

ALDEHYDES FORMATION DURING WATER DISINFECTION BY OZONATION AND CHLORINATION PROCESS

A. DĄBROWSKA^{1*}
B. KASPRZYK HORDERN¹
J. NAWROCKI¹

*Department of Water Treatment Technology
Faculty of Chemistry, A. Mickiewicz University
Drzymały 24, 60-613 Poznań, Poland*

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*to whom all correspondence should be addressed:
Tel: +48 61 829 34 343; Fax: +48 61 829 34 000
e-mail: agatadab@amu.edu.pl

ABSTRACT

The goal of this paper is an investigation into the influence of disinfection with ozone, chlorine (Cl₂) and chlorine dioxide (ClO₂) on the aldehydes formation. Three types of waters were treated with different doses of these disinfectants. The results obtained indicate that the level of carbonyls concentration can significantly increase with the time of Cl₂ and ClO₂ reaction with aldehyde precursors in treated water. There is no noticeable correlation between quantity of aldehydes and total organic carbon (TOC) value of disinfected water, but potential of organic by-products formation is evidently connected with the nature of organic material. The range of productivity of aldehydes in water treated with ClO₂ or Cl₂ is very similar. The productivities of aldehydes were calculated for all investigated waters treated with different doses of oxidant and were 2 – 10 µg of aldehydes per 1 mg TOC. Formaldehyde and acetaldehyde were the dominant carbonyl compounds identified in water before as well as after the reaction with disinfectants.

KEYWORDS: disinfection, chlorine, chlorine dioxide, ozone, organic byproducts, aldehydes,

1. INTRODUCTION

Chlorine, chlorine dioxide and ozone are the most popular compounds used as the effective oxidants in water treatment technology. Numerous by-products are associated with these disinfectants.

The most common ozonation by-products are short-chained carboxylic acids (Gagnon *et.al.* 1997, Kuo 1998) and aldehydes (Weinberg *et.al.*, 1993, Griffini *et.al.*, 1999, Westerhoff *et.al.*, 1999, Can and Gurol, 2003). Minimization of aldehydes and other organic ozonation by-product in drinking water is very desirable. It is known that formaldehyde and acetaldehyde, being relatively volatile, have produced respiratory tumors, glyoxal has promoted stomach tumors (Can and Gurol, 2003). The highly biodegradable aldehydes as well as the others biodegradable by-products formed during oxidation process are considered to be the part of biodegradable organic carbon (BOC). They are removed from water after ozonation, usually by biofiltration process to prevent the distribution system from the bacterial regrowth. Most drinking water treatment plants using ozone also use a secondary disinfectant to maintain disinfection in the distribution system. The reactions of aldehydes with chlorine may produce halogenated by-products

of potential concern, such as cyanogens chloride and chloral hydrate. Aldehydes can be also responsible for some flavour problems. The production of aldehydes may depend on several variables, such as ozone dosage, temperature, pH value of water, and concentration of natural organic matter (NOM). The total aldehyde concentration was observed to increase with increasing ozone dose and initial organic carbon concentration. Correlation between the aldehydes and assimilable organic carbon has been shown by Schechter and Singer (1995). Griffini *et al.*, (1999) have also observed a relationship between the biodegradable dissolved organic carbon and the sum of aldehydes and ketoacids.

Chlorine was the first chemical used to disinfect drinking water and is still the most common disinfectant used as a strong and effective oxidant (Richardson 1998, Richardson *et al.*, 1998, Minear 1995). The chlorinated organic compounds such as trihalomethanes (THMs) and haloacetic acids (HAAs) are considered to be the major by-products formed when chlorine is used to treat drinking water. The chlorinated organic compounds are responsible for the undesirable taste and odor in disinfected waters. Moreover chloroform, bromodichloromethane and bromoform have been shown to be carcinogens. Chlorination by-products are regarded as being of low biodegradability, that is the reason why their presence in water does not necessarily lead to bacteria regrowth in a distribution system even in the case of insufficient dose of chlorine. However, apart from THMs and HAAs, the other groups of organic compounds were identified in chlorinated waters: highly biodegradable aldehydes and ketones (Richardson 1998, Richardson *et al.*, 1999). Not much is known about organic by-products formed after disinfection with chlorine.

Chlorine dioxide is a powerful oxidant, more effective than chlorine for killing most microorganisms. ClO_2 is five times more soluble in water than chlorine and is effective over a wide pH range. Compared to chlorine, chlorine dioxide does not produce chlorinated by-products making it an alternative disinfectants. The total mutagenicity observed for water treated with chlorine dioxide is much lower than with chlorine (Richardson 1998). Chlorites (ClO_2^-) and chlorates (ClO_3^-) are the best studied inorganic by-products connected with ClO_2 . Very few studies have focused on determining the effect of chlorine dioxide dosage and contact time on aldehyde formation. Ivancev-Tumbas and Dalmacija (2001) reported that formaldehyde, acetaldehyde, glyoxal and methylglyoxale are the by-products of natural organic matter oxidation by ClO_2 . The authors (Dąbrowska *et al.*, 2003, Świetlik *et al.* 2004) have previously shown, that the reaction of ClO_2 with humic substances present in disinfected water is responsible for the formation of aldehydes and the formation of carbonyl compounds takes place as long as disinfectant is available in water.

The aim of our study was to discuss the problem of biodegradable by-products formed during water disinfection by both: ozonation and chlorination process. We compared the range of productivity of aldehydes in three different waters treated with chlorine and chlorine dioxide with that observed usually for ozonation. Aldehydes were investigated as representative organic compounds, formed together with the other biodegradable organic by-products, relatively more unstable in water and difficult to detect. Our investigations were concentrated on the Cl_2 and ClO_2 disinfectants, which are used generally in the final stage of water treatment and can potentially influence aldehyde formation in distribution systems. To determine carbonyl compounds we used the method originally described by Yamada and Somiya (1989). We optimised this method and the detection limit in the ppt range was achieved in our research. Process of derivatization i.e. the reaction of carbonyl compounds with PFBOA (O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine) has been used to obtain oximes that after extraction with organic solvent were analysed by gas chromatography with selective electron capture detector.

2. MATERIALS AND METHODS

2.1. Disinfectants

Three disinfectants were used: chlorine, chlorine dioxide and ozone. Cl_2 and ClO_2 were obtained directly from Mosina Water Intake. ClO_2 was produced by a reaction of sodium chlorite with hydrochloric acid. Cl_2 was dosed as hypochlorite (NaClO). Cl_2 and ClO_2 concentrations were measured with iodometric methods (Standard Methods, 1980) and their residual concentrations were determined with DR/4000U spectrophotometer (HACH). Ozone was produced from oxygen in the OZOMATIC® type Effizon SWO 15/30 ozone generator (OZOMATIC® GmbH, Germany). The required oxygen was supplied by PSA unit type AS12 (Air Sep Corporation, USA). The feedgas was introduced to the water through an injector and mixed with the water with static mixer. The residual ozone concentration was determined using the indigo method (Standard Methods, 1980).

2.2 Waters

Three types of waters were investigated: WI – infiltrated ground water after iron and manganese removal (from Mosina), WII - surface water (from Bogdanka river), WIII - shallow ground water after iron and manganese removal (from Poznań).

All waters were treated with various doses of chlorine, chlorine dioxide and ozone and then analyzed for aldehydes in order to observe the relation between disinfectant dose and the formation of biodegradable organic disinfection by-products.

The pH value of all investigated waters were about 7 and this parameter was not corrected. The molecular size distribution of NOM was conducted with size exclusion chromatography before and after the reaction with disinfectant.

2.3. Analysis of aldehydes

Analytical standards of aldehydes (i.e. formaldehyde, acetaldehyde, propanal, hexanal, heptanal, octanal, benzaldehyde, nonanal, decanal, glyoxal, methylglyoxal) and derivatising agent O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBOA) were purchased from Aldrich – Chemie (Steinheim, Germany) and BDH (Pool, UK; AnalaR and GPR grades). PFBOA was prepared gravimetrically as an aqueous solution in organic free water while aldehyde solutions were prepared in methanol. Hexane (J.T.Baker, Germany) was used as a solvent for extraction.

The method for determination of aldehydes using PFBOA as a derivatising agent was originally described by Yamada and Somiya (1989), Glaze et al. (1989a) and by Scilimenti et al. (1990). This analytical method is recommended by US Environmental Protection Agency for analysis of carbonyl compounds in water. We optimised this method and the detection limit in the ppt range was achieved in our research. The technique utilises a direct aqueous derivatisation with the reagent PFBOA, which reacts with the aldehydes to form the corresponding oximes. With most of the aldehydes, two geometric isomers are formed (E-PFBO and Z-PFBO), except for symmetrical carbonyls such as formaldehyde. The procedure of the aldehyde analysis is exactly the same for both: the standard solution and the water samples.

20 ml water samples were collected in glass vials with glass caps. 1-ml of 1 mg ml^{-1} aqueous PFBOA solution was added to the sample and kept at room temperature for one hour, then 4 drops of concentrated sulfuric acid (H_2SO_4) were added to complete the derivatization reaction. The oximes were extracted by shaking the solution with 1 ml of hexane for 1 minute. The extract was then purified with 3 ml of 0.1 N sulfuric acid solution. The hexane layer was separated and transferred to vials containing approximately 50 mg of sodium sulfate to dry the extracts. The extracts were analysed by gas chromatography using Fisons Instrument GC 8000 equipped with a ^{63}Ni electron capture detector. Injections of 0.5 μl of the extract were introduced via "on column" injector onto chromatographic column. The Rtx-5MS (Restek) fused silica capillary column (30m x 0.25mm x 0.25 μm film) was applied for analysis while the Rtx-1301 (Restek) fused silica capillary column (30m x 0.32mm x 0.5 μm film) was used as a confirmation column. Helium

and nitrogen were used as a carrier gas and a detector make-up gas respectively. The program of temperature for analysis was as follows: 80°C for 4 min, then increased to 240°C at 10°Cmin⁻¹, then raised to 270°C at 20°Cmin⁻¹, for 5 min. The CSW (Chromatography Station for Windows, Version 1,7 Eval, Build 270598, Czech Republic) system was used to collect and process the chromatographic data. Quantification was carried out by means of an external standard calibration curve. The 10-point calibration curve was made by plotting concentration versus peak area or, in the case of isomeric peaks, combined areas. Calibration curve was linear from the detection limit 0.1 µg l⁻¹ to at least 100 µg l⁻¹. Average relative standard deviation (RSD) was about 10% for each of the monitored aldehydes. The same method of derivatization and extraction process was used for all the waters, which were analysed as well as for the standard solutions.

2.4. Analysis of trihalomethanes

Analytical standards of THMs (i.e. chloroform, bromodichloromethane, chlorodibromomethane and bromoform) were purchased from Promochem (Warsaw, Poland) as Reference Materials for EPA Method 501. This ULTRASTANDARD mixture (Catalog Number THM-511, Lot Number M622Z) was gravimetrically prepared, 200 µg of each analyte in 1 ml of methanol. The THMs were measured using the liquid-liquid extraction, according to US EPA Method (1980). The extracts were separated and analysed by gas chromatography using Fisons Instrument GC 8000 equipped with a ⁶³Ni electron capture detector. The same system CSW described above, was used to collect and process the chromatographic data.

2.5. Total organic carbon measurement

Total organic carbon (TOC) was analysed by a LABTOC system (Pollution and Process Monitoring Ltd., England) total organic carbon analyser by the sodium peroxydisulfate/orthophosphoric acid wet oxidation/UV radiation method.

3. RESULTS AND DISCUSSION

3.1. Aldehydes in raw waters

Aldehydes are the compounds present everywhere in the environment. They are identified even in organic free water for laboratory use. We have previously found measurable amounts of aldehydes in various samples of purified waters and relatively high background level of carbonyl compounds in drinking water (Nawrocki *et al.*, 1996, Nawrocki *et al.*, 2002). We have determined the aldehydes in raw waters, before they were exposed to disinfection. The average total aldehyde concentration in examined raw waters are presented in Figure 1 and compared with value of total organic carbon (TOC) concentration.

In contrast to Schechter *et al.* (1995) we observed that there was no clear correlation between TOC and total aldehyde concentration in raw waters. The highest level of aldehyde concentration i.e. 13.4 µg l⁻¹ was determined in surface water with the highest concentration of TOC 6.4 mg l⁻¹, however the high level of aldehyde concentration was also determined in the shallow ground water (VIII), with the low concentration of TOC 2.7 mg l⁻¹. Among the aldehydes identified in raw waters were: formaldehyde, acetaldehyde, glyoxal and methylglyoxal. This is in agreement with other papers (Ivancev-Tumbas and Dalmacija 2001, Richardson 1998, Can 2003).

The average distribution of aldehydes in raw waters is shown in Figure 2. It is evident that formaldehyde and acetaldehyde are the most abundant aldehydes in all the examined raw waters. Formaldehyde together with acetaldehyde reached about eighty per cent in average distribution of carbonyl compounds in presented waters.

3.2. Ozonation process

The waters were subjected to ozonation process with the O₃ doses of 0.1; 0.2; 0.4; 0.8; 1.0 and 2.0 mg for 1 mg organic carbon defined as TOC. Generally it was observed a

correlation between dose of ozone and amount of aldehydes formed as disinfection by-products: aldehydes were formed in direct proportion to the ozone dose. This observation is consistent with the results of many authors (Weinberg et. al. 1993, Schechter and Singer 1995, Glaze et. al. 1989b).

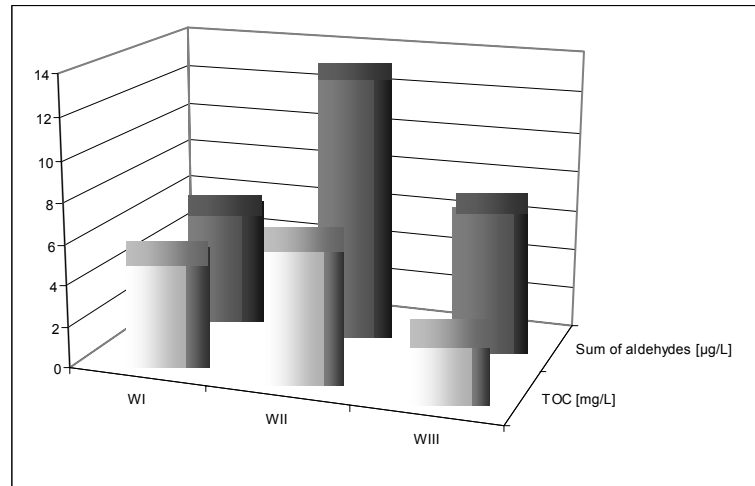


Figure 1. Total organic carbon (TOC) and concentration of aldehydes in raw waters: WI, WII, and WIII

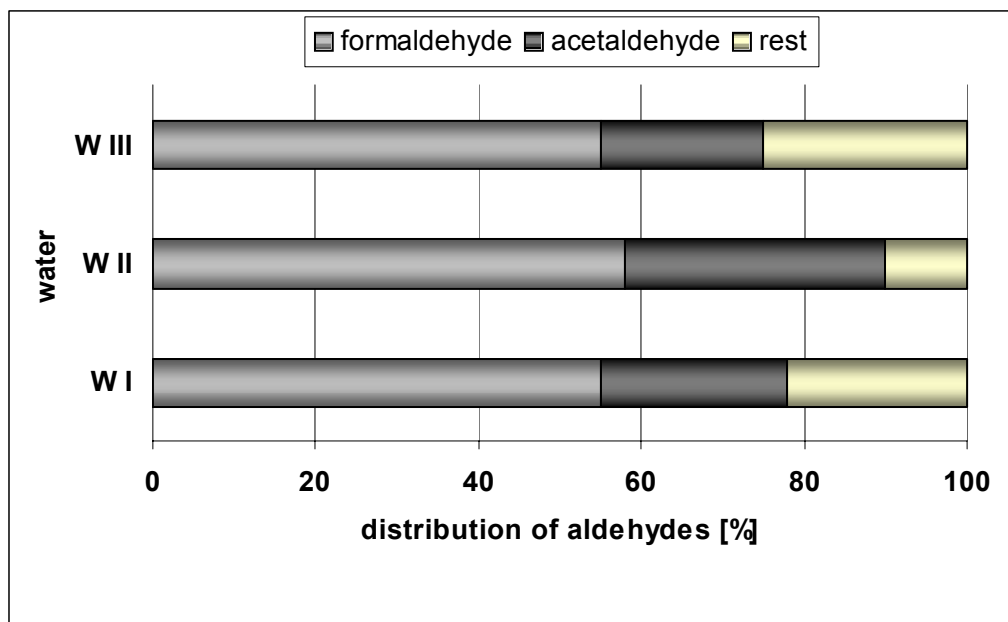


Figure 2. Average distribution of aldehydes in raw waters: WI, WII, and WIII.

The correlation between ozone dose and aldehydes produced in infiltrated ground water WI is shown in Figure 3. We observed an increase of aldehyde concentration in WI water for low doses of ozone from 0.1 to 0.8 mg mg⁻¹ TOC as well as for high doses of ozone i.e. for 1.0 and 2.0 mg mg⁻¹ TOC (Figure 4). However, the shallow ground water WIII did not show a similar increase of aldehyde production when the ozone dose was raised to 2.0 mg mg⁻¹ TOC. This suggests that competing reactions or destruction of aldehydes is occurring at the higher doses.

Additionally, it is significant to note that the three waters produced different amounts of aldehydes when were ozonated under similar conditions. This is consistent with many

researchers (Glaze *et al.*, 1989b; Weinberg *et al.*, 1993; Can and Gurol, 2003). In order to compare the results for different waters, the data were normalized by calculating the amount of aldehydes produced per mg TOC. The results of this calculation are shown in Table 1. The level of aldehyde concentration in water treated with disinfectant depends on the source of water, this means the productivity of aldehydes is connected with the characteristic of organic precursors in natural matter.

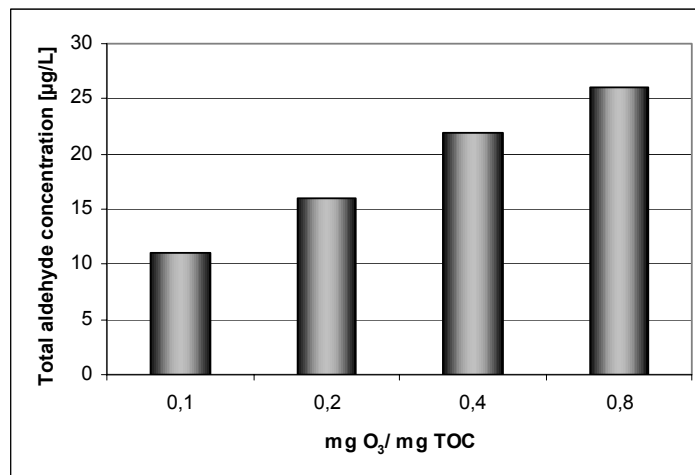


Figure 3. Correlation between total aldehydes and ozone dose in infiltrated ground water

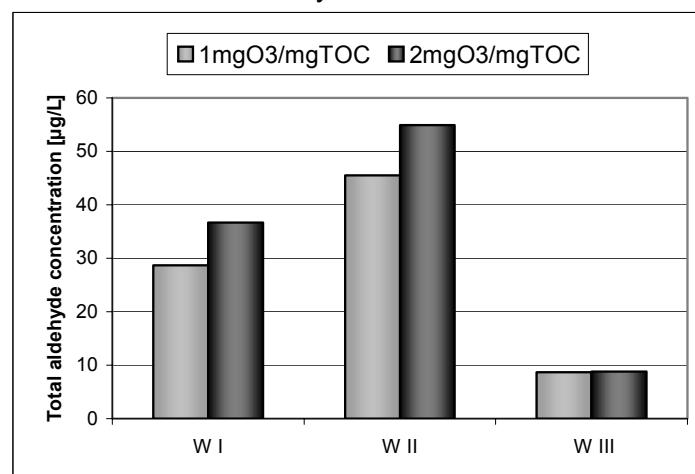


Figure 4. Correlation between total aldehyde concentration and high dose of ozone

Table 1. The amount of aldehydes produced per 1 mg TOC, ozone dose 1 mg l⁻¹

Parameter	Waters		
	W I	W II	W III
TOC [mg l ⁻¹]	5.0	6.4	2.7
Aldehydes [µg mg ⁻¹ TOC]	5.7	7.1	3.2

For all three waters, formaldehyde and acetaldehyde were dominant aldehydes produced during ozonation and accounted for about 80% of the total concentration of determined aldehydes. These results corroborate the findings of Weinberg *et al.* (1993) and Schechter and Singer (1995). It should be noted that formaldehyde and acetaldehyde are the main carbonyl compounds identified in water before as well as after the reaction with disinfectant.

3.3. Chlorination process

Because carboxylic acids and aldehydes are being considered as main by-products of ozonation process, there have been relatively few studies conducted to determine that chlorine and chlorine dioxide are disinfectants also responsible for the formation of biodegradable organic compounds. All the examined waters were treated with Cl_2 and ClO_2 with the dose of 0.2; 0.4; 0.8 and 1.2 mg for 1 mg TOC respectively. Then aldehydes were determined after 1 hour of reaction. Figure 5 presents the influence of chlorine dose on the aldehydes formation. The increase of aldehydes concentration can be observed for all samples but the three waters produced different amounts of aldehydes when were chlorinated under similar conditions. The high level of aldehydes (about $65.7 \mu\text{g l}^{-1}$) was determined in surface water WII already for Cl_2 dose of 0.4 mg mg^{-1} TOC. In case of infiltrated water WI and ground water WIII the highest concentration of aldehydes after chlorination was for Cl_2 dose of 1.2 mg mg^{-1} TOC and amounted $54.5 \mu\text{g l}^{-1}$ and $37.1 \mu\text{g l}^{-1}$ respectively.

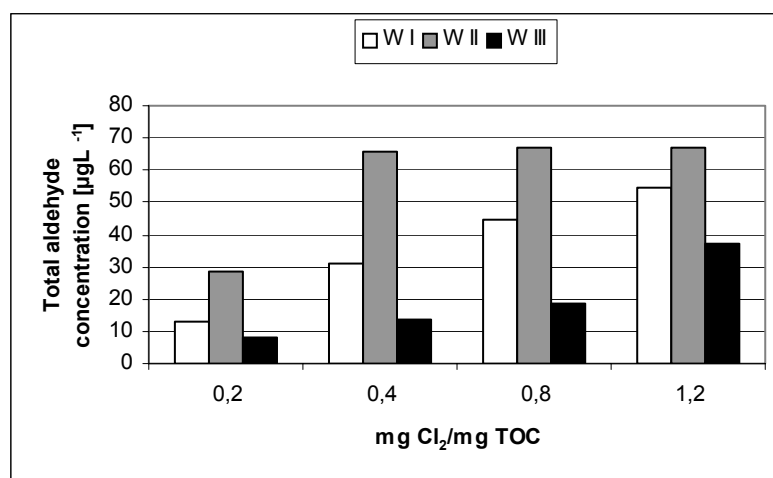


Figure 5. Correlation between total aldehyde concentration and dose of chlorine

The similar phenomenon was observed during disinfection process with chlorine dioxide: three sample of waters produced different amounts of aldehydes under similar condition. The results of this investigation are shown in Figure 6.

Taking into consideration the results of our experiments, there is evident that disinfection process with Cl_2 and ClO_2 contributes to the formation of biodegradable organic compounds, but it is difficult to determine one general principle about the relationships between disinfectant dose, TOC and the formation of organic by-products. However, we observed that the reaction time of Cl_2 and ClO_2 with natural organic matter plays an important role in disinfection process. Aldehyde concentration was controlled in the all examined waters after 4, 24 and 48 hours of reaction and the chlorine and chlorine dioxide residuals were measured at the same time. The results are shown in Figure 7. The effect of the reaction time on the total aldehyde concentration is presented as a percent increase of the total concentration of aldehydes in relation to the carbonyls formed after 1 hour of reaction.

After 48 hours of reaction with Cl_2 and ClO_2 about 100% increase of aldehydes concentration was observed when disinfectant doses of 1.2 mg mg^{-1} TOC were used. (About 50% increase of aldehydes was occurred only for sample WII, treated with Cl_2). The results show that the reaction of Cl_2 or ClO_2 with organic matter takes place as long as disinfectant is available in treated water. For low dose of disinfectants (i.e. 0.2 mg mg^{-1} TOC) the level of aldehyde concentration remained stable. Small dose of disinfectant can be used up quickly for a reaction with organic matter.

Consequently there is no disinfectant in treated water while some biodegradable organic compounds are present and this fact can lead to the formation of favourable conditions to bacterial regrowth in distribution system. When Cl_2 is used in disinfection process, together with biodegradable by-products formation occurs the formation of chlorination by-products, first of all trihalomethanes. Their presence can inhibit the bacteria development, even in the case of insufficient dose of chlorine.

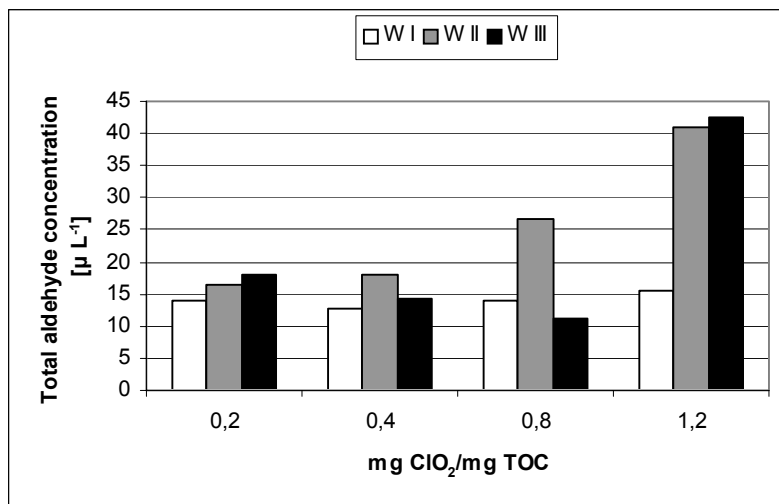


Figure 6. Correlation between total aldehyde concentration and dose of chlorine dioxide

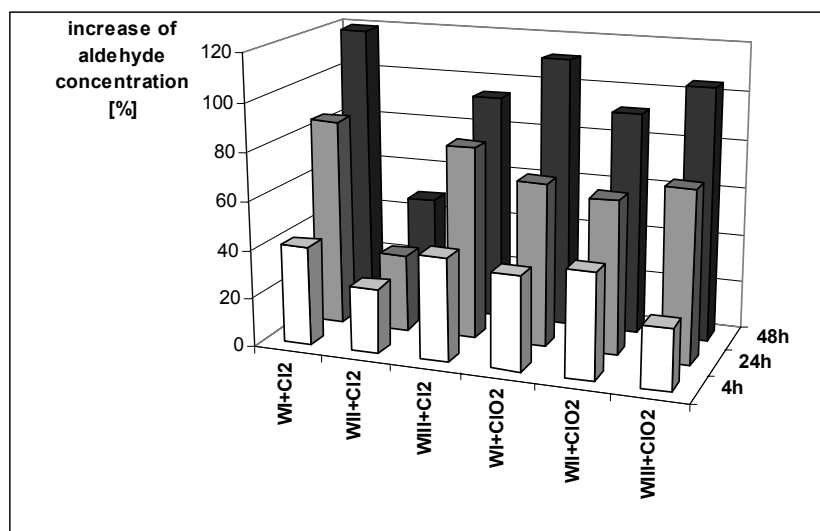


Figure 7. The increase of aldehydes concentration with the reaction time (relative to the total aldehyde formed after 1 hour of reaction), Cl_2 and ClO_2 doses: $1.2 \text{ mg mg}^{-1} \text{ TOC}$

Chlorine combined with chlorine dioxide are becoming widely used in disinfection process. We detected the aldehydes in water W I, which was treated with mixture of Cl_2 and ClO_2 . The following doses of chlorine in relation to chlorine dioxide were applied: 1.4:0; 1.0:0.4; 0.7:0.7; 0.4:1.0 and 0:1.4 mg l^{-1} . The results are presented in Figure 8a. The level of the generated aldehydes was stable, independently of the ratio of Cl_2 to ClO_2 . This confirmed that both oxidants were responsible for the production of aldehydes and their potentials of organic by-products formation were comparable. Moreover, it was

observed that the total sum of aldehydes was dependent on the total sum of both disinfectant concentrations.

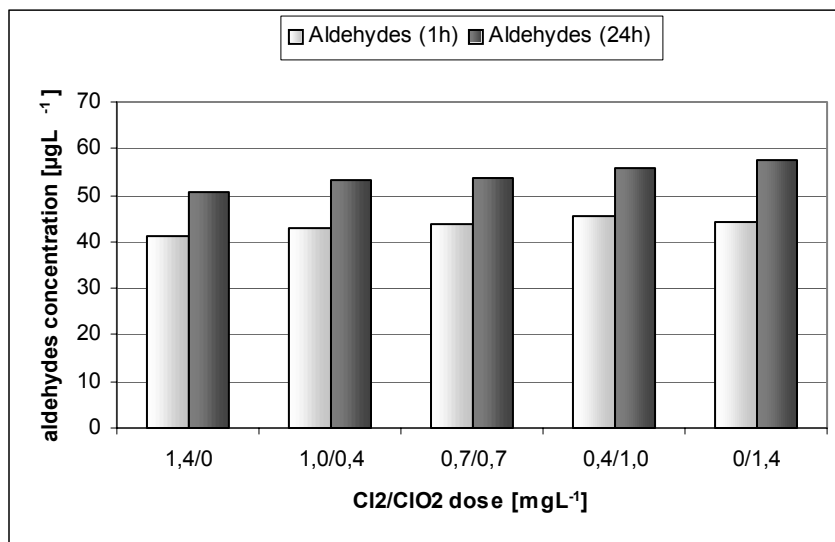


Figure 8a. Formation of aldehydes in infiltrated water during chlorination process with mixture of Cl₂/ClO₂

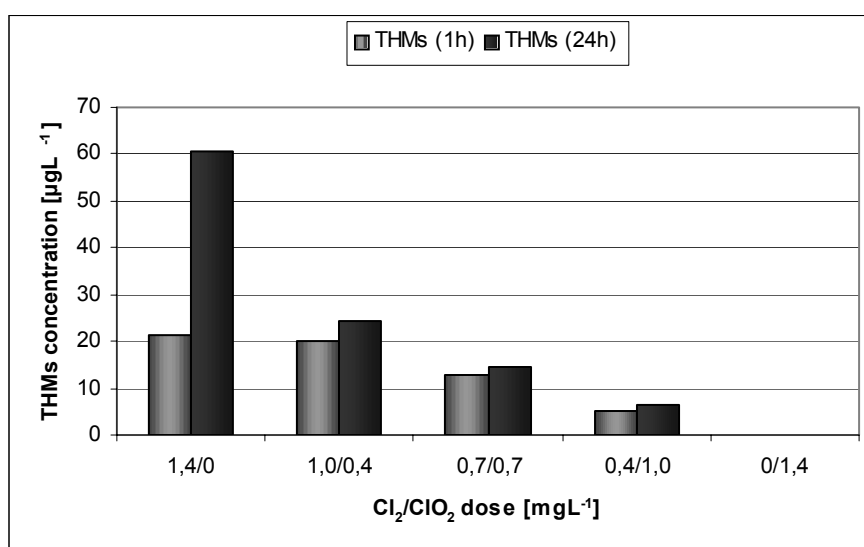


Figure 8b. Formation of trihalomethanes in infiltrated water during chlorination process with mixture of Cl₂/ClO₂

Additionally, in order to compare the lowly with the highly biodegradable by-products, THMs and aldehydes were monitored at the same time. In Figure 8b is shown the formation of trihalomethanes.

Decrease of THMs was significantly correlated with decrease of chlorine dose. The influence of the reaction time of disinfectants with organic matter on the by-products formation was evident: increase of aldehydes and THMs concentrations after 24 hours of reaction was revealed. As it was expected, the presence of ClO₂ did not affect the THMs formation. When chlorine combined with chlorine dioxide are used, apart from aldehyde formation, undesirable chlorinated by-products are formed. When ClO₂ without Cl₂ is used in final disinfection process, it provokes better conditions for bacteria regrowth in distribution system.

The productivities of aldehydes were calculated for all investigated waters treated with different doses of oxidant. The average ranges were 2 – 10 $\mu\text{g mg}^{-1}$ TOC. According to Weinberg *et al.* (1999) ozonation leads to aldehyde formation in the range 2-20 $\mu\text{g mg}^{-1}$ TOC depending on the parameters of ozonation process and nature of organic matter. We can observe that the range of aldehyde productivity is significant, when chlorine or chlorine dioxide is used and is comparable to that observed for ozonation. Moreover, these results have shown that the average ranges of productivity for both chlorine and chlorine dioxide were similar. It seems that productivity of organic by-products are correlated more with nature of organic matter than with TOC. It is then conceivable that the character of the background organic matter might be a more critical factor in determining the extent of aldehyde formation than the TOC level.

4. CONCLUSIONS

Significant production of aldehydes was found as a result of disinfection process by ozone, chlorine and chlorine dioxide.

For all three investigated waters, formaldehyde and acetaldehyde were the dominant carbonyl compounds identified in water before as well as after the reaction with disinfectants. They achieved about 80% of the total concentration of measured aldehydes.

All of the examined waters produced different amounts of aldehydes when were disinfected under similar conditions. This suggests, that potential of organic by-products formation does not depend directly on the disinfectant/TOC ratio, but is evidently connected with the nature of organic material comprising the TOC.

The formation of carbonyl compounds takes place as long as disinfectant is available in water.

The range of productivity of aldehydes in water treated with ClO_2 or Cl_2 is very similar.

The removal of natural organic matter as a precursor of the oxidation by-products is important, especially when ClO_2 disinfectant is used.

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