



# **Comparative Study of the Occurrence of Chlorophenols and Other Chloroaromatics in Surface-derived and Underground-derived Tap Waters**

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## **1. Introduction**

Phenol and chlorophenols are widely represented aromatic compounds in surface and drinking water. In respect to strong toxicity and ability of bioaccumulation of polychlorinated phenols they endanger the environment and human beings [6]. Similarly, chlorocatechols and chlorinated methoxyphenols i.e. chloroguaiacols and chlorosyringols, which are formed in the environment from chlorophenols and chlorobenzenes are of concern for human live and the environment [15]. The occurrence of the chlorophenols and their derivatives in the aquatic ecosystems is often connected with natural processes [9], which may be sometimes the major source of these compounds in surface water [16]. Nevertheless, phenol, chlorophenols, chlorobenzenes and polychlorinated biphenyls (PCBs) are mainly formed as a result of human activity because they are used as the precursors and the components of numerous chemicals including dyes, solvents plastics, resins, pharmaceuticals and pesticides [23,

2, 3]. It was also proven that the occurrence of chlorinated aromatics in drinking water is connected with disinfection of raw water with chlorine oxidants (water chlorination), which may be responsible for the increase of their content in treated water as it was observed by Dietz and Traud [5]. Chlorinated aromatics usually exhibit strong toxicity. For example, 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) are endocrine disruptors [13]. Those substances also provoke liver cancer and lymphomas in rodents and probably provoke cancer development in humans, thus they were classified by The International Agency for Research on Cancer as a probable and a possible carcinogens, respectively [11]. It was also proven that chlorobenzenes affect reproductive system in humans [12] and polychlorinated biphenyls suppress the immune system and change thyroid hormone levels, which are critical for normal growth and development. Studies in animals and humans suggest that PCBs are probable human carcinogens [23]. The European Council Directive that refers to the quality of water intended for human consumption, set admissible concentration for phenol and individual chlorophenol up to 500 ng/L and 100 ng/L, respectively. Moreover, the maximum level for individual pesticide and related products including persistent organochlorine compounds (chlorobenzenes, polychlorinated biphenyls) must not exceed 100 ng/L [7]. According to our best knowledge, there is insufficient information concerning the presence of the above described substances in tap waters derived from underground aquatic environments. Moreover, no study has been conducted that would compare the differences in the content of these compounds in surface-derived and underground-derived tap waters. Therefore, in this study we have assessed the differences in seasonal occurrence (samples were collected four times in the year) of phenol, chlorophenols, chlorocatechols, chloroguaiacols, chlorosyringols, chlorobenzenes and polychlorinated biphenyls in tap waters derived from surface and underground sources.

## **2. Methodology**

### **2.1. Sample collection**

The collection of tap water samples was conducted in Łódź city (central Poland) in the areas supplied both with water derived from surface intake situated on the Pilica River and groundwater intake situated within

the city. River water is taken by the Municipal Facility of Łódź Water-Works, Department of Water Production ‘Tomaszów’. The water is taken from surface current of the Pilica River, and then it is subjected to coagulation and sand filtration. Finally, the water is ozonated and disinfected with gaseous chlorine at a concentration of 1.5 g of active chlorine per 1 m<sup>3</sup> of water. Treated water is sent from the facility to Łódź City in a mean time of 48 h. Underground water is taken by a Department of Water Production ‘Łódź’. The facility takes water from 13 wells of 120 to 900 m in depth from quaternary and cretaceous leads. The water is filtrated, aerated and then chlorinated with chlorine dioxide at a concentration of 0.5 g of active chlorine per 1 m<sup>3</sup> of water. Treated water is pumped into underground reservoirs, and then within some hours it is sent to consumers. From each site, four samples were collected four times in the year of 2010 in March, June, September and December. Four samples of tap water in a volume of 1 L each were collected to analyze phenols, chlorobenzenes and chlorinated biphenyls, respectively. After the collection, 10 mL of methanol and 0.1 g of ascorbic acid were added to the samples to inhibit oxidation of phenols or/and microbes development.

## 2.2. Chemicals

Analytical standards (99.5%–99.9% purity) of hydroxybenzene (phenol), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,3,6-trichlorophenol (2,3,6-TCP) (internal standard), 2,4,5-trichlorophenol (2,4,5-TCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,5-tetrachlorophenol (TeCP), pentachlorophenol (PCP), 4-methylphenol, 1,2-dihydroxybenzene (catechol), 4-chlorocatechol (4-CC), 3,4,5-trichlorocatechol (3,4,5-TCC), tetrachloro-catechol (TeCC), 2-methoxyphenol (guaiacol), 4,6-dichloroguaiacol (4,6-DCG), 4,5,6-trichloroguaiacol (4,5,6-TCG), tetrachloroguaiacol (TeCG), 2,6-dimethoxyphenol (syringol), 3-chlorosyringol (3-CS), trichlorosyringol (TCS), veratrole, trichloroveratrole (TCV), chlorobenzene (CB), 1,2-dichlorobenzene (1,2-CB), 1,3-dichlorobenzene (1,3-CB), 1,4-dichlorobenzene (1,4-CB), 1,2,3-trichlorobenzene (1,2,3-TCB), 1,2,4-trichlorobenzene (1,2,4-TCB), hexachlorobenzene (HCB), 1,4-dibromobenzene (internal standard). PCBs mixture at a concentration of 10 ng/μL of 2,4,4’-trichlorobiphenyl “IUPAC No. 28”, 2,2’,5,5’-tertrachlorobiphenyl “IUPAC No. 52”, 2,2’,4,5,5’-pentachlorobiphenyl “IUPAC No. 101”,

2,3',4,4,5'-pentachlorobiphenyl "IUPAC No. 118", 2,2',3,4,4',5'-hexachloro-biphenyl "IUPAC No. 138", 2,2',4,4',5,5'-hexachlorobiphenyl "IUPAC No. 153", 2,2',3,4,4',5,5'-heptachloro-biphenyl "IUPAC No. 180"), and 2,3,3',4,4',4,4'-heptachlorobiphenyl "IUPAC No. 189" (internal standard) were bought from Sigma Aldrich (USA) and Promochem (Germany). Methanol, hexane, dichloromethane, diethyl ether, acetone, phosphoric acid (HPLC purity) and octadecyl C18 solid-phase discs were purchased from Baker JT (USA).

### **2.3. Sample preparation**

Solid-phase extraction, sample derivatization as well as gas chromatography-mass spectrometry analysis of phenol, chlorophenols and their derivatives were conducted according to previously published procedure [17].

In the laboratory, the internal standard solution (1.0 µg of 1,4-dibromobenzene dissolved in 1 mL of acetone) was added to the samples that were intended for chlorobenzenes analysis. Next, 200 g of sodium chloride was dissolved in water, and the samples were acidified with 10% phosphoric acid to pH 2.0. Finally, the samples were mixed using a magnetic stirrer (750 rpm) for 30 min.

The adsorption of chlorobenzenes from water was performed on octadecyl C18 discs (diameter of 50 mm, thickness of 1.0 mm) in the Baker Separex system. Before the compounds were adsorbed, the solid-phase had been conditioned using 10 mL volumes of diethyl ether, methylene chloride, methanol and deionized water acidified with 10% phosphoric acid (pH 2.0), respectively. After adsorption, the compounds were eluted with 10 mL volume of diethyl ether, and then with 10 mL volume of methylene chloride.

After elution, the solvents were dried with anhydrous sodium sulphate, concentrated to a volume of 0.5 mL, and then, the fraction was dissolved in a volume of 30 mL of hexane. Hexane fraction was extracted twice using 20 mL of 0.1 mol/L potassium carbonate. The hexane fraction was discarded, 1 mL of acetic anhydride was added for the derivatization of chlorobenzenes, and then, 0.5 mL of pyridine and 30 mL of hexane were added to the combined potassium carbonate fraction. The samples were shaken for 30 min and placed in a separator. After separation of the phases, the solvent (hexane) was collected and the water phase

was extracted twice with 20 mL of hexane. The combined hexane phases were dried with anhydrous sodium sulphate and evaporated under a gentle nitrogen stream to a volume of 0.1 mL for gas chromatography analysis.

Preparation of sample and solid-phase extraction of polychlorinated biphenyls was performed according to polish standard PN-C-04579-1:1999 Water and Wastewater – Tests for Polychlorinated Biphenyls (PCBs) Content – Determination of PCBs no 28, 52, 101, 118, 138, 153, 180 in water by gas chromatographic methods.

#### **2.4. Gas chromatography-mass spectrometry analysis**

The chromatographic analysis of all the compounds studied was done using a gas chromatograph (Hewlett-Packard type 5890, USA) connected with a quadruple mass spectrometer type 5972 (temperature MS – 162°C) equipped with a capillary column HP 5 (60 m x 0.25 mm) for chlorobenzenes separation and HP (30 m x 0.25 mm) for polychlorinated biphenyls separation, phase thickness 0.25 µm. In order to analyze chlorobenzenes, the column temperature was maintained at 40°C for 7 min, then increased to 80°C at the rate of 10°C/min, and to 110°C at the rate of 27°C/min, finally, the temperature was increased to 230°C at the rate of 40°C/min and eventually maintained for 15 min. The temperature of the splitless injector was 250°C. The carrier gas was helium (rate of flow, 0.9 mL/min). Splitless time – 0.7 min. Full scan EI of the chlorobenzenes to estimate their retention times and characteristic ions was performed in the range of mass  $m/z$  50–400: chlorobenzene ( $m/z$  77, 112, 114), 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene ( $m/z$  111, 146, 148), 1,4-dibromobenzene ( $m/z$  75, 155, 236), 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene ( $m/z$  109, 180, 182) and hexachlorobenzene ( $m/z$  282, 284, 286).

The chromatographic separation of polychlorinated biphenyls, after optimization, was as followings: initial temperature was 100°C maintained for 2 min, then, increased to 160°C at the rate of 25°C/min and finally increased to 280°C at the rate of 5°C/min and held for 10 min. The temperature of the splitless injector was 250°C. The carrier gas was helium (rate of flow, 0.9 mL/min). Splitless time – 0.7 min. Full scan EI of the polychlorinated biphenyls to estimate their retention times and characteristic ions was performed in the range of mass  $m/z$  50–450: PCB 28 ( $m/z$  256, 186), PCB 52 ( $m/z$  292, 220), PCB 101 and 118 ( $m/z$  326,

254) PCB 138, 153 (m/z 360, 290), PCB 180 and 189 (m/z 394, 324). The evaluation of all separated compounds was performed in the selective ion monitoring system (SIM). For each compound three m/z ions were chosen, dwell time per SIM ions – 100 ms. The order of elution, retention times and characteristic ions (relative intensity,%) used for quantification and confirmation of the compounds analyzed are listed in Table 1.

**Table 1.** List of chlorobenzenes and polychlorinated biphenyls retention times and quantification ions for GC/MS/SIM analysis

**Tabela 1.** Wykaz analizowanych chlorobenzenu i polichlorowanych bifenyli z podaniem ich czasów retencji oraz oznaczonych jonów fragmentacyjnych techniką GC-MS

Analytes	Retention time (min)	Characteristic ions (m/z) (relative intensity, %)		
		Quantification Ion	Confirmatory Ion 1	Confirmatory Ion 2
Chlorobenzenes				
Chlorobenzene	12.70	112(100)	77(76)	114(32)
1,2-Dichlorobenzene	15.45	146(100)	148 (66)	111 (44)
1,3-Dichlorobenzene	15.52	146(100)	148 (66)	111 (44)
1,4-Dichlorobenzene	15.79	146(100)	148 (66)	111 (44)
1,2,4-trichlorobenzene	16.56	180 (100)	182 (96)	109 (32)
1,4-Dibromobenzene (IS)	17.05	236 (100)	155 (53)	75(48)
1,2,3-Trichlorobenzene	17.97	180 (100)	182 (96)	109 (40)
Hexachlorobenzene	23.22	284 (100)	286 (88)	282 (55)
Chlorinated biphenyls				
Trichlorobiphenyl (28)	9.40	–	186(100)	256 (80)
Tetrachlorobiphenyl (52)	9.85	–	292(100)	220 (95)
Pentachlorobiphenyl (101)	11.03	–	326(100)	254 (65)
Pentachlorobiphenyl (118)	11.86	–	326(100)	254 (60)
Hexachlorobiphenyl (138)	12.14	–	360 (100)	290 (70)
Hexachlorobiphenyl (153)	12.52	–	360 (100)	290 (75)
Heptachlorobiphenyl (180)	13.46	–	394 (100)	324 (85)
Heptachlorobiphenyl (189)	15.30	–	394 (100)	324 (80)

## 2.5. Method performance: accuracy, precision, and detection limits

Method performance was verified on deionized and raw water samples containing known (spiked) concentrations of the compounds studied. The mean recovery for chlorobenzenes was from 72 to 95% at two spiking levels of 1.0 and 0.1 µg/L and for polychlorinated biphenyls from 75 to 95% at two spiking levels of 1.0 and 0.1 µg/L (Table 2). Standard deviations for these replicate determinations (n = 4) were lower than 8% for chlorobenzenes and below 9% for polychlorinated biphenyls. Recovery of the surrogates from raw water samples was also acceptable ranging from 70 to 92% for chlorobenzenes and from 82 to 95% for polychlorinated biphenyls. Based on a concentration factor of 10,000, the method detection limits (MDL) were estimated for 20 ng/L for chlorobenzenes and 5 ng/L for polychlorinated biphenyls.

**Table 2.** The mean ± SD recovery (n=4) of chlorobenzenes and chlorinated biphenyls from fortified deionized water

**Tabela 2.** Wartości średniej i odchylenia standardowego (n=4) dla odzysku chlorobenzenów i polichlorowanych bifenyli z zagęszczanej wody dejonizowanej

Analytes	Spiking level (µg/L)	Mean ± SD (%)	Spiking level (µg/L)	Mean ± SD (%)
Chlorobenzenes				
Chlorobenzene	1.0	74±8	0.1	72±6
1,2-Dichlorobenzene	1.0	75±6	0.1	72±7
1,3-Dichlorobenzene	1.0	78±9	0.1	75±7
1,4-Dichlorobenzene	1.0	88±5	0.1	86±5
1,2,4-Trichlorobenzene	1.0	89±6	0.1	91±6
1,2,3-Trichlorobenzene	1.0	92±5	0.1	89±4
Hexachlorobenzene	1.0	95±4	0.1	88±5
Chlorinated biphenyls				
Trichlorobiphenyl (28)	0.5	85±7	0.1	82±6
Tetrachlorobiphenyl (52)	0.5	89±8	0.1	85±9
Pentachlorobiphenyl (101)	0.5	90±5	0.1	86±5
Pentachlorobiphenyl (118)	0.5	92±7	0.1	89±7
Hexachlorobiphenyl (138)	0.5	91±4	0.1	89±7
Hexachlorobiphenyl (153)	0.5	95±7	0.1	92±6

### **3. Results and discussion**

The purpose of this study was to assess seasonal differences in qualitative or/and quantitative content of chlorophenols, chlorobenzenes and polychlorinated biphenyls present in surface-derived and underground-derived tap water.

Our results showed that phenol was determined in all samples studied and its concentrations were comparable in both surface-derived and underground-derived tap water ranging from 50 to 130 ng/L and from 30 to 130 ng/L, respectively (Table 3). The concentrations of phenol detected in our study were lower than that determined by Filipov et al. [8] in drinking water of Moscow (Russia), which ranged from 400 to 600 ng/L.

The formation of chlorophenols, and particularly 2,4,6-TCP in drinking water is mainly connected with raw water disinfection in which phenols and other aromatic compounds undergo electrophilic substitution with chlorines to form respective derivatives [14]. In the samples analyzed, several chlorophenols have been found including most frequently determined 2,4,6-TCP and PCP. The 2,4,6-TCP is usually detected more often in drinking water than other chlorophenols. For instance, Niemiński [18] observed common occurrence of 2,4,6-TCP in treated waters of the USA. In our study, 2,4,6-TCP was determined in all the seasons studied and its concentrations were higher in tap water derived from underground intake (20–250 ng/L) in comparison to water derived from surface intake (40–80 ng/L). Comparing to our results, Santori [21] determined 2,4,6-TCP in lower concentrations ranging from 8 to 238 ng/L in tap water of Rio de Janeiro. In our study, 2-CP was detected in trace concentration only in autumn in underground derived tap water, whereas 2,4-DCP was determined in comparable concentrations in tap water derived both from surface and underground water intakes. Moreover, we detected significant amounts of TeCP (ranging from 100 to 170 ng/L) in tap water derived from surface intake in spring and summer and in tap water derived from underground intake in summer (Table 3).



**Table 3.** Comparison of mean concentration values (ng/L) of phenol, 4-methylphenol and chlorophenols determined in spring, summer, autumn and winter of 2010 in tap water of Łódź city derived from surface and underground intakes (n = 4)

**Tabela 3.** Porównanie średnich wartości stężeń (ng/L) fenolu, 4-metylofenolu i chlorofenoli oznaczonych w wodzie pitnej m. Łodzi pochodzącej z ujęcia powierzchniowego i głębinowego (n = 4) w okresie wiosny, lata, jesieni i zimy 2010 roku

Analytes	Spring		Summer		Autumn		Winter	
	Surface derived tap water	Underground derived tap water	Surface derived tap water	Underground derived tap water	Surface derived tap water	Underground derived tap water	Surface derived tap water	Underground derived tap water
Phenol	50 ± 13	60 ± 19	12 ± 10	30 ± 22	110 ± 46	130 ± 31	130 ± 13	30 ± 0
4-Methylphenol	–	–	–	–	50 ± 24	30 ± 24	20 ± 0	20 ± 0
2-Chlorophenol	–	–	–	–	–	20 ± 0	–	20 ± 0
2,4-Dichlorophenol	120 ± 96	20 ± 0	20 ± 0	70 ± 17	50 ± 22	60 ± 26	–	–
2,4,5-Trichlorophenol	–	–	20 ± 0	30 ± 0	60 ± 17	20 ± 0	–	–
2,4,6-Trichlorophenol	80 ± 36	120 ± 86	60 ± 10	250 ± 35	50 ± 22	20 ± 0	40 ± 26	20 ± 0
Tetrachlorophenol	150 ± 71	–	100 ± 37	170 ± 85	–	–	20 ± 0	20 ± 0
Pentachlorophenol	–	520 ± 260	190 ± 57	40 ± 16	470 ± 170	520 ± 91	60 ± 22	170 ± 39

– below detection limit

In our study, PCP was determined in all of the seasons studied, and its concentrations were high both in surface-derived tap water (60–470 ng/L) and in underground-derived tap water (40–520 ng/L) (Table 3). In investigations conducted by other authors, PCP has been detected in drinking water in lower concentrations ranging from 10 to 100 ng/L [25]. Similarly, Santori [21] did not detect PCP (limit of detection 14 ng/L) in tap water of Rio de Janeiro (Brazil). Surprisingly, in our study PCP was detected in higher concentrations in underground-derived tap water, which was notable in spring, autumn and winter (Table 3). This finding may be connected with slower degradation of PCP in underground waters than in surface waters. For instance, Davis et al. [4] observed limited degradation of chlorophenols in underground aquifers situated near industrial site in Australia. It should be underlined that PCP concentrations determined in our study in some cases repeatedly exceeded admissible standards established for drinking water by ECU [7]. High concentrations of PCP detected in the waters studied may be due to significant pollution of Łódź city areas by textile and paper industries, which has been uncontrolled in recent years.

We also found trace amounts of chlorinated methoxyphenols i.e. 4,6-DCG, 3-CS, TCS and chlorocatechols including 4-CC, 3,4,5-TeCC and TeCC in both surface-derived and underground-derived tap waters (Table 4). Chlorocatechols and particularly TeCC could have been formed from PCP, which was present in significant amounts in the waters studied. It has been proven that PCP is converted to TeCC in aqueous environments when exposed to abiotic and biotic factors [3]. We noted that both 4-methylphenol and guaiacol were determined occasionally and in very low concentrations in the samples studied. In autumn, significant concentrations of 4,5,6-TCG in surface-derived (470 ng/L) and underground-derived (520 ng/L) tap water were detected. Moreover, notable amounts of TeCG in summer (160 ng/L) in tap water derived from surface intake were determined (Table 4). In some studies, it has been evidenced that 4,5,6-TCG and TeCG often occur in aquatic environments (that are used as the sources of drinking water) and their existence is connected both with human and natural activities [16].

**Table 4.** Comparison of mean concentration values (ng/L) guaiacol, chlorinated methoxyphenols and chlorocatechols determined in spring, summer, autumn and winter of 2010 in tap water of Łódź city derived from surface and underground intakes (n = 4)

**Tabela 4.** Porównanie średnich wartości stężeń (ng/L) gwajakolu, chlorowanych metoksyfenoli i chlorokatecholi oznaczonych w wodzie pitnej m. Łodzi pochodzącej z ujęcia powierzchniowego i głębinowego (n = 4) w okresie wiosny, lata, jesieni i zimy 2010 roku

Analytes	Spring		Summer		Autumn		Winter	
	Surface derived tap water	Underground derived tap water	Surface derived tap water	Underground derived tap water	Surface derived tap water	Underground derived tap water	Surface derived tap water	Underground derived tap water
Guaiacol	20 ± 0	–	20 ± 0	–	30 ± 13	40 ± 26	20 ± 0	20 ± 0
4,6-Dichloroguaiacol	–	–	–	–	–	–	–	20 ± 0
4,5,6-Trichloroguaiacol	–	–	–	–	470 ± 170	520 ± 91	–	–
Tetrachloroguaiacol	20 ± 0	–	160 ± 30	–	–	–	–	–
3-Chlorosyringol	–	–	20 ± 0	–	–	–	–	–
Trichlorosyringol	20 ± 0	20 ± 0	20 ± 0	–	–	–	–	–
4-Chlorocatechol	–	–	–	–	20 ± 0	20 ± 0	–	–
3,4,5-Trichlorocatechol	–	60 ± 17	–	20 ± 0	–	–	–	30 ± 18
Tetrachlorocatechol	–	20 ± 0	40 ± 20	20 ± 0	40 ± 10	–	–	20 ± 0

– below detection limit

Among chlorobenzenes, chlorobenzene was determined in all of the seasons studied (excluding winter) in the concentrations, which were comparable in both surface-derived (100–170 ng/L) and underground-derived (60–240 ng/L) tap water. Summer concentrations of chlorobenzene detected in tap water derived both from surface and underground sources significantly exceeded admissible standards established for drinking water by ECU [7]. Moreover, we found trace amounts of 1,2,4-TCB and HCB in surface-derived (summer) and underground-derived (spring) tap waters, respectively (Table 5). The contents of chlorobenzenes detected in our study were lower than that observed by Almeida and Boas [1] who found dichlorobenzene and trichlorobenzene in the concentrations range from 0.20 to 1.01  $\mu\text{g/L}$  in drinking water of Lisbon (Portugal). Similarly, Soh and Abdullah [22] determined significantly higher dichlorobenzenes concentrations (from 200 ng/L to 3.42  $\mu\text{g/L}$ ) in Malaysian drinking waters.

In our study, polychlorinated biphenyls were determined mainly in spring and summer in low concentrations. We have noticed that tetrachlorobiphenyl (52) occurred more often and in the higher concentrations than other PCBs studied. That compound was detected in summer and autumn in the concentrations ranging from 10 to 18 ng/L. Similarly, Salina et al. [20] noticed that tetrachlorobiphenyl (52) was the most common among PCBs, which occurred in drinking water of Mexico City in the concentration ranging from 18 to 40 ng/L. In tap waters studied, pentachlorobiphenyl (110), pentachlorobiphenyl (118), and hexachlorobiphenyl (153) were also found in trace concentrations (Table 5). Hong et al. [10] detected chlorinated biphenyls in comparable concentrations ranging from 1 to 46 ng/L in drinking water of Jiangsu Province in China, whereas Palmer et al. [19] determined significantly higher PCBs concentrations (mean 73 ng/L) in public water systems in the USA along the contaminated area of the Hudson river.

**Table 5.** Comparison of mean concentration values (ng/L) of chlorobenzenes and polychlorinated biphenyls determined in spring, summer, autumn and winter of 2010 in tap water of Łódź city derived from surface and underground intakes (n = 4)

**Tabela 5.** Porównanie średnich wartości stężeń (ng/L) chlorobenzenów i polichlorowanych bifenyli oznaczonych w wodzie pitnej m. Łodzi pochodzącej z ujęcia powierzchniowego i głębinowego (n = 4) w okresie wiosny, lata, jesieni i zimy 2010 roku

Analytes	Spring		Summer		Autumn		Winter	
	Surface derived tap water	Underground derived tap water	Surface derived tap water	Underground derived tap water	Surface derived tap water	Underground derived tap water	Surface derived tap water	Underground derived tap water
Chlorobenzenes								
Chlorobenzene	100 ± 70	60 ± 30	170 ± 65	240 ± 50	110 ± 30	120 ± 89	90 ± 12	70 ± 14
1,2,4-Trichlorobenzene	–	–	20 ± 0	–	–	–	–	–
Hexachlorobenzene	–	20 ± 0	–	–	–	–	–	–
Polychlorinated biphenyls								
Tetrachlorobiphenyl (52)	–	–	13 ± 2	18 ± 4	10 ± 2	–	–	–
Pentachlorobiphenyl (110)	–	–	16 ± 4	–	–	–	–	–
Pentachlorobiphenyl (118)	7 ± 2	5 ± 0	–	–	–	–	–	–
Hexachlorobiphenyl (153)	–	17 ± 12	–	–	–	–	–	–

– below detection limit

## 4. Conclusions

Summing up, in tap water of Łódź City derived both from surface and underground intakes; we determined phenol, chlorophenols, chlorocatechols, chloroguaiacols, chlorosyringols as well as some chlorobenzenes and polychlorinated biphenyls. Generally, we detected those compounds in low concentrations excluding pentachlorophenol and chlorobenzene, which contents significantly exceeded standards established by EEC. Although, we have not found any significant differences for most of the compounds studied, surprisingly, the concentrations of 2,4,6-TCP, PCP and total content of chlorophenols were higher (particularly in spring) in underground-derived tap water. Moreover, we have found seasonal differences in the total concentrations of chlorophenols and their derivatives both for surface-derived and underground-derived tap waters with the highest values noted for autumn.

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## **Analiza porównawcza występowania chlorofenoli i innych związków chloroaromatycznych w wodzie pitnej pochodzącej z ujęcia powierzchniowego i głębinowego**

### **Streszczenie**

Dotychczas niewiele miejsca poświęcono badaniom obecności trwałych i silnie toksycznych związków chloroaromatycznych, tj. chlorofenoli, chlorobenzenów i chlorowanych bifenyli w wodzie pitnej pochodzącej z ujęć głębinowych.

W niniejszej pracy przeprowadzono sezonową analizę porównawczą dotyczącą obecności tych substancji w wodzie pitnej pochodzącej z ujęcia powierzchniowego i głębinowego wybierając jako obszar badawczy aglomerację łódzką. Analizy przeprowadzono z wykorzystaniem techniki chromatografii gazowej sprzężonej ze spektrometrią mas.

Przeprowadzone analizy wskazały na powszechnie występowanie w badanych próbach fenolu (30–130 ng/L), chlorofenoli (20–520 ng/L) i chlorobenzenu (70–240 ng/L). W nielicznych próbach wykryto także chlorokatechole (20–60 ng/L), chlorowane metoksyfenole (20–520 ng/L) oraz polichlorowane bifenyly (5–18 ng/L).

Wyniki badań wskazały, że 2,4,6-trichlorofenol i pentachlorofenol występowały w wyższych stężeniach w wodzie pitnej pochodzącej z ujęcia głębinowego. Ponadto, najwyższe całkowite stężenia chlorofenoli oznaczono w sezonie jesiennym zarówno w próbach wody pitnej pochodzących z ujęcia powierzchniowego, jak i głębinowego.