Polish Journal of Environmental Studies Vol. 14, No. 3 (2005), 327-333

Original Research

The Occurrence of Chlorophenols, Chlorocatechols and Chlorinated Methoxyphenols in Drinking Water of the Largest Cities in Poland

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Received: 29 July, 2004
Accepted: 14 October, 2004

Abstract

The purpose of this work was to determine the occurrence of phenol, chlorophenols, chlorocatechols and chlorinated methoxyphenols in the drinking water of the Polish cities of Łódź (Lodz), Warszawa (Warsaw), Poznań and Wrocław. The compounds were adsorbed on octadecyl (C18) layer in a Baker-Separex system and eluted with methylene chloride, then analyzed using the methods of gas chromatography and mass spectrometry. In samples, chlorophenols, 4-chlorocatechol, chloroguaiacols, chlorosyringols and 5,6-dichlorovaniline were detected. Higher concentrations and number of chlorophenols and their chlorinated derivatives were noted in summer. Among the most toxic compounds, 2,4,5-trichlorophenol in drinking water of Warszawa (summer and winter) and Łódź (winter) and tetrachlorophenol in water of Wrocław (summer) were noted. Their concentrations were above the admissible standards of the EU and the US EPA. In some cases the concentrations of chloroguaiacols and 5,6-dichlorovanillin also were significant.

Keywords: chlorocatechols, chloroguaiacols, chlorophenols, chlorosyringols, drinking water

Introduction

Aromatic compounds, due to their toxicity and persistence in the environment, establish serious danger towards living organisms, including humans. One of the most important group of ecotoxins are chlorophenols. Those compounds are in common use as the precursors and components of many chemicals, including polymers, dyes or pharmaceuticals [1]. The compounds also are formed as a result of the use and degradation of phenolic pesticides such as 2-chlorophenol, 4-chlorophenol and 2,4,5-trichlorophenol [2] and phenoxyherbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) [3]. Chlorophenols emit high toxicity, including genotoxic [4], mutagenic [5] and carcinogenic activity [6]. Clinical investigation showed that people exposed to drinking water contaminated with chlorophenols (Jarvela, South Finland) suffer from infections, dermatitis, irritation of digestive tract and strong exhaustion [7]. Catechols and chlorocatechols similar to phenols, are synthesized and used by industry [8]. Those compounds also are created during degradation of pesticides and biphenyls. A related group of compounds are the methoxyphenols formed mainly as a result of bleaching (chlorinating) of wood pulp [9]. Until now the investigations have concerned the presence of chlorophenols in drinking water that were formed during chemical oxidation of aromatic compounds – (the substitution of aromatic ring by free atoms of chlorine derived from chlorinated oxidants) present in purifying water [10]. As far as we know there haven't been any investigations concerning the presence of chlorocatechols and chlorinated methoxyphenols in drinking water and nothing is known about the transformation of these compounds during chlorination. Both catechol [11], chlorocatechols [8] and methoxyphenols [13, 14] emit high toxicity including mutagenicity and carcinogenicity.

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Moreover, substitution of these compounds by chlorine atoms may increase their toxic action and prolong the period of their bioaccumulation in living organisms.

The aim of this study was to determine phenol, chlorophenols, catechol, chlorocatechols, chlorinated methoxyphenols (chlorosyringols, chloroguaiacols, 3,4,5-trichloroveratrole and 5,6-dichlorovanillin) in drinking water of the largest cities in Poland - Warszawa, Łodź, Poznań and Wrocław. The estimation of seasonal changes concerning the number and concentrations of the compounds determined (samples collected in summer and winter) also was analyzed.

Materials and Methods

Chemicals

The standards of these compounds were bought from Fluka AG: 1-hydroxybenzene (phenol), 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,3,6-trichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,3,4,5-tetrachlorophenol, pentachlorophenol, 4-methylphenol (p-cresol), 1,2-dihydroxybenzene (catechol), 4-chlorocatechol, 3,4,5-trichlorocatechol, tetrachlorocatechol, 2-methoxyphenol (guaiacol), 4,6-dichloroguaiacol, 4,5,6-trichloroguaiacol, tetrachloroguaiacol, 2,5-dimethoxyphenol (syringol), 3-chlorosyringol, trichlorosyringol, 1,2-dimethoxybenzene (veratrole), 3,4,5-trichloroveratrole and 5,6-dichloro-4-hydroxy-3-methoxybenzaldehyde (5,6-dichlorovanillin).

Collection of Samples

Drinking water was collected Łódź, Poznań, Warszawa and Wrocław. Three samples (n=3) of water were collected each in summer and winter.

In Warszawa, drinking water was collected from the area supplied by Central Water Supply that pumps it from the Vistula River. Moreover, water is delivered by South Water Supply and Praski Water Supply, reciving it into the southern and eastern parts of the city, respectively.

Tap water in Łódź was collected from the western area of the city that is supplied by surface water taken from Sulejowske Lake situated on the Pilica River, 50 km from Łódź. Most of the water destined for Łódź is obtained from several deep-seated wells situated within the city.

In Poznań tap water was collected from the southern area of the city that is supplied with water taken from the Warta River in Mosina, 20 km from Poznań. Moreover, water for Poznań is obtained from the water supply in Dębina that delivers river water to the northern part of the city.

Tap water in Wrocław was collected from the area supplied with water taken from the Odra River. "Mokry Dwór" water supply is situated a few kilometers from Wrocław and carries water to southern and western parts of the city. Remaining water is delivered to the centre of the city and is obtained from water supply situated at Michałów on the Oława River, 60 kilometers from Wrocław.

Individual water supplies carry water to 30% of the Łódź population, 35% of Warszawa population, 60% of Poznań population and 50% of Wrocław population.

Selected areas of the cities were supplied with water (river water) exposed to the strongest antropogenic contamination. The water taken from these places potentally should have contained the highest amounts and the diversity of compounds analyzed and their precursors.

Preparation of Samples

Samples were collected in 1 dm^3 volumes in dull HD polyethylene bottles. To samples 10 ml of methanol and 0.1 g of ascorbic acid were added to inhibit biodegradation and oxidation proccesses. The internal standard also was added (1 µg of 2,3,6-trichlorophenol in 1 ml of acetone) to samples. Next, 200 g of sodium chloride was added and samples were acidified with phosphoric acid to pH = 2 to decrease solubility of phenols in water (higher effectivity of adsorbtion of phenols by octadecyl layer). Finally, samples were mixed using an electromagnetic stirrer (750 rts/min) for 40 minutes.

Solid-Phase Extraction

Adsorption of chlorophenols and their derivatives was performed on "EMPORE Extraction Disks" in a Baker

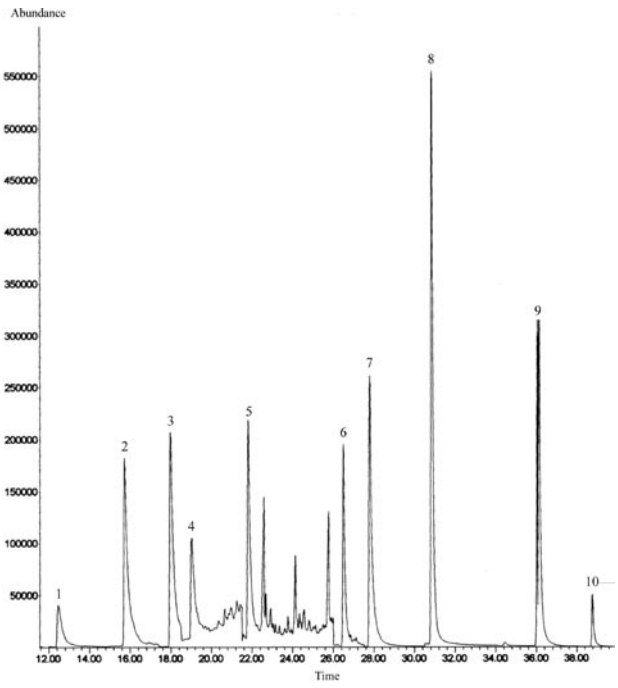

Fig. 1. Chromatogram of standards of chlorophenols and chlorocatechols separated by GC-MS method - **1**. phenol, **2**. 4-metylphenol, **3**. chlorophenol, **4**. guaiacol, **5.** dichlorophenol, **6**. dichlorophenol, **7**. chlorocatechol, **8**. tetrachlorophenol, **9**. pentachlorophenol, **10**. tetrachlorocatechol.

Separex system. The system "EMPORE spe" of extraction filters (disks) was equipped with its binding phase octadecyl C18, diameter of 50 mm and layer thickness of 1.0 mm. The filters (disks) were used in a special vacuum extraction apparatus "Baker Separex" made of borosilicate glass. The octadecyl layer was conditioned using 10 ml volumes of diethyl ether, methylene chloride, methanol and bidistilled water, respectively, and elution was made with two 5 ml volumes of dietyl ether and methylene chloride, respectively. Eluent was evaporated, individual phenols and their derivatives were dissolved in hexane, acetylated (derivatization) and concentrated down to a volume of 0.1 ml for gas chromatography separation.

Gas Chromatography-Mass Spectrometry

Chromatographic analysis was made using a gas chromatograph (Hewlett-Packard type 5890) connected with a quadruple mass spectrometer type 5972 (temperature MS - 152 °C) equipped with capillary column HP 5 (60 m x 0.25 mm). Column temperature was maintained at 60°C for 1 min then increased to 160°C at 5°C/min and finally increased to 280°C. The temperature of the injector was 260°C. The carrier gas was helium (rate of flow, 1 ml/min). Qualitative estimation was made in SCAN system (identification of individual compounds by comparision with standards or spectra from spectra library type NBS 75KL) and quantitative estimation was done in SIM system (identification by comparing with calibrated standards) (Fig. 1).

Results

Obtained results evidenced the presence in collected samples of phenol, some chlorophenols (4-chlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol and tetrachlorophenol) 4-chlorocatechol, 4,6-dichloroguaiacol, tetrachloroguaiacol, 3-chlorosyringol, trichlorosyringol and 5,6-dichlorovanillin. Generally, in summer higher numbers and concentrations of investigated compounds were noted. That particularly concerned the occurrence of chlorocatechols, chlorinated methoxyphenols and 5,6-dichlorovanilin that were not detected in winter. The concentrations of some determined compounds exceeded admissible standards established by the USA Environmental Protection Agency (EPA) (0,1 µg chlorophenol to 1 L of drinking water). That refered to 2,4,5-trichlorophenol (summer and winter, Warszawa and winter, Łódź) and tetrachlorophenol (summer, Wrocław). The concentrations of chlorophenols, 4-chlorocatechol and chlorinated methoxyphenols determined in drinking water in summer and winter are shown in Table 1.

Selected chromatograms of standard chlorophenols and compounds determined in drinking water are shown in Figs. 2-3.

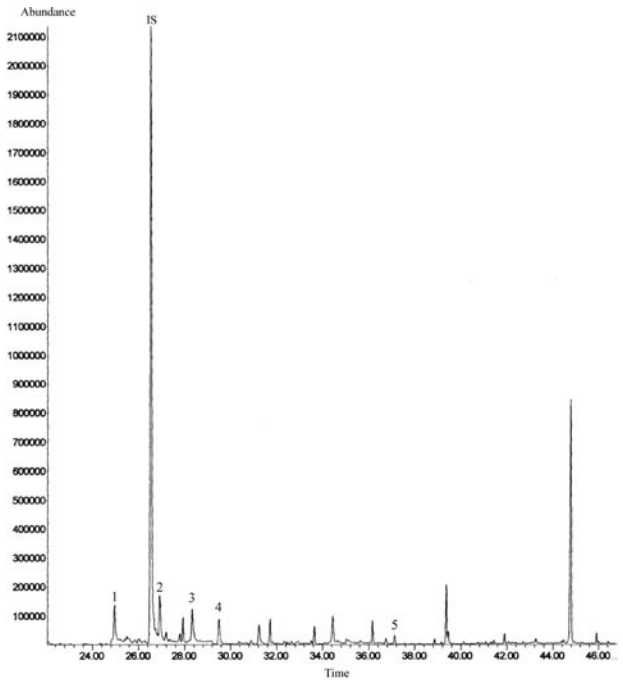

Fig. 2. Chromatogram of 2,4,6-trichlorophenol (**1**), 2,4,5-trichlorophenol (**2**), dichloroguaiacol (**3**), 3-chlorosyringol (**4**), trichlorosyringol (**5**) determined in drinking water of Warszawa in summer 2000.

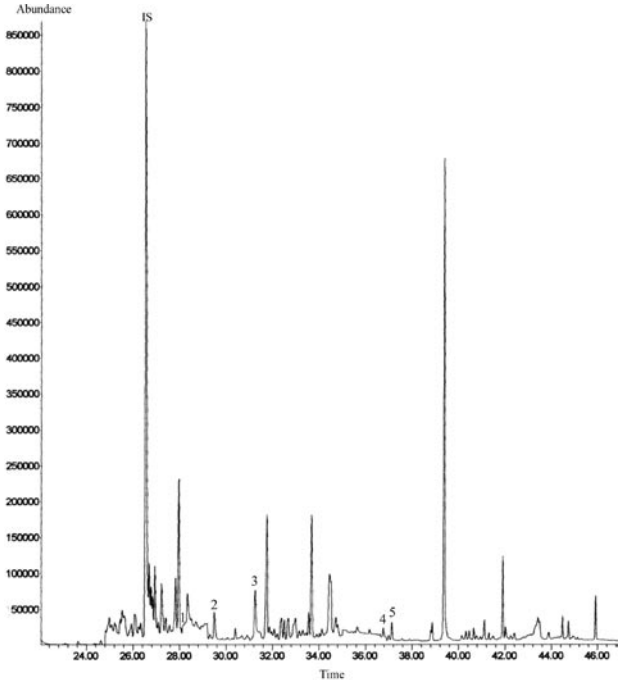

Fig. 3. Chromatogram of tetrachlorophenol (**1**), 4-chlorocatechol (**2**), tetrachloroguaiacol (**3**), 3-chlorosyringol (**4**) and trichlorosyringol (**5**) determined in drinking water of Wrocław in summer 2000.

Table 1. The means (n=3) of concentrations (µg/l) and their standard deviations obtained for phenol, chlorophenols, 4-chlorocatechol and chlorinated methoxyphenols determined in the drinking water of Łódź, Poznań, Warszawa and Wrocław in summer and winter 2000-01.

Determined compound	Łódź				Poznań			
	summer		winter		summer		winter	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
phenol	-	-	0.233	0.0305	-	-	-	-
4-chlorophenol	-	-	-	-	0.010	0.0015	-	-
2,4,5-trichlorophenol	-	-	0.486	0.0638	-	-	-	-
2,4,6-trichlorophenol	-	-	-	-	-	-	0.004	0.0010
tetrachlorophenol	-	-	-	-	0.035	0.0150	-	-
4-chlorocatechol	0.030	0.0100	-	-	0.047	0.0153	-	-
4,6-dichloroguaiacol	-	-	-	-	-	-	0.004	0.0015
tetrachloroguajacol	0.241	0.0100	-	-	0.109	0.0153	-	-
3-chlorosyringol	0.022	0.0029	-	-	0.024	0.0046	-	-
trichlorosyringol	0.040	0.0167	-	-	0.029	0.0023	-	-
5,6-dichlorovaniline	0.341	0.0222	-	-	-	-	-	-
Determined compound	Warszawa				Wrocław			
	summer		winter		summer		winter	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
phenol	-	-	-	-	-	-	trace c.	-
4-chlorophenol	-	-	-	-	-	-	-	-
2,4,5-trichlorophenol	0.330	0.0385	0.350	0.0100	-	-	-	-
2,4,6-trichlorophenol	0.075	0.0080	-	-	-	-	-	-
tetrachlorophenol	-	-	-	-	0.221	0.0130	-	-
4-chlorocatechol	-	-	-	-	0.131	0.0104	-	-
4,6-dichloroguaiacol	0.036	0.0046	0.007	0.0025	-	-	trace c.	-
tetrachloroguajacol	-	-	-	-	0.136	0.0136	-	-
3-chlorosyringol	0.015	0.0015	-	-	0.028	0.0056	-	-
trichlorosyringol	0.019	0.0020	-	-	0.044	0.0036	-	-
5,6-dichlorovaniline	-	-	-	-	-	-	-	-

"-" = none detected

Discussion of Results

Previous investigations have noted the occurrence of many chlorinated aliphatic and aromatic and some brominated compounds in drinking water [14, 15, 16] and special attention has been paid to the presence of phenol and chlorophenols exerting high toxicity, mutagenicity and carcinogenicity [11, 17, 18, 19, 20]. High toxicity of chlorophenols and their negative impact on organoleptic properties of drinking water, even in small concentrations (100-300 nanograms) has forced scientists to establish admissible standards for these compounds on 100 nanograms of individual chlorophenol and 1 microgram of total concentrations of chlorophenols per one litre of drinking water. Unfortunately, there has been little or no investigation concerning the occurrence of catechol, methoxyphenols and their chlorinated derivatives in drinking water. Both catechol [21, 22] chlorocatechols [8], guaiacol [23], chloroguaiacols [22] and syringol [24] reveal toxic properties including cytotoxic, mutagenic and cancerogenic activity. Moreover, substitution of discussing compounds by chlorine atoms usually increases their toxicity. In collected samples the occurrence of several chlorophenols (4-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol and tetrachlorophenol) was noted. Generally, it is

known that chlorophenols reach the surface water as a result of the activity of chemical, cosmetic, pharmaceutical and other industries [1]. Chlorophenols also are formed during production, use and degradation of phenoxyherbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) [25] or 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) [26]. Those compounds also are used as biocides. For example, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) are used as herbicides, 4-chlorophenol (4-CP) is used as a fungicide [2] and pentachlorophenol (PCP) is commonly applied as an insecticide [20]. Similarly, industrial activity [27] use and degradation of pesticides [28] and environmental transformation of biphenyls lead to creation of chlorocatechols such as 4-chlorocatechol and 3,4,5-trichlorocatechol (determined only in one sample water of Łódź). Tetrachloroguaiacol, 4,6-dichloroguaiacol, trichlorosyringol and 3-chlorosyringol are formed mainly as a result of the activity of the paper industry in the process of bleaching (chlorinating) wood pulp. This process leads to tearing of phenylpropanoid biopolymer structure of lignin and chlorination of its subunit-monomers (methoxyphenols) [9, 29]. Moreover, guaiacol and its chlorinated derivatives are producted as the components used in the chemical and pharmaceutical industries, plus in medicine and stomatology [23].

Some of described compounds are formed by living organisms. Catechol and vanillin are produced by plants [30] and the formation of chloroguaiacols and chlorosyringols results from the activity of fungi from *Basidiomycetes* order [31]. All of the described compounds undergo different biotic and abiotic transformations in the environment that lead to the creation of catechols from phenols – hydroxylation proccess [32] - or methoxyphenols - O-methylation [26]. The presence of compounds, expecially of those highs substituted in chlorine such as 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, tetrachlorophenol or trichlorosyringol, may also be related with processes of water chlorination (using oxidants such as gas chlorine or dioxide chlorine) that lead to the substitution of aromatic compounds by chlorine atoms [33, 34]. Tetrachlorophenol, for example, seldom exists in the aqueous environment and its presence most probably results from water chlorination.

It is quite probable that some of the detected phenols and especially their methoxylated derivatives were formed during chlorination of humus substances that occurr in water, as described by Biłyk [16]. High quantities of sludges containing humus substances characterizes Sulejowski Lake [35], whose water is used for the Łódź agglomeration. That may influence high concentrations of tetrachloroguaiacol and syringols determined in the drinking water of a given city. Lower quantity of organic matter usually present in the fluvial (river) water used for Warszawa, Wrocław and Poznań probably affects consideraly lower concentrations of those compounds.

The highest concentrations of chlorophenols of anthropogenic origin determined in annual cycle were noted in drinking water of Warszawa supplied from the section of the Vistula River situated within the city. The Vistula is strongly polluted by municipal activity of the city - in 2000 the values of physico-chemical parameters determined in river beneath the city exceeded the addmisible standards [36]. As it is also known, municipal sewage often contains chlorophenols [37].

The highest total concentrations of the compounds determined were noted in tap water collected in Łódź and Wrocław. Considerable concentrations of determined compounds in tap water of Łódź stem from mentioned high quantities of humus substances that become precursors of methoxyphenols during water chlorination. Determined 5,6-dichlorovanilin may be formed during water treatment from vanilin that is produced by conoferous trees, abudantly growing on the banks of Sulejowski Lake [30]. The presence of notable concentrations of phenols in drinking water collected in Wrocław may results from using gas chlorine in a final step of its purification. As we know, gas chlorine usually generates higher amounts of chlorinated compounds than chlorine dioxide [16] that it uses in the purification plants of Łódź, Warszawa and Poznań.

In winter a decrease in the number of compounds determined was noted in comparison to summer. That results mainly from inactivity of plants that usually produce some precursors of disccusing compounds and lower temperature of water (the temperature of surface water in Poland in winter is almost 20°C lower in comparision to summer). Lower temperatures decrease the solubility of phenols and their precursors and capacity of their migration in the environment. Tetrachlorophenol and 2,4,5-trichlorophenol were the most noxious compounds determined in samples. Concentration of 2,4,5-TCP in Warszawa water were 0.330 μg/l in summer and 0.350 μg/l in winter and its concentration in water collected in Łódź in winter was 0.486 μg/l. 2,4,5,6-TeCP existed at 0.221 μg/l in samples collected in summer in Wrocław. The concentrations of the discussing compounds exceeded admissible standards assigned by EU and US Environmental Protection Agencies. In some cases considerable concentrations of chlorinated methoxyphenols also were noted in summer. This refers to tetrachloroguaiacol (0.245 μg/l) and 5,6-dichlorovanillin detected in drinking water collected in Łódź.

References

1. BRUCE R. M. SANTODONATO J., NEAL M. W. Summary review of the health effects associated with phenol. Toxicol. Indust. Health. **3**, 535, **1987**
2. CERNAKOWA M., ZEMANOWICOWA A. Microbial activity of soil contaminated with chlorinated phenol derivatives. Fol. Microbiol. **43,** 411, **1998**.
3. DAUBARAS D. L., SAIDO K., CHAKRABARTY A. M. Purification of hydrochinol 1,2-dioxygenase and maleylacetate reductase: the lower pathway of 2,4,5-trichlorophenoxyacetic acid metabolism by *Burkholderia cepacia AC 1100*. Appl. Environ. Microbiol. **62**, 4276, **1996**.

4. TISH M., LOHNEIER A., SCHNIEZER P., BARTSCH M., MAIER M. Genotoxic effect of the insecticides pentachlorophenol and lindane on human nasal mucosal epithelium. Gene. **126**, 840, **2001**.
5. YOSHIDA R., OIKAWA S., OGAWA Y., MIYAKOSHI Y., OOIDA M. ASANUMA,; K. SHIMIZU, H. Mutagenicity of p-aminophenol in *Escherichia coli WP2 uvrA / pKM101* and its relevance to oxidative DNA damage. Mut. Res. **415**, 139, **1998**.
6. HOOVIELD M., HEEDERICK D. J., KOGEVINAS M., BOFFETA P., NEEDHAM L. L., PATTERSON D. G., BAS BUENO-DE-MESQUITA JR., BAS BUENO-DE-MESQUITA H. Second follow-up of a duch cohort occupationally exposed to phenoxy herbicides, chlorophenols, and contaminants. Americ. J. Epidemiol. **147**, 891, **1998**.
7. LAMPI P., VOHLONEN I., TUOMISTO J., HEINONEN O. P. Increase of specific symptoms after long-term use of chlorophenol polluted drinking water in a community. Eur. J. Epidemiol. **16**, 245, **2000**.
8. SCHWEIGERT N., MUNZIKER R. W., ESCHER B. J., EGGEN R. J. Acute Toxicity of (chloro)Catechols and (chloro-)Catechol-Copper Combinations in *Escherichia coli* Corresponds to Their Membrane Structure. Toxic. in Vitro Environ. Toxicol. Chem. **2**, 239, **2000**.
9. KNUUTINEN J. Analysis of chlorinated quaiacols in spent bleach liquor from a pulp mill. J. Chromat. **248**, 289, **1982**.
10. WAJON J. E., ROSENBLATT P. M., BURROWS E. P. Oxidation of phenol and hydroquinone by chlorine dioxide. Environ. Sci. Technol. **16**, 396, **1982**.
11. TSUTSUI T., MAYASHI N., MAIZUMI H., HUFF J., BARRET J. C. 'Benzene-, catechol-, hydroquinone- and phenol-induced cell transformation, gene mutation, chromosome aberrations, aneuploidy, sister chromatid exchanges and unscheduled DNA synthesis in *Syrian hamster* embryo cells. Mut. Res. **373**, 113, **1997**.
12. HAMAGUCHI F., TSUTSUI T.. Assessment of Genotoxicity of Dental Antiseptics: Ability of Phenol, Guaiacol, p-Phenolsulfonic Acid, Sodium Hypochlorite, p-Chlorophenol, m-Cresol or Formaldehyde to Induce Unscheduled DNA Synthesis in Cultured Syrian Hamster Embryo Cells. Jap. J. Pharmacol. **83**, 237, **2000**.
13. HIROSE M., TAKESADA Y., TANAKA H., TAMANO S., KATO T., SHIRAI T. Carcinogenicity of antioxidants BHA, caffeic acid, sezamol, 4-methoxyphenol and catechol at low doses, either alone or in combination and modulation of their effects in a rat medium-term multi-organ carcinogenesis model. Carcinogen. **19**, 207, **1997**.
14. BOVE F., SHIM Y., ZEITZ P. Drinking water contaminants and adverse pregnancy outcomes. A review. Environ. Health Perspect. **110**, 61, **2002**.
15. LUKSBATLEJ K., BODZEK D. Occurrence of triahalomethanes, particulary those containing bromine in Polish drinking waters. Polish J. Environ. Studies. **11**, 255, **2002**.
16. BIŁYK A., KABSH-KORBUTOWICZ M., CIEPŁOCH B. Transformations of organic compounds in proccesses of water puryfication. Raport SPR Nr 29/94 PWr. I-15. Wrocław, pp. 131, **1994**. (In Polish)
17. BOGE G., ROCHE H. Cytotoxicity of phenolic compounds on *Dicentrachus labrax* erythrocytes. Bull. Environ. Contam. Toxicol. **57**, 171, **1996**.
18. GŰLDEN M., SEIBERT H., VOSS J. U. The use of cultured skeletal muscle cells in testing for acute systemic toxicity. Toxicol. in vitro. **8**, 779, **1994**.
19. MAA Y. F., HSU CH. C. Aggregation of recombinant human growth hormone induced by phenolic compounds. Inter. J. Pharmaceut. **140**, 155, **1996**.
20. KLOBUCAR G. J., LAJTNER J., ERBEN R. Lipid peroxidation and histopathological changes in the digestive gland of a freshwater snail *Planorbarius corneus* (Gastropoda, Pulmonata) exposed to chronic and sub-chronic concentrations of PCP. Bull. Environ. Contam. Toxicol. **58**, 128, **1997**.
21. HAGIWARA H., TAKESADA Y., TANAKA H., TAMANO S., HIROSE H., ITO N., SHIRAI T. Dose- dependent Induction of Glandular Stomach Preneoplastic and Neoplastic Lesions in male F334 Rat Treated wiht Catechol Chronically. Toxicol. Pathol. **29**, 180, **2001**.
22. NIMMAGUDDA R., SYNDER R., SYNDER R. Oxidative modifications produced in HL-60 cells on exposure to benzene metabolites. J. Appl. Toxicol. **15**, 403, **1995**.
23. SHAPIRO S., GUGGENHEIM B. Inhibition of oral bacteria by phenolic compounds. Part 1. QSAR analysis using molecular connectivity. Quant. Struct-Act. Relat. **17**, 327, **1998**.
24. OKADA N., SATOH K., ATSUMI T., TAJIMA M., ISHIHARA M., SUGITA Y., YOKOE I. SAKAGAMI H., FUJISAWA S. Radical Modulating Activity and Cytotoxic Activity of Synthesized Eugenol-Related Compounds. Anticanc. Res. **20**, 2955, **2000**.
25. DAUGHERTY D. D., KAREL S. F. Daugherty D. D., Karel S. F. Degradation of 2,4-dichlorophenoxyacetic acid by *Pseudomonas cepacia DBO1 (pR 01D1)* in a dual-substrate chemostat. Appl. Environ. Microbiol. **60**, 3261, **1994**.
26. LAINE M. M., JORGENSEN K. S. Straw compost and bioremediated soil as inocula for the bioremediation of chlorophenols - contaminated soil. Appl. Environ. Microbiol. **43**, 1507, **1996**.
27. CHAE H., YOO J. Mathematical modelling and simulation of catechol production from benzoate using resting cells of *Pseudomonas putida*. Proc. Biochem. **32**, 423, **1997**.
28. SAURET-IGNAZI G., GAGNON J., BEGUIN C., BARELLE M. MARKOWICZ Y., PELMONT J., TOUSSAINT T. Characterization of a chromosomally encoded catechol 1,2-dioksygenase [E.C. 1.13.11.1.] from *Alcaligenes eutrophus CH34*. Arch. Microbiol. **166**, 42, **1996**.
29. CESPEDES R., MATURANA A., BUMANN U., BRONFMAN B., GONZALEZ B. Microbial removal of chlorinated phenols during aerobic treatment of effluents from radiata pine kraft pulps bleached with chlorine-based chemicals, with or without hemicellulases. Appl. Microbiol. Biotechnol. **46**, 631, **1996**.
30. WEISS M., MIKOLAJEWSKI S., PEIPP H., SCHMIDT U., SCHMIDT J., WRAY V., STRACK D. Tissue-specific and development - dependent accumulation of phenylpropanoids in larch mycorrhizas. Plant Physiol. **114**, 15, **1997**.

31. SWARTS M. J., VERHAGEN F. J., FIELD J. A., WIJNBERG J. B. Trichlorinated phenols from *Hypholoma elongatum.* Phytochem. **49**, 203, **1998**.
32. POWLOWSKI J., SEALY J., SHINGER V., CARDIEUX E. On the role of Dmpk, an auxiliary protein associated with multicomponent phenol hydroxylase from *Pseudomonas sp. strain CF600.* J. Biol. Chem. **272**, 945, **1996**.
33. KOWAL A. L., ŚWIDERSKA-BRÓŻ, M. Purification of water. PWN. Warszawa-Wrocław. pp 345, **1997**. (In Polish)
34. KUKLENYIK Z., ASHLEY D. L., Calafat AM. Analyzing drinking water for disinfection by-products. Analyt. Chem. **74**, 260A, **2002**.
35. GALICKA W.. Limnological characteristic of lowland barrier reservoir on the Pilica River in 1981-1993. Uniwersity Publishing, Łódź, pp. 1-143, **1996**. (In Polish)
36. CHORZEWSKA B., LASOTA D., MILEWSKA B., PACHOLSKA E., TUMMEL J. A report of environment condition in mazowieckie province. Chapter IV waters. WIOŚ, Warszawa, **2001**. (In Polish).
37. OŻADOWICZ R., MICHAŁOWICZ J., DUDA W. Chlorophenols, chlorocatechols, chlorinated methoxyphenols and monoterpenes in the Ner River and in municipal effluents of Łódź city. State and antropogenical changes of quality of waters in Poland. Editor J. Burchard. Łódź University Publishing, Łódź, **2002**. (In Polish)