Chlorine dioxide disinfection by-products in the Nová Bystrica-Čadca-Žilina long distance water supply system

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Abstract In a process of water disinfection it is necessary to distinguish between primary disinfection focused on removal or inactivation of microbiological contaminants from raw water, and secondary disinfection focused on maintenance of residual concentration of the disinfectant in distribution system. Current practice related to disinfection follows two approaches. The paper presents results from a stage task solution “Research of physical-chemical changes in water quality during its distribution” at the Nová Bystrica-Čadca-Žilina long distance water supply system (LDWSS) focused on the presence of disinfection by-products by using chlorine dioxide.

Keywords By-product; chlorine dioxide; disinfection; water treatment

Introduction

In a process of water disinfection it is necessary to distinguish between primary disinfection focused on removal or inactivation of microbiological contaminants from raw water, and secondary disinfection focused on maintenance of residual concentration of disinfectant in distribution system.

In some countries, it is required or recommended to maintain residual concentration of disinfectant in order to meet limits of microbiological parameters, minimize bio-film formation, prevent secondary contamination in distribution systems and to indicate whether contamination occurs as a result of disinfectant concentration reduction. Other countries follow the opinion that residual concentration of disinfectant is not required for good water quality, microbiologically safe groundwater or for some surface water resources treated by multilevel technologies, and degrade so disinfection by-product formation and reduction of risk connected with their formation, respectively (Gallagher et al., 1994; Griese et al., 1991; Hoehn et al., 1996).

Brief characteristics of long distance water supply system

The Nová Bystrica-Čadca-Žilina long distance water supply system (LDWSS) supplies northern part of the Žilina region with water from the Nová Bystrica water supply reservoir. The Nová Bystrica water treatment plant has been constructed for designed capacity of water treatment 1,060 ls⁻¹. Current operation capacity is 248 ls⁻¹. Treatment technology has been designed as a two-stage technology with technological levels: dosage of chlorinated ferric sulfate, rapid mixing, slow mixing (mechanical and hydraulic), sedimentation, calcium hydrate dosage, rapid filtration and disinfection. Since problems with preparation of primary coagulant have occurred early during the pilot operation, the provider has used an alternative dosage of aluminium sulfate. Initial water disinfection was designed using chlorine–ammonization methods. However, chlorine dioxide has been used for disinfection since 1997.

doi: 10.2166/ws.2006.071
Water supply system supplies with water 31 municipalities and cities of the Žilina region with the total number of 164,000 inhabitants. The water supply system is made of welded steel pipes with bituminous lining. The stretch Nová Bystrica-Krásno to Kysuca-Žilina (49 km) is made of pipes with a diameter of 800 mm and the stretch Krásno to Kysuca-Čadca (7 km) is made of pipes with a diameter of 600 mm. The total length of water supply is 607.4 km including 53 water reservoirs and 30 pumping stations (Büchnerová et al., 2001). Figure 1 original disinfection by chlorine–ammonization was sufficient for bacteriological and biological safety of drinking water distributed by the long distance water supply (Kriš et al., 1996), but it gave rise to quality deterioration considering nitrite parameter at the end of long distance water supply at Žilina. In addition, another problem related to iron presence has occurred in connection with reduced water abstraction from the network in the early 1990s. After introducing the chlorine dioxide disinfection at the Nová Bystrica WTP such problems with nitrites have been eliminated completely and iron experienced a rapid concentration decrease (Munka, 2002; Škultétová et al., 2000).

Monitoring of water disinfection by-products in supply system
The monitoring of the water supply system was carried out in the following periods: September and November 2000; February, May, August and November 2001. During these samplings the following water disinfection by-products have been determined:

- trihalogenmethanes: chloroform (CHCl₃); bromodichloromethane (CHBrCl₂); dibromochloromethane (CHBr₂Cl); bromoform (CHBr₃)
- dichlorophenols: 2,3-DCP; 2,4-DCP; 2,5-DCP; 2,6-DCP
- trichlorophenols: 2,4,5-TCP; 2,4,6-TCP
- perchlorophenol: PCP
- benzene and its derivates: benzene; chlorobenzene; ethylbenzene; 1,2-DCB; 1,3-DCB; 1,4-DCB; toluene; xylene
- other substances: 2,4-D acid (2,4-dichlorophenoxyacetic acid); 1,1,2-trichloroethylene (TCE); 1,2-dichloroethane; tetrachloromethane (CCl₄); 1,1,2,2-tetrachloroethylene (PCE)
- humic substances

At the same time (except for the sampling carried out in September and November 2000) the aliphatic carboxyl acids have been also determined (butanoic, pentanoic, hexanoic, heptanoic, octanoic, nonanoic, decanoic, undecanoic, dodecanoic, tetradecanoic, hexadecanoic and octadecanoic acid). Chlorine dioxide was determined in regular monthly intervals during the period from July to December 2001 and chlorites were determined in regular monthly intervals during the period from June to December 2001.

Results and discussion
Concentrations of chlorine dioxide in the water supply system
Chlorine dioxide concentrations at the start of the water supply system ranged from 0.20–0.50 mg/l. The concentrations at the Krásno to Kysuca water reservoir were determined and ranged from 0.02–0.25 mg/l. The higher concentrations were observed within its higher entering concentrations. The most frequent concentration was 0.10 mg/l. The highest concentration at the Čadca water reservoir was determined at a value of 0.15 mg/l, but the concentrations mostly ranged from 0.02–0.05 mg/l. Concentrations lower than 0.02 mg/l were observed at the Považský Chlmec water reservoir (only in one case the concentration reached value of 0.05 mg/l). Based on this course of concentrations it shows that such disinfection used in the long distance water supply system results in rather significant reduction of chlorine dioxide concentrations together with formation of chlorites already at 19 km long stretch from the Nová Bystrica WTP. Following the above
facts it can be stated that this stretch to Považský Chlmec was disinfected mostly by chlorites.

Results from monitoring of disinfection by-products and other organic substances

During the September 2000 sampling only chlorobenzene, ethylbenzene, 1,1,2,2-tetrachloroethene, xylenes and humic substances were determined above a detection limit. Chlorobenzene concentrations were slightly increased (Nová Bystrica WTP 1.5 µg/l; Považský Chlmec water reservoir 6.3 µg/l, while the limit-MH for drinking water is 10 µg/l) and 1,1,2,2-tetrachloroethene was detected only in concentration levels of approximately 0.2 mg/l (limit-NMH for drinking water is 10 µg/l). Xylenes, similarly to chlorobenzene, experienced an upward trend and their maximum concentration did not exceed 4% of the limit (Nová Bystrica WTP 1.4 µg/l, Považský Chlmec water reservoir 3.8 µg/l, while the limit-MH for drinking water is 100 µg/l). Humic substances in raw water reached the value of 2.0 mg/l, but water treatment reduced their concentration to 0.70 mg/l.

During the November 2000 sampling only chloroform was determined from THM on the level of 3 µg/l (limit for THM is 40 µg/l) and 1,1,2,2-tetrachloroethene was detected in the same concentrations as in previous sampling (0.2 µg/l). Humic substances in raw water reached the value of 3.4 mg/l, but at the outflow from water treatment plant their concentrations reached a value of 0.80 mg/l.

During the February 2001 sampling chlorobenzene was detected in concentrations of 3.8–6.6 µg/l with downward trend and its concentration in raw water reached 8.9 µg/l. At the Považský Chlmec water reservoir the 1,1,2,2-tetrachloroethene concentration reached a value of 0.9 µg/l. The content of humic substances in raw water was 1.2 µg/l and in treated water their content decreased to 0.6 µg/l.

During the May 2001 sampling only xylenes were detected in concentrations up to 2.1 µg/l and humic substances with a value of 1.0 mg/l. During the August 2001 sampling only humic substances were determined (raw water 0.9 mg/l; treated water 0.3 mg/l). During the November 2001 sampling only chloroform from THM substances was determined in concentrations ranging from 1.5–2.7 µg/l, benzene 0.5 µg/l, toluene in raw water 1.3 µg/l (limit-MH for drinking water is 50 µg/l), xylene less than 1.5 µg/l and humic substances (raw water only 0.7 mg/l).

During the samplings the aliphatic carboxyl acids were also determined because of their possible presence in the distribution system for distribution of water disinfected by chlorine dioxide (targeted analysis). The February 2001 sampling has proved that all aliphatic carboxyl acids were below the detection limit. During the May 2001 sampling only hexadecanoic (less than 0.40 µg/l) and octadecanoic (less than 30 µg/l) acids were observed in higher concentrations and the rest was determined in lower concentrations. The numbers from May 2001 sampling are the same as for August 2001 sampling. The only difference is that hexadecanoic acid concentrations were lower than 50 µg/l and for octadecanoic acid less than 0.40 µg/l. The highest concentrations during the November 2001 sampling were determined for octadecanoic acid (0.30 µg/l).

Table 1 shows the results from monitoring disinfection by-products and other organic substances at the Nová Bystrica-Čadca-Zilina long distance water supply system. For disinfection by-products the maximum determined concentration is given. This relates to their limit under the Decree no. 151/2004 Coll. and it is expressed in % from that value. In proportional expression the maximum concentrations of disinfection by-products ranged from 1.4–66.0% with the lowest content of xylenes and the highest concentrations of chlorobenzene.
Chlorite concentrations in the Nová Bystrica-Čadca-Žilina long distance water supply system

Samples taken from the Nová Bystrica WTP outflow demonstrated rather quick decomposition of chlorine dioxide already after its dosage into the treated water, when concentrations of chlorine dioxide and chlorites reached almost the same values. At a chlorine dioxide concentration lower than 0.20 mg/l at the outflow from the Nová Bystrica WTP its concentrations ranged from 0.02–0.5 mg/l already at Krásno to Kysuca. For chlorine dioxide concentration of 0.18 mg/l at the outflow from the Nová Bystrica WTP the concentration of chlorites was simultaneously determined at a value of 0.21 mg/l, but already at the Krásno to Kysuca water reservoir the chlorine dioxide concentration decreased to 0.02 mg/l, while chlorite concentration increased to 0.35 mg/l. In the Čadca water reservoir the concentration of chlorites decreased to 0.31 mg/l and in Považský Chlmec to the value of 0.27 mg/l. From Figures 1 and 2 it is evident that water disinfection at the stretches Krásno upon Kysuca water reservoir – Čadca water reservoir and Krásno upon

![Figure 1](https://iwaponline.com/ws/article-pdf/6/2/209/418041/209.pdf)

**Figure 1** Scheme of the Nová Bystrica-Čadca-Žilina long distance water supply system

<table>
<thead>
<tr>
<th>Water disinfection by-product</th>
<th>Maximum concentration</th>
<th>Limit Decree no.151/2004</th>
<th>Percentage limit (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>6.6 µg/l</td>
<td>10 µg/l (MH)</td>
<td>66</td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethene</td>
<td>1.0 µg/l</td>
<td>10 µg/l (NMH)</td>
<td>10</td>
</tr>
<tr>
<td>Xylenes</td>
<td>1.4 µg/l</td>
<td>100 µg/l (MH)</td>
<td>1.4</td>
</tr>
<tr>
<td>Benzene</td>
<td>&lt;0.5 µg/l</td>
<td>1.0 µg/l (MHRR)</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.3 µg/l</td>
<td>50 µg/l (MH)</td>
<td>2.5</td>
</tr>
<tr>
<td>Chloroform</td>
<td>3.0 µg/l</td>
<td>40 µg/l (MH)</td>
<td>8</td>
</tr>
<tr>
<td>Humic substances</td>
<td>Raw water: 1.2–3.4 mg/l</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Treated water: 0.6–1.0 mg/l</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td><strong>Aliphatic carboxyl acid</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexadecanoic acid</td>
<td>&lt;0.50 µg/l</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Octadecanoic acid</td>
<td>&lt;0.40 µg/l</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Other carboxyl acids</td>
<td>&lt;0.10 µg/l</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 1** Results from monitoring of water disinfection by-products and other organic substances in the Nová Bystrica-Čadca-Žilina water supply system
Kysuca water reservoir—Považský Chlmec water reservoir has been assured mostly by using chlorites.

Conclusions

Within the monitoring of disinfection by-products at the Nová Bystrica-Čadca-Zilina long distance water supply system the following substances have been determined: trihalogenmethanes, dichlorophenols, trichlorophenols, perchlorophenol, benzene and its derivatives, organic substances, humic substances, aliphatic carboxyl acids and chlorites.

The results show that from the above substances only the following were determined above the detection limit: chlorobenzene; 1,1,2,2-tetrachloroethene; xylenes; toluene; chloroform; humic substances; chlorites; hexadecanoic and octadecanoic acids. The highest concentration was determined for chlorobenzene (6.6 μg/l that represents 66% of limit under the Decree no. 151/2004 Coll.), chloroform (1.4 μg/l, 1.4%), toluene (1.3 μg/l, 2.5%) and 1,1,2,2-tetrachloroethene (1.0 μg/l, 10%). Aliphatic carboxylic acids reached the concentrations lower than 0.50 μg/l. The maximum concentrations of chlorites (NMH 0.20 μg/l) ranging from 0.30–0.35 μg/l were detected at sites where the chloride dioxide concentration is very low. Referring to own consumption of chlorine dioxide and course of its decomposition reactions in GSSW it was recommended for the provider to use chlorine dioxide dosages in concentrations of 0.25–0.27 mg/l at most, and simultaneously to monitor microbiological and biological water quality, especially at stretches where distributed water is disinfected only by chlorites.

References


