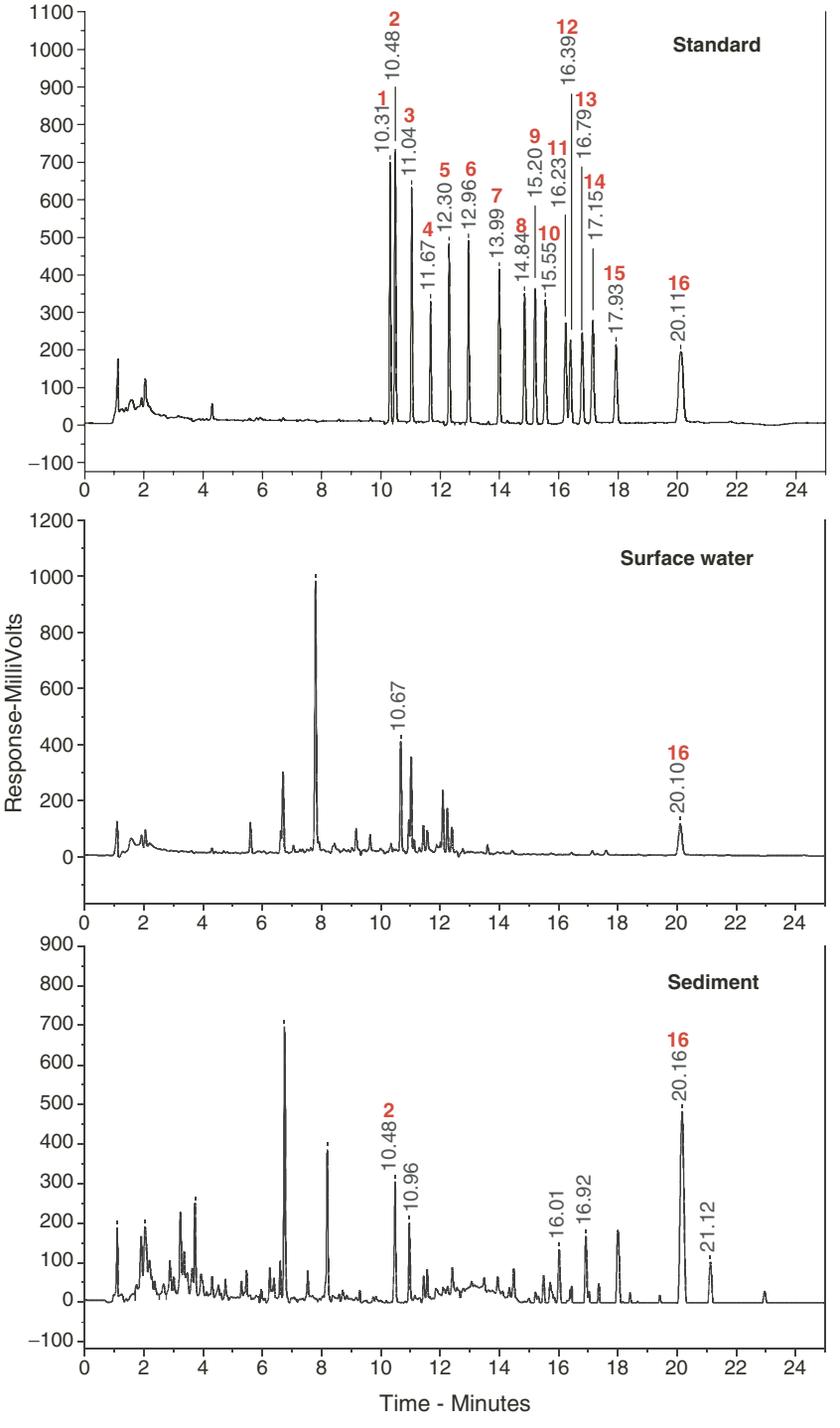

Figure 2. GC chromatograms of pesticides detected by ECD. (Top) GC-ECD chromatogram of a standard solution of 16 pesticides, as listed in table 1, dissolved in hexane at a concentration of 50 µg/L. (Bottom) GC-ECD chromatograms of surface-water extract (middle) and a sediment-sample extract.

Table 2. Concentration of organochlorine pesticides (OCP) observed in water and sediment samples collected from Lake Volvi.

Detected compounds	Water (ng/L) (no. of samples: $n=33$)				Sediment (μg/kg dry wt) (no. of samples: $n=64$)			
	Mean	Minimum	Maximum	Frequency of detection (%)	Mean	Minimum	Maximum	Frequency of detection (%)
HCB	1.2	1.0	10.2	10	1.4	1.1	7.6	12
Lindane	2.6	1.2	29.9	14	1.5	1.3	4.0	15
β-HCH	2.2	1.4	22.3	20	1.2	1	3.7	12
Heptachlor	1.4	1.3	7.8	14	1.1	1.2	2.1	6
Methoxychlor	32.2	3.7	145.5	83	17.4	1.5	77.9	85
2,4-DDT	7.2	1.4	142.2	23	34.8	8.1	119	88
α-Endosulphan	1.9	1.4	10.8	34	n.d.[a]	–	–	–

[a]n.d.: not detected.

The frequencies of the compounds detected in the samples varied between 10 and 83% and between 6 and 88% in water and sediment samples, respectively (table 2). In water, methoxychlor was detected at higher levels, with a mean concentration of 32.2 ng L^{-1}, while the lowest reached 3.7 ng L^{-1}. The other OCPs mentioned above were detected in most of the sediment samples. The highest concentration levels in sediments were observed for 2,4-DDT (34.8 μg kg^{-1} dry wt, mean concentration) followed by methoxychlor (17.4 μg kg^{-1} dry wt), while heptachlor was detected and confirmed at low levels with a mean concentration of 1.1 μg kg^{-1} dry wt by multiple injections ($n=3$).

The obtained results regarding the water–sediment distribution pattern of the detected compounds reflect the great capacity of the lake sediments to adsorb and accumulate such compounds. Neither DDT nor its degradation products (4,4-DDE or 4,4-DDD) were detected in water samples, while the degradation product 2,4-DDT was observed in sediment samples.

For α-endosulphan and methoxychlor, seasonal variations in the detected pesticide residue levels in water were observed in several sampling sites of the lake. The highest concentrations were found during the winter and the lowest during the spring. The sediment concentrations have a similar but less clear seasonal trend than the water concentrations. The concentrations of lindane in water samples were highest at sampling site 7 and for methoxychlor at sampling site 2. Differences in the concentrations observed between the sediment samples were less noticeable than between the water samples.

It is clear that water pollution from organochlorine pesticides during the sampling period was not very high. In any case, the concentrations detected were lower than the qualitative target levels set by the European Union [11]. The bioconcentration factor, defined as the concentration in the sediments divided by the concentration in water, reached values up to 4000 during this monitoring study.

In this preliminary study, the presence of organochlorine pesticides in a stable level of concentrations in the sediments during the sampling period could be proved, indicating that the sedimentary reservoir examined could act as a potential release source of the compounds and consequently could sustain aqueous contamination. The concentrations and distribution of the OCPs detected in sediments and water samples from Lake Volvi support this assumption.

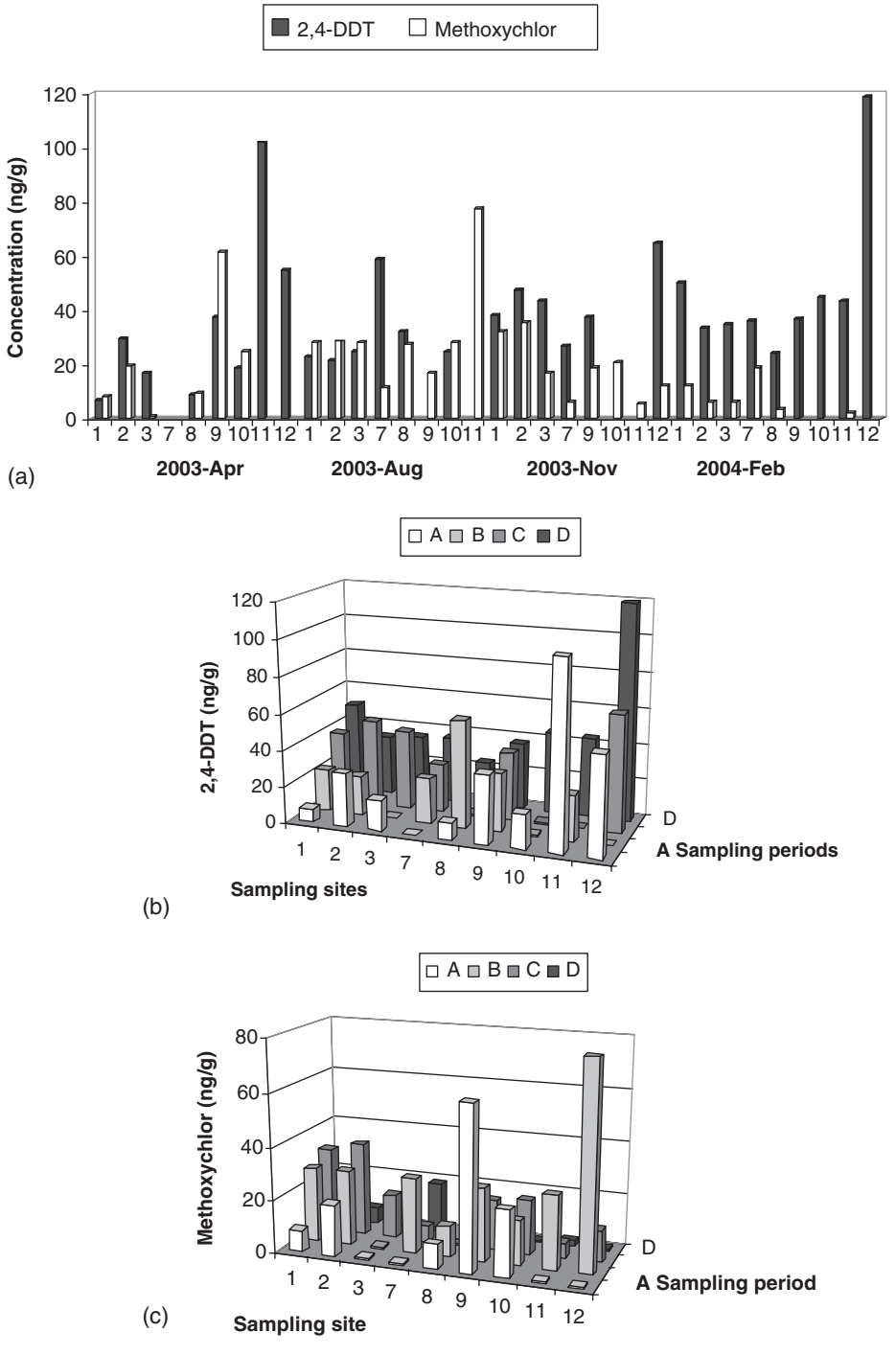

Figure 3. (a) Concentration profiles of 2,4-DDT and methoxychlor in sediments. (b) Concentration levels of 2,4-DDT in sediments in nine sampling sites for the four sampling periods. (c) Concentration levels of methoxychlor in sediments in nine sampling sites for the four sampling periods.

5. Statistical treatment

Of the 16 pesticides monitored, only 2,4-DDT and methoxychlor were found in detectable concentrations in sediments throughout the whole sampling period. Figure 3 shows the variation of these two analytes during the four sampling periods and for all the sampling sites.

A correlation analysis for the two analytes, taking into account either all the sampling sites or specific sites proved that no significant correlation exists in any of the cases ($r < 0.1$). This is probably because these two pesticides are not used simultaneously during the growth period, or at least they do not enter the lake simultaneously. The data concerning 2,4-DDT concentration in sediments are given in figure 3a, and the corresponding data for methoxychlor in figure 3b.

According to this classification, a correlation matrix was prepared, including each pair of sampling sites and taking into account the four samplings. The results are presented in tables 3 and 4 for 2,4-DDT and methoxychlor, respectively. In many cases, significant correlation coefficients were calculated, and this is additional to support the above hypothesis.

Table 3. Correlation matrix for all sampling sites for 2,4-DDT[a].

	1	2	3	7	8	9	10	11	12
1	1								
2	0.473664	1							
3	0.65884	**0.926052**	1						
7	**0.93635**	0.241365	0.381795	1					
8	−0.06773	**−0.81947**	−0.79309	0.259428	1				
9	0.141908	0.710737	0.791673	−0.21223	**−0.9586**	1			
10	0.424352	−0.0697	0.306079	0.241639	−0.13113	0.404425	1		
11	−0.6442	−0.43703	−0.3168	−0.76806	−0.15462	0.300038	0.411512	1	
12	0.645091	0.496467	0.783263	0.35964	−0.56196	0.739242	**0.831197**	0.101542	1

[a]Significant correlation coefficients are shown bold.

Table 4. Correlation matrix for all sampling sites for methoxychlor[a].

	1	2	3	7	8	9	10	11	12
1	1								
2	**0.830442**	1							
3	0.542951	0.422205	1						
7	0.322014	−0.11278	−0.34002	1					
8	−0.23882	−0.04093	**−0.92294**	0.339923	1				
9	−0.32676	0.233768	−0.44766	−0.54898	0.58199	1			
10	0.202831	0.712236	−0.0054	−0.54973	0.29968	**0.839527**	1		
11	0.594834	0.431388	−0.33841	0.790507	0.565695	−0.08393	0.072974	1	
12	0.575072	0.444374	−0.3686	0.761237	0.603877	−0.0243	0.122029	**0.998213**	1

[a]Significant correlation coefficients are shown bold.

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