

JAN DOJLIDO*, EDWARD ZBIEĆ*

CHANGES OF ORGANIC COMPOUNDS DURING THE WATER TREATMENT IN WARSAW, POLAND

The changes of organic compounds during the water treatment were studied. Investigations were carried out in two big waterworks in Warsaw, Poland. The raw water is taken from surface water, from two sources, i.e. the Vistula River and Zegrzyńskie Lake. The following groups of organic compounds were determined: organochlorine pesticides, PCBs, chlorinated benzene, volatile chlorinated hydrocarbons, phenols and chlorophenols. Organic compounds present in raw water were removed during treatment. In the process of water chlorination, big increase of the chloroorganic compounds produced was observed.

1. INTRODUCTION

The Warsaw Waterworks intake the water from two sources: the Vistula River and Zegrzyńskie Lake (figure 1).

The water intake on the Vistula is situated at a distance of 510 km from its spring. Before the Vistula reaches Warsaw it collects water from the drainage area which covers ca 84,800 km². Within this area with Silesian region, we can found numerous industrial plants. As a result, the Vistula River in Warsaw is highly polluted and the quality of intake water is too poor to be appropriate for communal intake.

Zegrzyńskie Lake is an impoundment created by the dam built across the course of the Narew River. The water quality of Zegrzyńskie Lake results from mixing the waters of two rivers: the Narew (drainage area of 28,262 km²) and the Bug (drainage area of 39,420 km²). In the basins of the rivers, there are some industrial plants and agricultural land with many food processing plants. The Narew River is draining the Mazurian Lakes, thus it is carrying humic acids. In hot periods, some algal blooms occur in the body of water of Zegrzyńskie Lake. Organoleptic properties of tap water

* Institute of Meteorology and Water Management, Podleśna 61, 01-673 Warszawa, tel/fax (+48 22) 35 49 26, Poland.

in Warsaw sometimes are not appropriate, which is connected with organic pollutants in water.

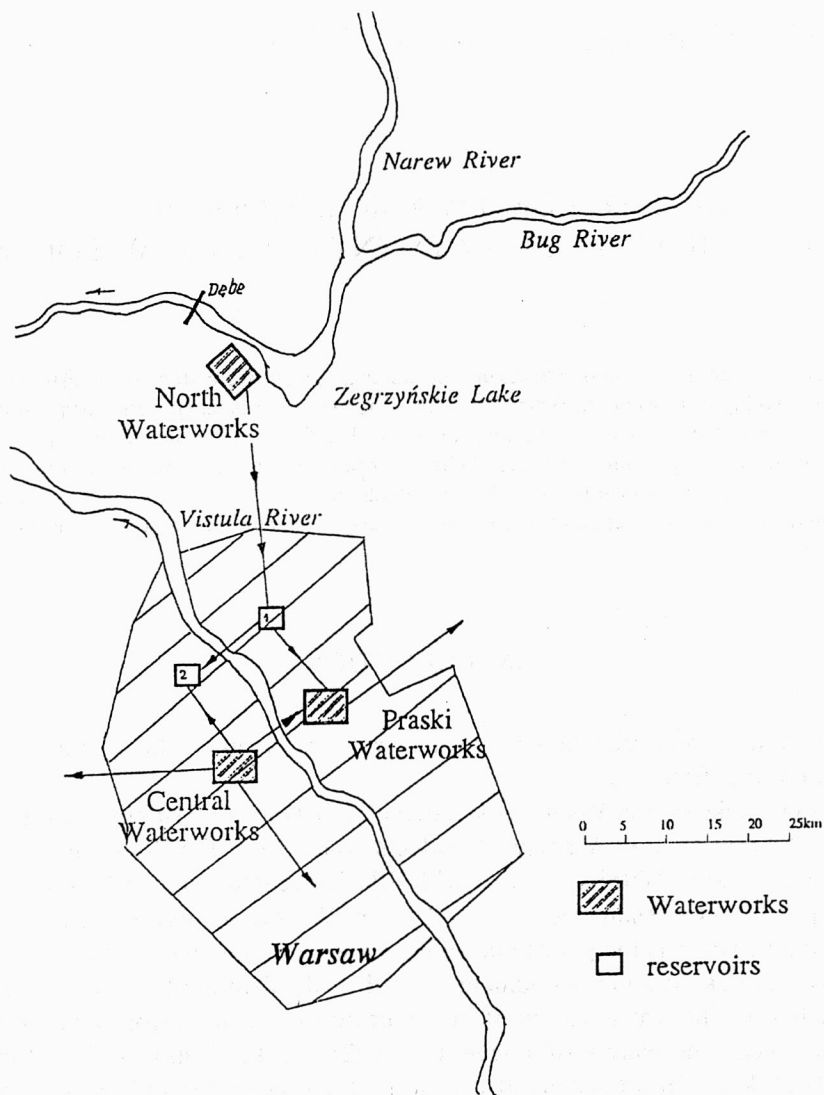


Fig. 1. Water supply system in Warsaw

The goal of this paper was to determine individual organic compounds in raw water and in drinking water after their treatment in the Warsaw Waterworks.

2. THE WARSAW WATERWORKS

2.1. THE CENTRAL WATERWORKS

The water is taken from the Vistula River (ca 500,000 m³/d) partly by bank intake, partly by bank infiltration. There are two process lines of treatment (figure 2).

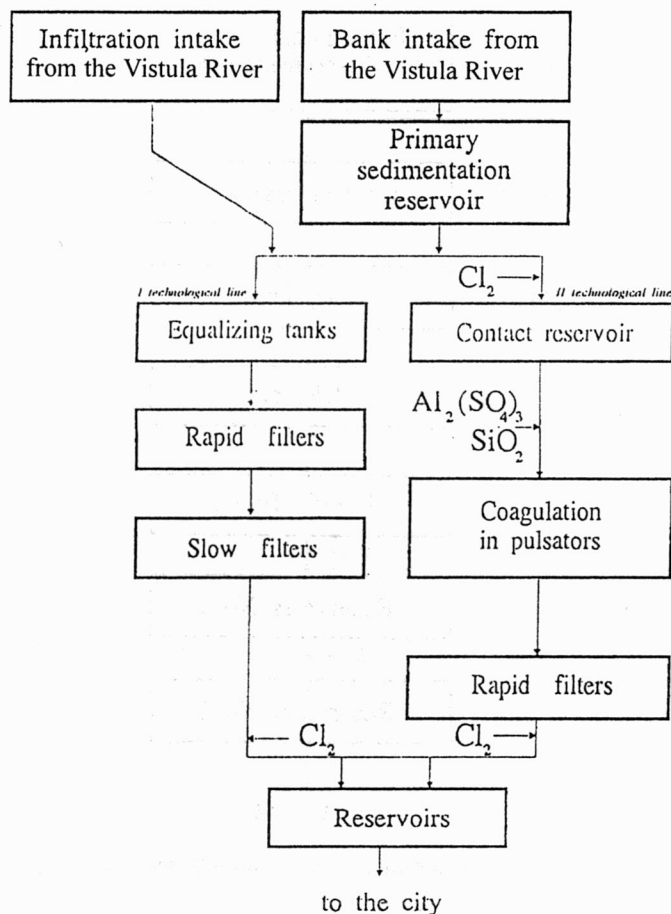


Fig. 2. Technological scheme of Central Waterworks

I technological line. After entering an equalizing tank (ca 30') wastewater is passed through two rapid filters, slow filters and thereafter is subjected to chlorination.

II technological line. If in the Vistula water some algae live, primary chlorination is necessary. Then water is coagulated by aluminium sulphate and activated silica. After leaving pulsator water passes through rapid filters and then is chlorinated.

2.2. THE NORTH WATERWORKS

The water is taken from Zegrzyńskie Lake (ca 200,000 m³/d, figure 1). During investigation period the following processes of treatment were applied: primary chlorination, ozonation, volume coagulation, filtration through rapid filters and chlorination (figure 3).

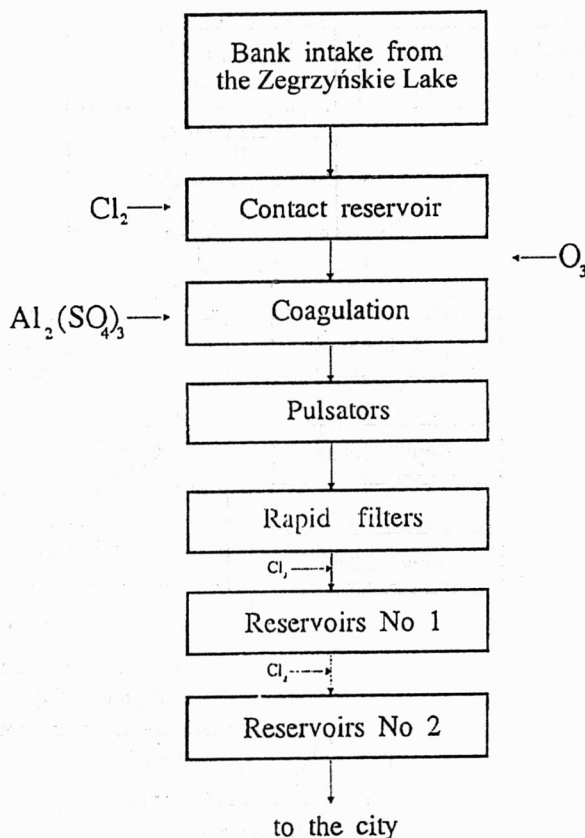


Fig. 3. Technological scheme of North Waterworks

3. MATERIALS AND METHODS

Our investigations were conducted from July 1992 to September 1993. The samples of raw water and treated tap water were taken every month (samples were taken 15 times).

The organic compounds were extracted from water by means of *n*-hexane.

Using a gas chromatograph Hewlett Packard type 5890 series II with capillary columns the following compounds were determined:

organochlorine pesticides: γ -HCH, DDT and its metabolites, DMDT, PCBs,
 chlorinated benzene: chlorobenzene, *p*-dichlorobenzene, *o*-dichlorobenzene, 1,2,3-trichlorobenzene, hexachlorobenzene,
 volatile chlorinated hydrocarbons: tetrachlorocarbon, 1,1,1-trichloroethylene, 1,1,2,2-tetrachloroethylene, tetrachloroethane,
 phenols: phenol, 2-nitrophenol, 4-nitrophenol, 2-methyl-4,6-dinitrophenol, 2,4-dinitrophenol, 2,4-dimethylphenol,
 chlorinated phenols: 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 4-chloro-3-methylphenol, pentachlorophenol.

4. RESULTS

The results of determinations are presented in tables 1–10.

Table 1

Pesticides and PCBs in raw water from the Vistula and in water after treatment (in ppb)

| | | γ -HCH | <i>p,p'</i> -DDE | <i>p,p'</i> -DDD | <i>p,p'</i> -DDT | <i>p,p'</i> -DMDT | PCBs |
|------------------------|------|---------------|------------------|------------------|------------------|-------------------|--------|
| Raw water | min. | 0.0015 | 0.0016 | 0.0008 | 0.0037 | n.d. | 0.0016 |
| | max. | 0.0152 | 0.0492 | 0.0198 | 0.0573 | 0.0212 | 0.0185 |
| | mean | 0.0056 | 0.0169 | 0.0058 | 0.0169 | 0.0030 | 0.0070 |
| Tap water | min. | 0.0005 | 0.0005 | 0.0003 | 0.0011 | n.d. | 0.0004 |
| | max. | 0.0028 | 0.0089 | 0.0089 | 0.0132 | 0.0015 | 0.0077 |
| | mean | 0.0017 | 0.0033 | 0.0022 | 0.0044 | 0.0003 | 0.0025 |
| Change of mean (times) | | -3.3 | -5.1 | -2.6 | -3.8 | -10.0 | -2.8 |

n.d. – not detected.

Permissible concentrations in Poland: surface water: chloroorganic insecticides – 0.05 ppb, tap water: γ -HCH – 5.0 ppb, DDT and its metabolites – 30.0 ppb.

Table 2

Pesticides and PCBs in raw water from Zegrzyńskie Lake and in water after treatment (in ppb)

| | | γ -HCH | <i>p,p'</i> -DDE | <i>p,p'</i> -DDD | <i>p,p'</i> -DDT | <i>p,p'</i> -DMDT | PCBs |
|-----------|------|---------------|------------------|------------------|------------------|-------------------|--------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Raw water | min. | 0.0005 | 0.0016 | 0.0005 | 0.0018 | n.d. | 0.0006 |
| | max. | 0.0195 | 0.0178 | 0.0125 | 0.0235 | 0.0257 | 0.0168 |
| | mean | 0.0034 | 0.0068 | 0.0039 | 0.0117 | 0.0026 | 0.0054 |

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|------------------------|------|--------|--------|--------|--------|--------|--------|--------|
| Tap water | min. | 0.0003 | 0.0008 | 0.0002 | 0.0009 | n.d. | 0.0002 | 0.0002 |
| | max. | 0.0029 | 0.0066 | 0.0065 | 0.0075 | 0.0030 | 0.0132 | 0.0132 |
| | mean | 0.0010 | 0.0030 | 0.0015 | 0.0037 | 0.0004 | 0.0024 | 0.0024 |
| Change of mean (times) | | -3.4 | -2.3 | -2.6 | -3.2 | -6.5 | -2.3 | -2.3 |

Table 3

Chlorobenzenes in raw water from the Vistula and in water after treatment (in ppb)

| | | Chloro- benzene | <i>p</i> -dichloro- benzene | <i>o</i> -dichloro- benzene | Trichloro- benzene | Hexachloro- benzene |
|----------------|------|--------------------|--------------------------------|--------------------------------|-----------------------|------------------------|
| Raw water | min. | 0.010 | n.d. | n.d. | n.d. | n.d. |
| | max. | 0.191 | 0.283 | 0.021 | 0.0049 | n.d. |
| | mean | 0.043 | 0.025 | 0.0036 | 0.0006 | - |
| Tap water | min. | 0.056 | 0.019 | 0.006 | 0.0027 | n.d. |
| | max. | 2.614 | 0.604 | 1.037 | 0.0728 | n.d. |
| | mean | 0.423 | 0.170 | 0.410 | 0.0236 | - |
| Change of mean | | 2.7 | 6.8 | 113.9 | 39.3 | - |

Permissible concentrations in Poland: tap water: chlorobenzenes without hexachlorobenzene - 5.0 ppb, - hexachlorobenzene - 0.015 ppb.

Table 4

Chlorobenzenes in raw water from Zegrzyńskie Lake and in water after treatment (in ppb)

| | | Chloro- benzene | <i>p</i> -dichloro- benzene | <i>o</i> -dichloro- benzene | Trichloro- benzene | Hexachloro- benzene |
|----------------|------|--------------------|--------------------------------|--------------------------------|-----------------------|------------------------|
| Raw water | min. | 0.006 | n.d. | n.d. | n.d. | n.d. |
| | max. | 0.098 | 0.028 | 0.010 | 0.0028 | n.d. |
| | mean | 0.034 | 0.004 | 0.001 | 0.0003 | - |
| Tap water | min. | 0.045 | 0.003 | n.d. | n.d. | n.d. |
| | max. | 0.781 | 0.128 | 0.206 | 0.0194 | 0.0024 |
| | mean | 0.218 | 0.031 | 0.041 | 0.0089 | 0.0002 |
| Change of mean | | 6.4 | 7.8 | 41.0 | 29.7 | increase |

Table 5

Volatile chlorinated hydrocarbons in raw water from the Vistula and in water after treatment (in ppb)

| | | Tetrachloro-carbon | Trichloro-ethylene | Tetrachloro-ethylene | Tetrachloro-ethane |
|----------------|------|--------------------|--------------------|----------------------|--------------------|
| Raw water | min. | 0.0003 | 0.0004 | 0.0002 | n.d. |
| | max. | 0.0145 | 0.3325 | 0.0338 | 0.229 |
| | mean | 0.0031 | 0.0286 | 0.0048 | 0.024 |
| Tap water | min. | 0.0030 | 0.0111 | n.d. | 0.011 |
| | max. | 0.0909 | 2.7736 | 0.1891 | 2.262 |
| | mean | 0.0199 | 0.4299 | 0.0265 | 0.395 |
| Change of mean | | 6.4 | 15.0 | 5.5 | 16.5 |

Permissible concentrations in Poland: tap water: tetrachlorocarbon – 5.0 ppb, trichloroethylene – 30.0 ppb, tetrachloroethane – 10.0 ppb.

Table 6

Volatile chlorinated hydrocarbons in raw water from Zegrzyńskie Lake and in water after treatment (in ppb)

| | | Tetrachloro-carbon | Trichloro-ethylene | Tetrachloro-ethylene | Tetrachloro-ethane |
|----------------|------|--------------------|--------------------|----------------------|--------------------|
| Raw water | min. | n.d. | 0.0004 | n.d. | n.d. |
| | max. | 0.0143 | 0.0421 | 0.0108 | 0.004 |
| | mean | 0.0020 | 0.0061 | 0.0024 | 0.0003 |
| Tap water | min. | 0.0024 | 0.0024 | 0.0010 | n.d. |
| | max. | 0.0218 | 0.6568 | 0.0300 | 0.012 |
| | mean | 0.011 | 0.0750 | 0.0053 | 0.0021 |
| Change of mean | | 5.5 | 12.3 | 2.2 | 7.0 |

Table 7

Phenols in raw water from the Vistula and in water after treatment (in ppb)

| | | Phenol | 2-nitro-phenol | 4-nitro-phenol | 2-methylo-4,6-dinitro-phenol | 2,4-dinitro-phenol | 2,4-dime-thylphenol |
|-----------|------|--------|----------------|----------------|------------------------------|--------------------|---------------------|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Raw water | min. | 0.12 | n.d. | n.d. | n.d. | n.d. | n.d. |
| | max. | 1.83 | 0.4 | 0.3 | 0.32 | 0.28 | 0.4 |
| | mean | 0.58 | 0.13 | 0.11 | 0.12 | 0.09 | 0.18 |

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|------------------------------|------|----------|----------|----------|----------|----------|----------|
| Tap | min. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| water | max. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | mean | — | — | — | — | — | — |
| Change of mean (times) | | decrease | decrease | decrease | decrease | decrease | decrease |

Table 8

Phenols in raw water from Zegrzyńskie Lake
and in water after treatment (in ppb)

| | | Phenol | 2-nitro- phenol | 4-nitro- phenol | 2-methylo- 4,6-dinitro- phenol | 2,4-dinitro- phenol | 2,4-dime- thylphenol |
|------------------------------|------|----------|--------------------|--------------------|--------------------------------------|------------------------|-------------------------|
| Raw | min. | 0.09 | n.d. | n.d. | n.d. | n.d. | n.d. |
| water | max. | 2.46 | 0.8 | 0.2 | 0.35 | 0.75 | 0.4 |
| | mean | 0.45 | 0.19 | 0.09 | 0.11 | 0.16 | 0.13 |
| Tap | min. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| water | max. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | mean | — | — | — | — | — | — |
| Change of mean (times) | | decrease | decrease | decrease | decrease | decrease | decrease |

Table 9

Chlorophenols in raw water from the Vistula
and in water after treatment (in ppb)

| | | 2-chloro- phenol | 2,4-dichloro- phenol | 2,4,6-tri- chlorophenol | 4-chloro- 3-methylo- phenol | Pentachloro- phenol |
|-------------------|------|---------------------|-------------------------|----------------------------|-----------------------------------|------------------------|
| Raw | min. | n.d. | n.d. | n.d. | n.d. | n.d. |
| water | max. | 0.5 | 0.2 | 0.16 | n.d. | 0.21 |
| | mean | 0.13 | 0.04 | 0.03 | — | 0.03 |
| Tap | min. | 0.4 | 0.6 | 0.05 | n.d. | n.d. |
| water | max. | 22.4 | 5.3 | 4.42 | 0.52 | 0.38 |
| | mean | 8.11 | 1.88 | 0.94 | 0.12 | 0.14 |
| Change of mean | | 62.4 | 47.0 | 31.3 | increase | 4.7 |

Table 10

Chlorophenols in raw water from Zegrzyńskie Lake
and in water after treatment (in ppb)

| | | 2-chloro-phenol | 2,4-dichloro-phenol | 2,4,6-tri-chlorophenol | 4-chloro-3-methylo-phenol | Pentachloro-phenol |
|----------------|------|-----------------|---------------------|------------------------|---------------------------|--------------------|
| Raw water | min. | n.d. | n.d. | n.d. | n.d. | n.d. |
| | max. | 0.3 | 0.5 | 0.11 | n.d. | 0.07 |
| | mean | 0.06 | 0.09 | 0.02 | — | 0.01 |
| Tap water | min. | 0.3 | 0.1 | n.d. | n.d. | n.d. |
| | max. | 5.9 | 2.9 | 1.15 | 0.05 | 0.14 |
| | mean | 2.21 | 1.34 | 0.46 | 0.01 | 0.06 |
| Change of mean | | 36.8 | 14.9 | 23.0 | increase | 6.0 |

4.1. PESTICIDES AND PCBs

Chlorinated pesticides were always detected in raw water, but their concentration in the Vistula was considerably higher than in Zegrzyńskie Lake. In both waterworks a substantial decrease in pesticide concentrations was noticed 10 times.

In the case of PCBs, which were detected in both sources of water, we dealt with a similar situation: their concentrations decreased 2–3 times during the treatment.

4.2. CHLORINATED BENZENES

Hexachlorobenzene was not detected in raw water and was only once found in tap water. Chlorobenzene always occurred in raw and drinking water. Other chlorinated benzenes were found periodically in intake water and in low concentrations. In general, the concentration of chlorinated benzenes was much lower in Zegrzyńskie Lake water than in the Vistula. During the treatment period the concentration of chlorinated benzenes increased substantially – the mean increase ranged from 2 to over 100 times (maximally the concentration of chlorobenzenes increased 400 times).

Volatile chlorinated hydrocarbons. These compounds were detected in intake water, but more often and in higher concentrations in the Vistula water. After the treatment their concentrations were much higher. Their mean concentrations increased 6–16 times in Central Waterworks and 2–12 times in North Waterworks.

Phenols. Phenol, nitrophenols and methylophenol were detected sporadically in the Vistula and Zegrzyńskie Lake water. But in tap water, phenols were not detected, which can be attributed to the water treatment or to their change to chlorophenols.

Chlorophenols occurred in intake water only occasionally and in small concentrations. But during the chlorination process the concentrations of chlorophenols highly increased (4–50 times).

5. DISCUSSION

The sources of water intake for the Warsaw Waterworks are polluted with many organic compounds. The Vistula River, draining large industrial region of Silesia, is more polluted than Zegrzyńskie Lake, but, in addition to industrial pollutants, the lake water contains high concentration of humic acids. Both the Vistula River and Zegrzyńskie Lake waters are eutrophic.

The water treatment in Warsaw is rather simple, it consists in filtration and coagulation.

The citizens of Warsaw are not satisfied with the quality of tap water. Sometimes its smell and taste are bad, sometimes it is overchlorinated.

The results obtained in this study showed that many organic compounds, mainly chlorinated derivatives, occur in the Warsaw tap water. In general, their concentrations are below the permissible level, but sometimes they exceed it. The treatment of water in the Waterworks in Warsaw should be improved.

6. CONCLUSIONS

The concentrations of chloroorganic pesticides and polychlorinated biphenyls present in the Vistula and Zegrzyńskie Lake water are low. Those compounds are removed during treatment, hence their concentrations in tap water are found to be very low, much below the permissible values.

Chlorinated benzenes occurred periodically and in low concentration in raw water. During the treatment their content increases, sometimes noticeably, but their concentration in tap water is still below permissible limit.

Volatile chlorinated hydrocarbons occurred in low concentrations in raw water. After chlorination their concentrations increase considerably, but are still below the permissible values for drinking water.

Phenols in the intake water occur sporadically and in small concentrations, but in tap water no phenols are detected.

Chlorophenols are found in raw water in small concentration, but during the treatment their concentrations increase, sometimes to the level that can change the taste and odour of tap water in Warsaw.

ACKNOWLEDGEMENT

This research was supported by the State Committee for Scientific Research. No 6 0757 91 01.

ZMIANY ZAWARTOŚCI ZWIĄZKÓW ORGANICZNYCH
PODCZAS OCZYSZCZANIA WODY W WARSZAWIE

Przebadano zmiany zawartości związków organicznych podczas oczyszczania wody. Badania były prowadzone w dwóch dużych stacjach oczyszczania wody w Warszawie. Wodę surową pobierano powierzchniowo z dwu źródeł: z Wisły i z Jeziora Zegrzyńskiego. Oznaczano następujące grupy związków organicznych: chloroorganiczne pestycydy, PCB, chlorowane benzeny, lotne chlorowane węglowodory, fenole i chlorofenole. Związki organiczne obecne w wodzie surowej były usuwane podczas oczyszczania. Podczas chlorowania wody zaobserwowano duży wzrost stężeń powstających związków chloroorganicznych,

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