MASS-SELECTIVE DETECTION OF PERSISTENT ORGANIC POLLUTANTS BY GC/MS. ISOLATION, CONCENTRATION, IDENTIFICATION AND DETERMINATION OF ISOMERIC-SPECIFIC COMPOSITION OF PCB IN NATURAL AND DRINKING WATERS OF DNIEPER RIVER BASIN IN KIEV REGION*

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In concentrates of natural and drinking waters of Dnieper river basin in Kiev region with enrichment factor of $2{,}0\cdot10^5$–$4{,}0\cdot10^5$ PCB ($PCB52^4$, $PCB66^4$, $PCB101^5$, $PCB118^5$, $PCB105^5$, $PCB153^6$, $PCB138^6$, $PCB180^7$, $PCB200^8$) have been identified and their isomeric-specific composition (tetrachloro- – heptachloroisomers) has been determined at MDL level as low as 10–400 pg/L.

Keywords: natural, drinking water, solid-phase extraction, microtraces, semivolatile organic compounds, polychlorinated byphenyls, identification, determination, GC/MS.

INTRODUCTION

The Dnieper river is the most important source for production of drinking water in Ukraine. Quality of natural water in it seriously deteriorated within last decades due to an excessive and uncontrolled pollution from numerous sources. Organic compounds from former and present discharges are being accumulated in sediments and ground water, from where they can penetrate into the artesian water resources and drinking water obtained by appropriate technology. Greatest problem is the fact, that there are no systematic data on identity of organic pollutants, especially toxic ones and on their content. As a result, environmental managers and politicians do not have full information in case they need to make decisions on water quality. Especially this concerns data obtained by high performance and highly informative physico-chemical methods of analysis and investigation. Therefore at present the actual up-to-date ecological state of the river basin is not known.

This gap is to be filled. Systematic analytical investigations on isolation, concentration [1–4], identification [5–8] and determination [9–14] of trace amounts of volatile and semivolatile organic compounds in natural, drinking [10,15] and mine [16] waters were carried out using chromatographic and mass-spectrometric (GC/FID, GC/ECD, GC/MS, MS, HPLC/FLU, HPLC/REF) methods at the levels from μg/l to pg/l.

Methodology of investigation of semivolatile organic compounds including persistent toxic organochlorine pesticides (OCP) and polychlorinated byphenyls (PCB) in these waters comprises the following steps [1−16]:

- adequate sampling, conservation of water samples and removal of solid phase by filtration;
- solid-phase extraction of sorbable organic compounds from waters (acid medium) by porous polymeric sorbents;
- elution of concentrated organic compounds from the sorbents with organic solvents of different polarity;

- evaporation of solvents from eluates using rotary evaporator at mild temperatures to anhydrous residual (to dryness) (removal of solvents using rotary evaporator);
- re-extraction of organic compounds obtained by methanol with simultaneous derivatization of compounds of acidic character (mild methylation) and then their full derivatization by diazomethane (hard methylation) with the aim of their derivatives volatility increase by GC/MS analysis (obtaining the general concentrates of organic contaminants of waters); (derivatization of compounds with acidic properties with the aim of their volatility increase in GC/MS analysis);
- identification and determination of mutagen MX microtraces in the general concentrates after methylation by GC/MS in the selected ion monitoring (SIM) mode;
- liquid extraction of nonpolar and weakly polar organic compounds from general concentrates after methylation of compounds with acidic properties; solvents which have been used for this aim (hexane, cyclohexane, benzene) are characterized by equal dipole moments ($\mu_{г}=0{,}08$; $\mu_{ц}=0$; $\mu_{б}=0$ [17]) but by different increasing dielectric constants ($\varepsilon_{г}=1{,}890_{20}$; $\varepsilon_{ц}=2{,}023_{20}$; $\varepsilon_{б}=2{,}284_{20}$ [17]) (fractionation of the general concentrates by means of different solvents);
- high performance chromatographic separation of the complex mixtures of organic compounds of the general concentrates obtained and of their fraction concentrates;
- identification of organic pollutants microtraces in the general concentrates and in concentrates of their fractions by GC/MS in SCAN mode;
- treatment of dry mass of general concentrates and/or of their fraction concentrates by concentrated H_2SO_4 and/or by oleum (anhydrous H_2SO_4 + 15–60 % SO_3);
- liquid-phase extraction of OCP and PCB from organic-acidic mass obtained after treatment by H_2SO_4 and/or by oleum;
- high performance chromatographic separation of OCP and PCB of purificated concentrates obtained (SIM mode);
- identification of OCP and PCB in the standard mixture by GC/MS (SCAN mode);
- identification and determination of OCP and identification and determination of isomeric-specific composition of PCB by GC/MS at the level of $1\cdot10^{-9}$–$1\cdot10^{-12}$ g/L (SIM mode).

This methodology of investigation has been used for identification and determination of semivolatile organic compounds of different classes and for monitoring of persistent OCP and PCB in natural (surface) and drinking waters of Dnieper river basin in Kiev – Dnepropetrovsk – Zaporozhie – Nikopol – Nikolaev region [1–16].

The contaminants of neutral and acidic character that belong to about 50 classes of semivolatile organic compounds have been identified in general concentrates and concentrates of their fraction in SCAN mode with enrichment factor $2{,}0\cdot10^{3}$–$5{,}0\cdot10^{4}$. They are following: highest normal and isomeric alkanes, normal and isomeric aliphatic monocarboxylic acids, highest normal aliphatic monocarboxylic acids ethyl esters, normal and isomeric aliphatic dicarboxylic acids, unsaturated aliphatic monocarboxylic acids with one, two and three double bonds, unsaturated aliphatic dicarboxylic acids, branched (methylene attached) unsaturated aliphatic dicarboxylic acids, oxo- and hydroxyderivatives of the aliphatic mono- and dicarboxylic acids, aliphatic tricarboxylic acids, aliphatic dichlorocarboxylic acids, aromatic mono-, di- and tricarboxylic acids, mono- and dichlorobenzoic acids, phthalic acid alkyl esters, phenolcarboxylic acids, steroids, highest aliphatic alcohols, aliphatic carbonyl compounds, aliphatic chloroketones, alkyl-, cycloalkyl- and alkenylbenzenes, chloroalkylbenzenes, alkylphenols and alkylchlorophenols, alkylarylureas, nitrogen heterocycles, aryl sulfones, sulfur heterocycles, nitrogen and sulfur heterocycles, nitrogen and phosphorus compounds and others [5–8,10].

In SIM mode 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (mutagen MX) and its geometric isomer (*E*)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (*E*-MX), OCP (α-, β-, γ-BHC, DDD, DDE, DDT) and PCB (trichloro- – octachloroisomers) were identified and determined.

In SIM mode for MX and *E*-MX after methylation as methyl derivatives concentration in drinking waters of Dnieper river basin was determined (characteristic ions, m/z 73, 107, 137, 147, 169, 199, 201, 203, 205, 217, 219, 221, 241, 243, 245, 247, 249, 276).

In SIM mode (10 groups of characteristic ions) for 16 OCP analysis of natural, drinking waters and sediments was carried out (the first, α-, β-, γ-, δ-BHC, m/z 109, 181, 219; the second, heptachlor, m/z 100, 135, 272; the third, aldrin, m/z 101, 263; the fourth, heptachlor epoxide, m/z 237, 263, 353; the fifth, endosulfans I and II, m/z 170, 195, 243; the sixth, dieldrin, m/z 108, 246, 263, 318; the seventh, endrin, m/z 170, 195, 263, 281; the eighth, endrin aldehyde, m/z 165, 235, 250, 346; the ninth, endosulfan sulfate, m/z 272, 387; the tenth, DDE, m/z 165, 246, 248 and DDD, DDT, m/z 165, 235, 237).

In SIM mode for PCB isomers concentration in natural, drinking waters and sediments of Dnieper river basin was determined (trichloro-, m/z 256, 258, 260; tetrachloro-, m/z 290, 292, 294; pentachloro-, m/z 324, 326, 328; hexachloro-, m/z 358, 360, 362; heptachloro-, m/z 392, 394, 396; octachloro-, m/z 426, 428, 430).

Special attention was paid to pollutants of mine water in the western area of the Donetsk coal basin as one of industrial sources of pollution of Dnieper river basin natural water [1,15,16].

The data on actual state of pollution of surface, drinking, mine waters and sediments of the Dnieper river by semivolatile organic substances (OCP – α-, β-, γ-BHC, DDE, DDD, DDT; organophosphorus pesticides – metaphos, carbophos, rogor; phthalates; chlorophenols; polynuclear aromatic hydrocarbons; PCB; nonionic surfactants; etc.) have been generalized for period of 1987–1994 [10,15,16].

Aim of this paper is identification and determination of isomeric-specific composition of PCB in natural and drinking waters of Dnieper river basin on the example of Dnieper and Desna water treatment stations of Kiev.

EXPERIMENTAL

Procedures for preparation of general concentrates of microcontaminants of semivolatile and nonvolatile organic compounds from natural and drinking waters, of their hexane extract and its purification

Developed and modernized procedures (solid-phase extraction of semivolatile and nonvolatile organic compounds by porous polymeric sorbents from acid medium, elution of complex mixtures of sorbed compounds, their concentration, methylation of compounds with acidic character, fractionation of organic compounds by solvents with different polarity) have been used for preparation of general concentrates of micropollutants of natural and drinking waters which were described in detal in [2–4].

Isolation of PCB from general concentrates has been carried out by two consecutive liquid extractions with hexane (on 25 mL of hexane each time).

Hexane extract has been treated by concentrated sulfuric acid and/or by oleum.

Separation of hexane layer from organic-acidic mass has been fulfilled further.

Preparation of PCB concentrates from natural and drinking waters of Dnieper river basin in Kiev region

As an investigation object natural and drinking waters of Dnieper and Desna water treatment stations were chosen for the period of 1997–1999.

The general concentrates of micropollutants of natural and drinking waters and concentrates of their hexane fraction have been obtained.

After treatment of hexane extract by concentrated sulfuric acid and/or by oleum and separation of hexane layer from organic-acidic mass and solvent evaporation to 50 μL enrichment factor of purified concentrate was $2{,}0\cdot10^5$–$4{,}0\cdot10^5$ depending on from the volume of initial water, which was taken for analysis (10–20 L).

The last concentrates mentioned have been used for identification and determination of isomeric-specific composition of PCB by GC/MS in SIM mode.

Procedure for investigation of PCB from natural and drinking waters using GC/MS in SIM mode

Hexane concentrates after purification isolated from the general concentrates were investigated by GC/MS on gas chromatograph HP5890 Series II with mass-selective detector HP5970B and on gas chromatograph HP5890 with mass-selective detector HP5971 with quadrupole mass analysers. The concentrates of organic water contaminants (1 μL) were injected into an injector port of the chromatograph splitless by Hamilton syringe.

Chromatographic conditions: carrier gas – helium, inlet pressure – 50 kPa, oven temperature program from 60 to 270°C, 8 °C/min rate, then isothermally at 270 °C for 15 min, columns SE-30 (25m·0,25mm·0,25μm) (Supelco) and HP-1 (12m·0.2mm·0.32μm) (Hewlett-Packard).

Mass-spectrometric conditions: EI was realized under 0,2 mA current and ionization energy of 70 eV, the mass-spectra were registered by means of an electron multiplier under -2,2 – -2,4 kV and pressure of $2{,}0\cdot10^{-5}$ Torr in an ion source chamber in mass range 35–650 a.m.u. and SCAN frequency of 0,6–0,7 Hz.

Reference mixture no. 4-8707 Aroclor 1254 Supelco with concentration of 200 mg/L was used for calibration of chromato-mass-spectrometers in SCAN mode and with concentration of 2 mg/L in SIM mode.

RESULTS AND THEIR DISCUSSION

Chromatogram of PCB Aroclor 1254 reference mixture of 200 mg/L concentration was performed by GC/MS in total ion current (TIC) (SCAN mode). Identification of separated peaks of complex mixture of these compounds was carried out by comparing mass-spectra of real mixture with mass-spectra which are presented in Wiley library with high probability (97–99 %). Mass-spectra of tetrachloro- – octachloroisomers of PCB have intensive characteristic ions $M^{+\cdot}$, $[M+2]^{+\cdot}$, $[M+4]^{+\cdot}$ and definite ratio of intensities which are given in table 1.

Table 1. Characteristic ions of PCB $M^{+\cdot}$, $[M+2]^{+\cdot}$, $[M+4]^{+\cdot}$ and ratio of their intensities $I_M^{+\cdot}$ / $I_{[M+2]}^{+\cdot}$ / $I_{[M+4]}^{+\cdot}$

Isomers of PCB	Characteristic ions $M^{+\cdot}$, $[M+2]^{+\cdot}$, $[M+4]^{+\cdot}$ with m/z	Ratio of intensities $I_M^{+\cdot}$ / $I_{[M+2]}^{+\cdot}$ / $I_{[M+4]}^{+\cdot}$
Trichloro-	256, 258, 260	10:6:3**
Tetrachloro-	290, 292, 294	8:10:5
Pentachloro-	324, 326, 328	6,6:10:6,6
Hexachloro-	358, 360, 362	5:10:8
Heptachloro-	392, 394, 396	5:10:10
Octachloro-	426, 428, 430	3,6:8,4:10

** Identification of trichloroisomers of PCB was carried out by standard mixture of Aroclor 1248. Ratio of intensities of characteristic ions $I_M^{+\cdot}$ / $I_{[M+2]}^{+\cdot}$ / $I_{[M+4]}^{+\cdot}$ was taken from [9].

Chromatogram of reference mixture of 2 mg/L PCB concentration was performed by GC/MS in SIM mode and ratio of characteristic ions intensities for tetra- – octachloroisomers was determined. Coinsiding retention times and ratio of intensities of characteristic ions in two modes were obtained. Therefore retention times and definite ratio of intensities of these ions $M^{+\cdot}$ /

$[M+2]^{+\cdot}$ / $[M+4]^{+\cdot}$ served as characteristic ones for identification of these isomers for analysis of mixtures isolated from real objects of investigation in chosen time intervals which are close to retention times.

Tipical chromatogram of PCB concentrates (SIM mode) isolated from real object of investigation is presented in figure 1.

Retention times of identified individual PCB and analytical parameters of this method in these conditions (noize, signal/noize ratio, limit of detection LOD, limit of quantification LOQ and method detection limit MDL) are presented in table 2.

Table 2. Retention times of identified individual PCB and analytical parameters of method

t, min	PCB	m/z	Height of peak H, conv. unit	Noize N	Signal/ Noize ratio S/N	Limit of detection LOD a), mg/L	Limit of quantification LOQ b), mg/L	Method detection limit MDL c), ng/L
15,818	PCB52[4]	290	1406					
15,819		292	1826	66	28	0,14	0,72	0,7
15,819		294	845					
17,277	PCB66[4]	290	948					
17,278		292	1223	66	19	0,22	1,08	0,11
17,278		294	632					
17,380	PCB101[5]	324	1404					
17,381		326	2347	36	65	0,66	0,31	0,03
17,382		328	1534					
18,795	–	324	2594					
18,795		326	4380	36	122	0,03	0,16	0,015
18,795		328	2876					
19,404	PCB118[5]	324	1959					
19,404		326	3107	36	86	0,05	0,23	0,025
19,405		328	1971					
20,011	PCB105[5]	324	1055					
20,010		326	1129	36	31	0,13	0,64	0,0625
20,010		328	811					
19,945	PCB153[6]	358	905					
19,946		360	1771	30	59	0,07	0,34	0,035
19,946		362	1469					
20,557	PCB138[6]	358	1082					
20,557		360	2081	30	69	0,06	0,29	0,03
20,560		362	1609					
22,102	PCB180[7]	392	105					
22,115		394	246	32	252	0,02	0,08	0,01
22,114		396	241					
25,5	PCB200[8]	426						
25,5		428						
25,5		430						

a) – was determined at S/N=2; b) – was determined at S/N=10; c) – was determined at enrichment factor $k=2,0\cdot10^5$.

Identification and determination of PCB isomers in investigated concentrates was carried out by GC/MS in SIM mode using characteristic ions.

Calibration plot for mixture of PCB constructed in coordinates “height of chromatographic peak – concentration of model compounds” is linear in all the range of measurements from 1,0 to 4,0 mg/L (r = 0,997–0,998, n = 3).

Taking into account the linearity of the calibration plots the concentration of PCB in initial water can be calculated by any initial concentration of its model PCB by the formula

$$C_{xi} = H_{xi} \cdot (C_{0i} / H_{0i}) \cdot (1 / k),$$

where H_{0i} and H_{xi} are heights of peaks on the chromatogram of PCB in model and real mixtures, respectively; C_{0i} is concentration of PCB in model mixture; C_{xi} is concentration of PCB in real mixture; and $k = V_w / V_{conc}$ is enrichment factor equal to the ratio of water sample volume to volume of the corresponding concentrate.

For calculation of concentration of respective isomers in mixture the following isomeric content of PCB Aroclor 1254 model mixture was used: tetrachloro- – 11 %, pentachloro- – 49 %, hexachloro- – 34 %, heptachloro- – 6 % [18].

Calculation of isomeric-specific content was carried out by the mean value of total concentration of PCB calculated by the mean value in each group of isomers or by the mean value of total concentration of PCB calculated by the mean value in all groups of isomers.

Example of calculation of total concentration and isomeric-specific composition of PCB is presented in table 3 (natural water of Dnieper river, input; see table 4).

Table 3. Calculation of total concentration and isomeric-specific composition of PCB

t, min	PCB	m/z	Total concentration of PCB $C\cdot10^9$, g/L	Mean value of total concentration of PCB $C\cdot10^9$, g/L	Mean value of total concentration of PCB in each group of isomers $C\cdot10^9$, g/L	Mean value of total concentration of PCB in all groups of isomers $C\cdot10^9$, g/L	Isomeric-specific composition calculated by the mean value in each group of isomers $C\cdot10^9$, g/L	Isomeric-specific composition calculated by the mean value in all groups of isomers $C\cdot10^9$, g/L
16,023	PCB52^{4}	290	3,78	4,31±0,55 (12,7 %)	5,91±1,60 (27,1 %)	7,15±1,72 (24,1 %)	0,65±0,18 (27,7 %)	0,79±0,19 (24,1 %)
		292	3,74					
		294	5,40					
17,515	PCB66^{4}	290	6,86	7,51±0,81 (10,8 %)				
		292	6,55					
		294	9,11					
17,574	PCB101^{5}	324	1,54	1,39±0,17 (12,3 %)	3,89±2,55 (65,7 %)		1,90±1,25 (65,6 %)	3,50±0,84 (24,0 %)
		326	1,05					
		328	1,58					
18,994	–	324	1,41	1,28±0,07 (5,1 %)				
		326	1,25					
		328	1,19					
19,731	PCB118^{5}	324	6,50	8,99±1,30 (14,5 %)				
		326	10,90					
		328	9,58					
20,273	PCB153^{6}	358	8,42	8,14±1,65 (2,0 %)	6,80±1,35 (19,8 %)		2,31±0,46 (19,9 %)	2,43±0,58 (23,9 %)
		360	8,16					
		362	7,85					
20,832	PCB138^{6}	358	5,39	5,45±0,04 (0,7 %)				
		360	5,45					
		362	5,52					
22,358	PCB180^{7}	392	17,1	11,98±2,60 (21,7 %)	11,98±2,60 (21,7 %)		0,72±0,16 (22,2 %)	0,43±0,10 (23,3 %)
		394	10,2					
		396	8,63					

Content of isomers calcullated by the mean value in each group of isomers (tetrachloro- – heptachloroisomers) is presented in table 4,1*, figure 2,a–d, curve 1,3 and content of isomers calculated by the mean value in all groups of isomers is presented in table 4,2*, figure 2,a–d, curve 2,4.

Determination of isomeric-specific content of tetrachloro- – heptachloroisomers was carried out by GC/MS in SIM mode at the MDL level as low as 10–400 pg/L.

Table 4. Results of determination of PCB (pg/l) in natural and drinking waters of the Dnieper and Desna water treatment stations, Kiev (1997–1999)

Isomers of PCB***	Natural water of Dnieper river, input		Drinking water				Natural water of Desna river, input		Drinking water			
			after chlorination stage		tap water				after chlorination stage		tap water	
	1*	2*	1*	2*	1*	2*	1*	2*	1*	2*	1*	2*
Tetrachloro-	650	790	690	1000	470	390	280	510	660	510	1000	540
Pentachloro-	1910	3500	2450	4450	1410	1750	1000	2270	1400	2290	620	2390
Hexachloro-	2310	2430	3300	3090	400	1210	1890	1580	1750	1590	680	660
Heptachloro-	720	430	920	540	360	210	500	280	280	280	430	290

*** – total content of isomers with this degree chlorination;
1* – content of isomers calculated by the mean value of total concentration of PCB in each group of isomers (tetrachloro- – heptachloroisomers);
2* – those in all groups of isomers.

Relationship of content change for all four PCB isomers groups in natural and drinking waters of Kiev Dnieper and Desna water treatment stations are shown in figure 2 for evidence and data analysis for content of isomers calculated by the mean value of total concentration of PCB in each group of isomers (tetrachloro- – heptachloroisomers) (table 4,1*) and those in all groups of isomers (table 4,2*). Values of absciss axis correspond to: 1 – input water, 2 – raw water after chlorination stage, 3 – tap water.

Analysis of presented data shows that content of all four PCB isomers groups in natural and drinking waters of Dnieper water treatment station has the following relationship $C_{tap} < C_{input} < C_{after\ chlorination\ stage}$ (figure 2,a–d). The relationship demonstrates that additional amount of PCB is formed when chlorinating as compared with input water. The dependence appears to be connected with higher content of easily chlorinated polyoxyphenolic compounds (flavons, flavonons, flavonoids, antocians, crenic, apocrenic, fulvic acids etc.) in natural water. The relationship has been traced for all of PCB isomers groups (table 4). Maximum of PCB content falls on pentachloro- and hexachloroisomers.

Somewhat different picture is observed for natural and drinking waters of Desna water treatment station. Content change for each isomers groups calculated by the mean value of total concentration of PCB has its own dependence. Content of tetrachloroisomers increases simultaneously in the row $C_{input} < C_{after\ chlorination\ stage} < C_{tap}$ (table 4,1*, figure 2,a). At the same time for the content of pentachloroisomers analogous relationship of concentration change as well as in Dnieper waters $C_{tap} < C_{input} < C_{after\ chlorination\ stage}$ is observed (table 4,2*, figure 2,b). Content of hexachloroisomers decreases in the row $C_{input} > C_{after\ chlorination\ stage} > C_{tap}$ (table 4,1*, figure 2,c). At the same time for the content of heptachloroisomers somewhat unusual dependence $C_{after\ chlorination\ stage} < C_{tap} < C_{input}$ is observed (table 4,1*, figure 2,d).

Calculated data of PCB content appreciated in all groups of isomers in natural and drinking waters of Desna water treatment station for three isomers (tetrachloro-, pentachloro-, heptachloroisomers) do not show practically change of their content when preparing tap water. Only for hexachloroisomers the dependence of concentration change as well as in Dnieper waters is observed (table 4,2*, figure 1,c). Maximum of PCB content in this water in the same way falls on pentachloro- and hexachloroisomers.

The latter relationship illustrates that very insignificant amount of PCB is formed when chlorinating as compared with input water. The relationship seems to be connected with another ratio of easily chlorinated polyoxyphenolic compounds (flavons, flavonons, flavonoids, antocians, crenic, apocrenic, fulvic acids etc.) and humic acids in this natural water.

Illustrations of content change of PCB isomers for Dnieper and Desna water treatment station may be considered as coinciding only for pentachloro- and hexachloroisomers.

CONCLUSIONS

In concentrates of natural and drinking waters of Dnieper river basin in Kiev region with enrichment factor of $2{,}0 \cdot 10^5$–$4{,}0 \cdot 10^5$ PCB (PCB52^4, PCB66^4, PCB101^5, PCB118^5, PCB105^5, PCB153^6, PCB138^6, PCB180^7, PCB200^8) have been identified and their isomeric-specific composition (tetrachloro- – heptachloroisomers) has been determined at MDL level as low as 10–400 pg/L.

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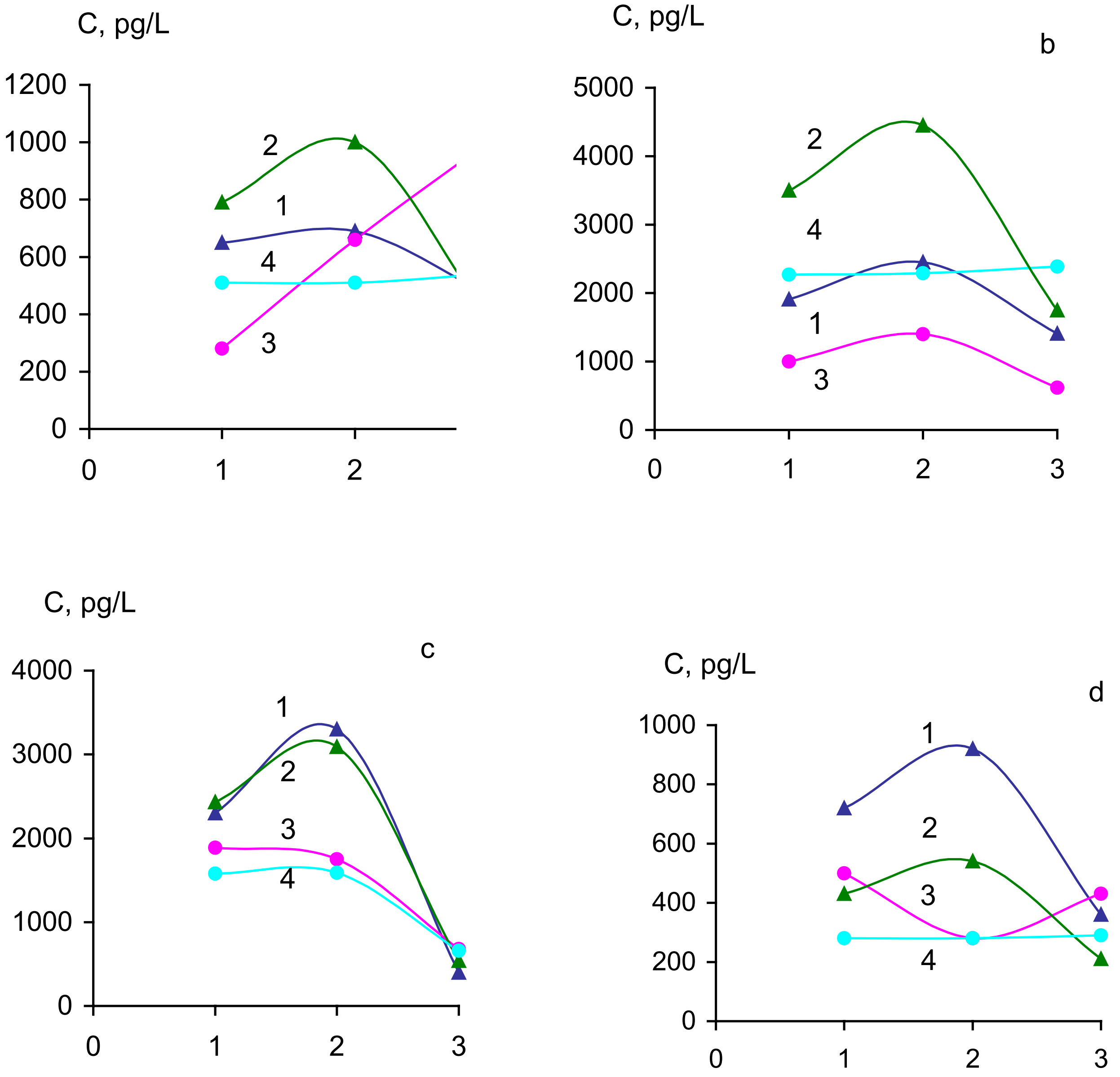

Figure 2. Isomeric-specific composition of PCB isomers (a – tetrachloro-, b – pentachloro-, c – hexachloro-, d – heptachloro-) in natural and drinking waters of Dnieper (curve 1, 2) and Desna (curve 3, 4) water treatment stations. Values of absciss axis correspond to: 1 – input water, 2 – raw water after chlorination stage, 3 – tap water.

Figure 1. Total ion chromatogram in SIM mode of PCB (tetrachloro- – heptachloroisomers) concentrate isolated from drinking water after chlorinated stage of Dnieper water treatment stations.

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