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Magdalena Domańska

KINETICS OF CHANGE IN THE CONCENTRATIONS OF CHLORINE AND CHLORINE DIOXIDE IN WATER DISTRIBUTION SYSTEMS

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A distribution system is a sensitive, dynamic,
living individual with its own peculiar characteristics,
not just a network of tubes joined together.

T.E. Larson

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INTRODUCTION

Awareness about the relationship between the incidence of infectious diseases and the quality of water and air dates back to ancient times. But scientific evidence to support this observation comes from the first half of the 19th century and was provided by Dr John Snow. While analysing the rate of incidence of cholera for each borough of London, he discovered and documented that the disease was spread in drinking water. Several decades later, in 1883, the comma-shaped bacterium *Vibrio cholerae* was detected by Robert Koch. In 1855, Theodor Escherich isolated the organism *Bacterium coli commune*, now named *Escherichia coli*, which is a basic indicator of fecal water contamination. In microbiological analysis it is conventional to use an indicator that helps assess the microbiological quality of drinking water. Defined by Robert Koch, the indicator of microbiological quality includes the so-called colony forming unit (CFU), a measure of viable bacterial numbers, which indicates the probable number of bacterial colonies formed and is determined by surface inoculation of 1 cm^3 of water in standard media. The strong evidence for the finding that contaminated water may be blamed for the spread of serious diseases has contributed largely to the widespread use of disinfection as a final step in tap water treatment prior to supply to the user [Roeske 2007].

Initially the efficiency of the disinfection method applied was analysed in terms of the number of microorganisms that had been killed before the water entered the distribution system. Currently, when making decision on the choice of the disinfection mode to be used, consideration is given to such problems as water stability in the pipeline and by-product formation linked with the use of strong oxidants for improving the biological composition of the water.

Water stability is defined as such a state that guarantees compliance of the physicochemical and biological parameters of the water with relevant sanitary requirements during supply to the user *via* a drinking water distribution system. Tap water is defined as stable when the following conditions are fulfilled: the water itself is non-corrosive, does not adversely affect the solubility of the materials with which it comes into contact, does not support processes of precipitation (especially that of calcium carbonate), has a composition that prevents heterotrophic microorganism growth responsible for the deterioration of microbiological quality, and does not promote reactions concomitant with a rise in pollutant concentrations.

Tap water stability is influenced by the type and quantity of primary pollutants that are present in the water taken in for drinking purposes. Groundwaters show a lesser degree of pollution than do surface waters, so their treatment consists primarily in removing excess iron, manganese, free carbon dioxide, hydrogen sulphide and ammonia nitrogen. Surface waters carry a wider spectrum of pollutants, which not only act by different mechanisms, but also follow different patterns of removal. As for these pollutants, careful consideration should primarily be given to live pathogenic microorganisms or their resting spores, microcistins, as well as phytoplankton and the products of its metabolism. Among the organic pollutants whose dissolved fractions are particularly difficult to remove are principally humus substances classified as main precursors of oxidation and disinfection by-products. Another group of troublesome organic pollutants includes pesticides, chlorinated organic compounds, polycyclic aromatic hydrocarbons, radioactive elements and heavy metals. The category of troublesome surface water pollutants also comprises inorganic nitrogen forms such as ammonia nitrogen, nitrite nitrogen and nitrate nitrogen; they predominantly enter the watercourse together with mineral fertilizers, industrial wastewater discharge, and rainfall or snowfall, but they may as well penetrate surface water directly from atmospheric air (free dissolved nitrogen) [Kowal, Świderska-Bróż 2007].

The group of secondary water pollutants encompasses products of oxidation and disinfection, excess concentrations of coagulant hydrolysis products, synthetic organic polymers, nitrite ions, aggressive carbon dioxide, and biodegradable fractions of organic pollutants. The quantity of disinfection by-products formed depends principally on the chemical structure and concentration of their precursors, the dose and type of oxidants used, as well as on the time of contact. The amount of secondary pollutants is also influenced by the pH and temperature of tap water.

Lack of chemical stability manifests in undesirable changes in the physicochemical composition of the water whereas the lack of biological stability is characterised by microbial regrowth in the water-pipe network, fittings and plumbings. A contributory factor in the loss of biological stability is the presence of substrates susceptible to autotrophic transformation or biodegradable substrates, which in microbiologically catalysed reactions act as electron donors and/or energy sources [Biłozor, Danielak 1997]. Quantitative analyses of biodegradable substrates in most instances reduce to the determination of assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC) [Świderska-Bróż 2003]. The growth of autotrophic bacteria in tap water is promoted by the presence of dissolved oxygen, ammonium ion, speciation forms of iron and manganese, and also hydrogen sulphide and hydrosulphate ion. Water recontamination in the pipes is attributable to insufficient disinfectant concentration.

Historically, the underlying causes of water quality degradation during delivery from the treatment plant to the customer were specified in the 1960ies by E.T. Larson, who analysed the contribution of corrosion, pipe deposits and flow rate to water deterioration under such conditions [Larson 1966]. His research has revealed that a water distribution system is the host to autotrophic iron-oxidising, nitrifying and sulphate-reducing bacteria, and also to heterotrophic bacteria that affect the biological stability of the water.

Another major factor affecting the biological stability of the water travelling through the distribution system is the presence of biofilms that form on the internal surfaces of the pipes and thus change the taste, smell and colour of the water. Biofilms are to blame for biological corrosion, which is conducive to the occurrence of severe technological and operating problems [Van der Kooij et al. 1999]. The heterotrophic bacteria colonising the biofilm, specifically those of the *Legionella, Mycobacterium* and *Pseudomonas* genera, have the potential to transmit diseases from drinking water to human organism.

Among the fundamental causes behind the loss of chemical and biological stability is the prolongation of water residence in the distribution system, and, in extreme cases, water stagnation, an event frequently observed in fittings and plumbings due to temporal decline in water demand. Such conditions support the development of biofilms as a result of disinfectant decay and a rise in AOC concentration, which in many instances is attributable to the growth of autotrophic bacteria [Dohnalik, Wytrwał 2005]. LeChevallier [1999] emphasised the need of maintaining "a disinfectant residual in the drinking water systems", an issue that had been of fundamental importance in Environmental Engineering for nearly a century. According to LeChevallier, there are obvious reasons behind the use of disinfection, such as protection by inhibiting microbial growth in the system, or destruction of the microorganisms that might penetrate the distribution system as a result of recontamination originating, for example, during repair work. The suitability of using a residual disinfectant has also been substantiated by Zhang et al. [2002], who have demonstrated that among the major factors responsible for the increase of bacterial numbers in tap water (*e.g.* water temperature, quantity of biodegradable organic carbon, corrosion products and deposits accumulating in water-pipe networks) is the concentration of the disinfectant. According to Zang et al. biological stability will be achieved when tap water temperature stays below 15ºC, assimilable organic carbon concentration does not exceed 100 $\mu g \cdot dm^{-3}$, chlorine concentration does not fall below 0.5 $mg \cdot dm^{-3}$, and chloramine concentration is not lower than 1 $mg \cdot dm^{-3}$. Besner et al. [2001], during their study at two water treatment plants in Montreal, observed that the number of coliform events increased at higher water temperature and decreased at a residual chlorine concentration exceeding 0.1 $mg \cdot dm^{-3}$. In real systems, however, it is impossible to provide such technological conditions as those proposed by Zangh et al. [2002], because of the difficulties that are inherent in the control of disinfectant concentrations in the water distribution system.

In tap water produced from surface water AOC concentrations are reduced by ozonation and filtration through active carbon beds, where organic compounds are removed by adsorption. The reduction in total organic carbon (TOC) obtained in this process ranges from 20 to 25%, whereas that in biodegradable dissolved organic carbon (BDOC) varies between 30 and 45%. However, the decrease in organic carbon concentrations is parallelled by a rise in the quantity of short-chain organic acids, which are precursors to the formation of disinfection by-products [Raczyk-Stanisławiak et al. 2007].

Tap water with an appropriate composition will be biologically stable in the absence of a disinfectant residual, if the materials from which the pipes have been made do not deteriorate this composition during contact [Van der Kooij et al. 1999]. In engineering such conditions are difficult to achieve, as reported by LeChevallier [1999], who investigated the contribution of the pipe material to bacterial growth on the pipe surface during service. The effect of pipe material used on the quality of the water being transported has been described in more detail in the theoretical part of this monograph (Section 2.4. Kinetics of chlorine (chlorine dioxide) decay in water distribution systems).

The rules and regulations of water disinfection that were in force in the EU member states in the nineteen-nineties have been described by Hydes [1999]. At that time, tap water disinfection was mandatory for waterworks in Spain, Portugal and Great Britain. Maintenance of disinfectant concentration in the entire water distribution system was compulsory in Spain and Portugal. In Germany, Austria, and also in Poland water had to be disinfected only if its microbiological composition failed to meet the sanitary standard desired. Hambsch [1999] observed that in Germany the user gave preference to water with no disinfectant additives. In the Netherlands, disinfectant residual maintenance in tap water is not a requisite of sanitary regulations. Nevertheless, much attention is attached to developing preventive strategies and taking actions that could reduce the risk of recontamination. Among them is the use of certified building materials for the construction of distribution networks and infrastructure, pressure maintenance at levels higher than 2 bars (which enables quick identification of leakage), and installing protective valves to prevent contamination [Van der Kooij et al. 1999].

For many years it was a common practice not to chlorinate groundwater. And Poland was no exception in this matter. Investigations have revealed, however, that over periods when the tap water was lacking in a disinfectant residual, enhanced growth was observed not only in the number of heterotrophic bacteria (due to the increase in the concentration of biodegradable organic carbon released from plastic pipes), but also in the number of autotrophic bacteria in biofilms. In addition, it has been found that in many instances tap water contamination should be attributed to poor workmanship on pipe damage repair, and also to negligence during disinfection of the infrastructure.

The AWWA Water Quality Division Disinfection Systems Committee Report [2000] pertaining to small water producing plants shows that in the United States 97% of surface water and 86% of groundwater was subject to residual disinfection. According to Shaw and Regli [1999], in the United States it is compulsory only for waterworks treating surface water to maintain a disinfectant residual in the distribution system. As reported by Haas [1999], attempts are made in the United States to maintain the concentrations of disinfectants in water-pipe network systems within the range of 0.05 to 0.1 $mg \cdot dm^{-3}$.

The presence of a disinfectant in tap water reduces the risk of microbial growth in the distribution system and water recontamination. Water distribution systems should be monitored not only for quantifying the disinfectant, but also for enabling temporary control of microorganism numbers in tap water. When a disinfectant is present in the water, this minimises the potential for microbial growth and prevents water contamination caused by microorganisms migrating from the biofilm. With the rise in chlorine concentration a decrease was observed in bacterial counts not only in the water but also in biofilms. This phenomenon was found to be limited only when AOC concentration took lower values than 0.6 $mg \cdot dm^{-3}$. It is essential to note that microorganism growth in the pipes is largely influenced by the length of service (pipe age) of the water distribution system, as well as by the material from which the pipes have been made. A major factor that stimulates bacterial growth in the biofilm is the phosphorus content in the water [Haas 1999].

Tryby et al. [1999] emphasise the benefits of maintaining the desired disinfectant level in tap water with additional chlorine portions added at selected points of the distribution system. They have defined this procedure as a post-disinfection of tap water. The same authors indicate that a requisite for maintaining the desired water quality in the system requires consideration of many different aspects, such as proper performance of the technical infrastructure, continuous education of the operating staff, or development of methods for water-pipe network control and monitoring.

The study reported by Sudoł [2007], which involved 132 water distribution systems accounting for 61.8% of the overall length of Poland's water-pipe networks, produced the following finding. 78% of the tap water samples analysed for composition displayed free chlorine concentration values higher than that of 0.3 $mg\ Cl_2 \cdot dm^{-3}$, which had been established as admissible in water for human consumption. This substantiates not only the significance of disinfectant control, but also the suitability of the guiding principle (adopted by large waterworks) that the maintenance of disinfectant concentrations exceeding those allowable for the distribution system is better than the loss of biological stability of the water supplied to the user. Also LeChevallier [1999], who attached great significance to the consumer's health, expressed the opinion that providing biological stability of tap water is more important than reducing the disinfectant content of the water below the level of microbial regrowth in the distribution system. The problem is that, depending on the composition of the water, its specific smell and taste may be perceived even at chlorine residual concentrations lower than 0.05 mg $Cl_2 \cdot dm^{-3}$ [Van der Kooij et al. 1999].

It is really difficult for large distribution systems to provide full protection of the water against loss of biological stability during flow from the waterworks to the consumer. What should be done is to reduce the risk that such loss will occur, since both quantitative and qualitative methods are available for assessing such a risk. Analysis of water quality variation is very difficult because of the changing technological, hydraulic, economic and environmental conditions [Zimoch 2009]. For poorly computerised waterworks where archives containing data on water-pipe networks are readily available, it is possible to assess the risk and effects of failure occurrence (and this includes loss of biological stability) based on statistical analysis of those data [Rak et al. 2009].

A rapid decay of the disinfectant and, consequently, an increased risk of microbial regrowth in the distribution system is frequently linked with a long time of water residence in the pipes. Water residence, also defined as "water age", extends as a result of low flow velocities, which occur mainly at the peripheries of the pipeline, but are also observed during re-dimensioning of pipe diameters.

With the aim of exemplifying the problem of tap water disinfection, as well as making use of literature data, preliminary tests were carried out within the scope of this study on chlorine concentration variations for two different water distribution systems in Poland, Strzelin (4 April 2007) and Bychowo (25 April 2007).

The Strzelin Water Distribution System possesses a modernised water treatment plant with a daily capacity of 7200 m^3. The water being treated there is drawn from the intakes located in Brzegowa Street, Ludów Polski and Górzec. The non-uniformity of water distribution is balanced by two tanks located at the highest point in the town, each with a capacity of 1000 m^3. The distribution system consists of steel, cast-iron and plastic pipes. The overall length of the water-pipe network, which is fed by WTP Strzelin, totals 77 km. Of these, a 29.7 km length of pipes has been laid within the area of the town. The remaining part of the network delivers water to the nearby villages. Water is disinfected in a continuous mode with sodium hypochlorite in amounts varying from 0.1 to 0.3 mg$Cl_2 \cdot dm^{-3}$, whereas post-chlorination is not performed continuously. Sodium hypochlorite is periodically added to raw water at the intakes in Ludów Polski, Górzec and Dankowice.

Tests on free chlorine content of tap water were carried out at 15 sampling points located within the city of Strzelin, as well as in villages receiving water from WTP Strzelin. No free chlorine was detected in tap water at any of the sampling points within the city area, but free chlorine was present in the water sampled at WTP Strzelin. Although the tap water in the Strzelin Water Distribution System was lacking in free chlorine, the microbiological quality of the water received by the customers did not deteriorate.

The other object tested for the presence of free chlorine was the Water Distribution System Bychowo. The Bychowo Water Distribution System includes the Water Treatment Plant (WTP) Bychowo with a water pumping station and eight intermediate pumping stations: Krościna Mała, Małuszyn, Strupina, Gródek, Brzeźno, Kosinowo, Rzepotowice and Marcinowo. The productivity of the aquifer amounts to 600 $m^3 \cdot h^{-1}$, and the overall length of the water distribution system exceeds 300 km. The waterworks feeds 74 villages and hamlets by supplying water disinfected with sodium hypochlorite in a continuous mode at WTP Bychowo, post-chlorination being carried out temporarily at some of the intermediate pumping stations. At the stage of design, the Bychowo Water Distribution System was intended for water supply to a larger number of users characterised by an increasing water demand, such as the large state-owned farms (PGRs) that were developing in those days. The system was also designed to feed the municipality of Trzebnica, as well as the village Prusice. As a result of conversion to market economy in Poland, the PGRs have been replaced with smaller farms (which have become the main water consumers), water demand in industry and services has fallen significantly, and the city of Trzebnica has developed its own water intakes. Redimensioning of the water-pipe network brought about some operating problems. Episodes of deteriorated microbiological quality and unpleasant putrid odour have become a recurrent feature of the water supplied to the users.

Water samples for the study were collected at 15 points along the Bychowo Water Distribution System. Chlorine residual concentrations, which ranged between 0.15 and 0.35 mg $Cl_2 \cdot dm^{-3}$, in the majority of the sampling points approached 0.15 mg $Cl_2 \cdot dm^{-3}$. The highest value was measured only at WTP Bychowo. During the study, the presence of free chlorine was detected at all of the sampling points, which, however, should be attributed to the post-chlorination procedures carried out temporarily at the local intermediate pumping stations.

These test results have substantiated the need of adopting a flexible approach when modelling the rate of chlorine decay in tap water. And this requires application of such hydraulic models that incorporate the kinetics of the processes responsible for the changes in disinfectant concentrations during water flow in the pipes. Nowadays, monitoring of water quality variations in the distribution system is performed using computer programs that not only simulate the hydraulic conditions in the pipeline during service, but also model the chemical and biological processes occurring in the tap water during transmission to the consumer. Amongst the most popular programs is EpaNet (developed by L. Rossman and co-workers at US Environmental Protection Agency), Mike Net, ISYDYW and PICCOLO [Zimoch 2008a]. With these packets it is possible to calculate the flows and pressures that occur in the water distribution system under defined operating conditions.

Elton et al. [1995] proposed a model of chlorine decay in a large distribution system in Great Britain, feeding water to 8 million inhabitants. When modelling the rate of chlorine decay in the system, they took into account the following factors: time of water residence in the pipeline, water composition, and the effect of internal pipe surfaces on the rate of chlorine decay in the water being transported. The model was tared using the chlorine concentration values measured in the water at selected points of the network.

Sudoł [2007] demonstrated that only 8.3% of Poland's waterworks possessed hydraulic models of their water-pipe networks, and that these models might have had the potential to support monitoring of tap water quality. The results obtained by Sudoł [2007] make it clear that water quality in distribution systems needs to be monitored in order to prevent biological stability loss. In waterworks the managerial staff fail to adopt a systematic approach to monitoring, although this is a key issue in controlling the functioning of a water distribution system [Zimoch, Trybulec 2005].

Zimoch [2008a] made use of the EpaNet program in her study on the water distribution system in the city of Wrocław. The investigations involved modelling of chloroform concentration variations [Zimoch 2009], as well as the contribution of changes in the rate and direction of flow to the occurrence of iron(II) and iron(III), manganese, redox potential and permanganate COD in the water [Kłos, Zimoch 2005]. Zimoch and Trybulec [2005] examined the fate of chloroform (a by-product of water disinfection with chlorine) in their study on the water distribution system in Katowice. Taking the distribution subsystems in Kraków and Wrocław as examples, Zimoch [2008, 2009a] tested an original monitoring program, *Jakość wody* (*Water quality*), designed for assessing the risk that the water in the distribution system might deteriorate. The use of this program makes it possible to determine the reliability parameters for the supply of water of the desired quality not only at an arbitrary monitoring point, but also in the entire system.

According to Zimoch [2006, 2007], there is a need of both carrying out and developing continuous water quality monitoring in order to enable rational management of the distribution process. Information derived from monitoring can be a guideline on formulating developmental strategies for the waterworks and reducing the operating cost of the water distribution system. This analysis substantiates the necessity of systematically correcting the monitoring system, with emphasis placed on the sampling points and the range of sample analysis.

Olsińska et al. [2007] made use of computer simulation to visualise the performance of the distribution system when choosing the location and operation mode for the post-chlorination plant. Their model of chlorine decay in the water distribution system was calibrated using the EpaNet software; chlorine decay constants were taken from relevant literature, at the assumption that their values are constant. Ozdemir and Ger [1998] claim that such approach is incorrect, because with the switch of hydraulic conditions from transient flow to laminar flow an increase is observed in the values of chlorine decay constants. Assumption of the same values for the constants of chlorine decay during water flow in the pipeline promotes errors; it is necessary take into account not only the hydraulic conditions involved, but also the quality of the water being transported. In spite of its incorrectness, the approach is preferably adopted, since it allows for simplifying the computations required.

In recent years, the use of chlorine dioxide in water disinfection has become increasingly frequent. World Health Organization (WHO) Guidelines on the permissible chlorine dioxide concentration in water for human consumption, as well as on the concentration values that may cause complaints from water consumers, do not specify a recommendable permitted concentration value for chlorine dioxide because of its rapid decay in the water distribution system [Roman 1999]. Instead, it is recommended that permissible levels of chlorite and chlorate ions should be determined based on the state-of-the-art knowledge about their potential effect on human organism. The literature contains many references to the rate constants of chlorine decay in tap water [Fisher et al. 2011, Świderska-Bróż, Wolska 2007, Lu et al. 1999, Hua et al. 1999], but no data are available on the rate constants of chlorine dioxide decay.

Engineering strategies should be aimed at developing methods that would reduce disinfectant concentration, improve the smell and taste of the water received by the user, and implement water treatment technologies inhibiting the formation of disinfection by-products, instead of removing the disinfectant from the water being transported in the distribution system. It is essential to note, however, that disinfectant residual concentrations should be maintained at a level guaranteeing biological stability of the tap water. These conditions can only be fulfilled if there is a disinfectant control and monitoring system based on the best available knowledge of the mechanism governing the process.

What provided a spur to this research, which attempts to find the relationship between the rate of chlorine decay and the rate of chlorine dioxide decay in tap water, is the strong preference recently observed in water treatment plants to use chlorine dioxide, although the kinetics of its decay is still insufficiently understood.

2. REVIEW OF LITERATURE

2.1. Methods of tap water disinfection: Historical background

The first device for water disinfection involving UV radiation was designed in England in 1877. In the United States the implementation of the process in water treatment plants dates back to the 1930ies but in Europe UV disinfection has found wide acceptance only since the 1970ies [Dera 1997]. First experiments on the application of ozone as a disinfectant were accomplished in 1886 in France, where use was made of an apparatus designed by Werner von Siemens, who patented his invention in 1857. Because of the high cost involved in ozonation, scientists and engineers directed their attention to a less costly disinfectant, which appeared to be chlorine. In gaseous state, chlorine is a toxic substance characterised by a yellowish green colour, a pungent odour, and a specific weight 2.5 times as high as that of air. Liquefaction of chlorine over the temperature range of 15 to 20ºC requires excess pressure of 5 to 6 bars [Roeske 2007]. When liquefied, chlorine displays a higher coefficient of expansion than does any other liquid. At 100ºC chlorine develops a corrosive action on iron and steel. The high toxicity of gaseous chlorine poses a grave danger to the environment. In a full-scale tap water disinfection process chlorine was first applied in Maidstone (England) in 1897, and soon its use as water disinfectant became common practice. Initially, chlorine was used in the form of chlorine water (obtained by mixing gaseous chlorine with water), which was applied using a chlorator. Contact between chlorine and water induces the following reaction [Evans 2004]:

$$\mathrm{H_2O + Cl_2 \leftrightarrow OCl^- + 2H^+ + Cl^- \leftrightarrow HOCl + HCl} \tag{1}$$

which yields a weak hypochlorous acid (HOCl) and a strong hydrochloric acid (HCl). The proportions of gaseous chlorine, hypochlorous acid and hydrochloric acid depend on the pH and ionic composition of the water being chlorinated.

It is common practice for small-sized water treatment plants to use sodium hypochlorite as a disinfectant, which during contact with water undergoes dissociation:

$$\mathrm{NaOCl \leftrightarrow OCl^- + Na^+} \tag{2}$$

combined with the release of bactericidal hypochlorite ion [Kowal, Świderska-Bróż 2007]. Commercial sodium hypochlorite has an active chlorine content of 145 $g \cdot dm^{-3}$. Storage of sodium hypochlorite may induce the formation of chlorite and chlorate ions as a result of the following reactions:

$$\mathrm{OCl^- + OCl^- \rightarrow ClO_2^- + Cl^-} \tag{3}$$

$$2OCl^- + OCl_2^- \rightarrow ClO_3^- + 3Cl^- \tag{4}$$

To limit the occurrence of reactions (3) and (4), it is advisable to shorten the duration of storage for the concentrated sodium hypochlorite solution, dilute the sodium hypochlorite solution to the concentration of about 6%, and also reduce the temperature of the solution to approximately 10ºC. Sodium hypochlorite should be stored in rooms with limited exposure to light, as this will extend the life of the disinfectant [Kowal, Świderska-Bróż 2007].

If treated water contains ammonia, disinfection with chlorine water or sodium hypochlorite contributes to the formation of mono- and dichloramine, as well as trichloronitrogen, *via* the following reactions:

$$NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+ \tag{5}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \tag{6}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \tag{7}$$

At neutral pH and a Cl_2 to N_{NH4} ratio lower than 4, formation of monochloramine dominates (Fig. 1). Upon chlorination, the proportion of mono- and dichloramines, as well as that of trichloronitrogen, depends primarily on the pH and on the ratio of chlorine dose to ammonia concentration. The rise in the Cl_2 to N_{NH_4} ratio is associated with the occurrence of a number of consecutive and parallel reactions, the most meaningful among them being ammonium ion oxidation to free nitrogen:

$$2NH_4^+ + 3HOCl \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \tag{8}$$

and to nitrates:

$$NH_4^+ + 4HOCl \rightarrow NO_3^- + H_2O + 6H^+ + 4Cl^- \tag{9}$$

The water chlorination curve (Fig. 2) displays a characteristic maximum and minimum of the function known as the breakthrough point. At the Cl_2 to N_{NH_4} ratio ranging between 5 and 8, as a result of reactions (8) and (9), chloramine concentrations in the water are in decline. With the rise in pH, once the level of 6.5 has been achieved, ammonium ion oxidation to nitrates tends to dominate, which is in accordance with reaction (9).

Characterised by a high stability during passage in water distribution systems, chloramines are frequently used in the USA, Mexico and Australia not only for disinfection, but also for maintaining biological stability in large water supply systems. To achieve the desired chloramine concentrations, the water is treated with appropriate chlorine doses, and in the absence of ammonium ion additionally with ammonia or ammonium salts, mostly ammonium chloride. Chloramines account for the specific taste and odour of the water, which are the most frequent causes of consumer complaint. Both taste and odour can be removed by filtration through activated carbon, where chloramines decompose, predominantly with the release of ammonium and chloride ions [Kowal 1990].

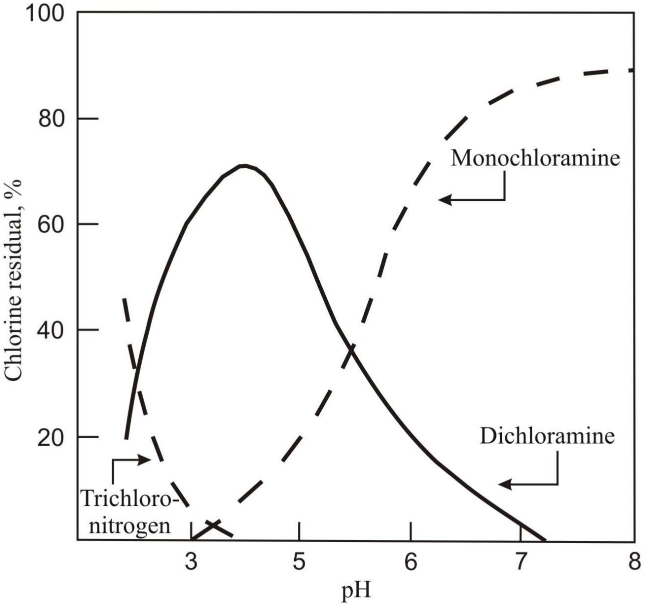

Fig. 1. Proportions of monochloramine, dichloramine and trichloronitrogen in free chlorine related to the pH of the water [Pauling 1950]

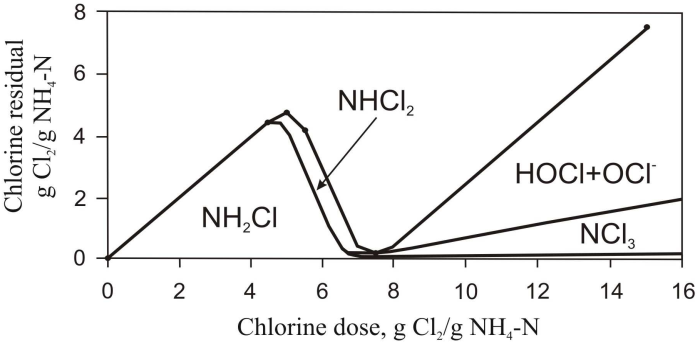

Fig. 2. Proportions of chloramines, hypochlorous acid and hypochlorite ion in ammonia-containing water after 2-hour contact at various Cl_2 to N_{NH_4} ratios [Pauling 1950]

In recent years, use has also been made of the sodium salt of dichloroisocyanuric acid for water disinfection. With the molecular formula $C_3Cl_2N_3O_3Na \cdot 2H_2O$, the disinfectant is a highly stable preparation (99.55% stability after 6-month storage). In Poland sodium salt of dichloroisocyanuric acid is marketed under the brand name of Jasol Solid (a French product), in the form of 3.2 g white pellets (with specific chlorine-like smell), containing 1.5 g of free chlorine. Jasol Solid has a conformity certificate, and its properties have been specified in the Polish standard PN-EN12931:2008 (*Chemikalia do uzdatniania wody przeznaczonej do spożycia. Bezwodny dichlorocyjanuran sodu*).

Although it belongs to the family of chlorocyanates, dichloroisocyanuric acid does not yield products of cyanide type (which is due to its ring structure); it decomposes at temperatures higher than 240°C [Wnęt, Granops 2010]. Sodium dichloroisocyanurate decomposes as a result of hydrolysis, according to:

$$NaCl_2(NCO)_3 + 2H_2O \rightarrow NaH_2(NCO)_3 + 2HClO \qquad (10)$$

Since sodium dichloroisocyanurate is predominantly applied for the disinfection of water intended for military uses, the results of investigations into the quality of the water disinfected *via* this route, or into the formation of by-products, have not been made available. These days, the number of small-sized water treatment plants that use sodium dichloroisocyanurate for continuous or immediate disinfection is growing steadily.

Chloride dioxide as a water disinfectant was first used in Belgium in the year 1900 [Roeske 2007]. However, its use in water treatment plants on a larger scale has been possible only since 1944, when the opportunity arose to transport sodium hypochlorite in liquid state (in solid state, this component for chloride dioxide production displays explosive properties). In 1953, at 150 water treatment plants in the United States use was made of chlorine dioxide for the disinfection of drinking water. The use of chlorine dioxide as a disinfectant in the second half of the 20th century solved the troublesome problem of disinfecting water that contained phenol compounds. In contrast to chlorine, chlorine dioxide is not a contributing factor in the formation of chlorophenols responsible for the unpleasant taste and odour, which meet the customer's disapproval [Walker et al. 1986]. More information on chlorophenols can be found in Section 2.3. By-products of drinking water disinfection.

Considering reaction (16), pure gaseous chlorine dioxide can be obtained by injecting nitrogen-saturated liquid chlorine into sodium chlorite in solid state [EPA… 1999]. However, this mode of chlorine dioxide production is rarely used in engineering. These days, the use of chlorine dioxide for water disinfection follows an upward trend, which is attributable to the noticeably lower quantity of DBPs that form with this disinfectant.

In water treatment plants chlorine dioxide is in most instances produced from sodium chlorite and hydrochloric acid according to the reaction:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \qquad (11)$$

which is also accompanied by the following reactions:

$$5ClO_2^- + 2H^+ \rightarrow 3ClO_3^- + Cl_2 + H_2O \qquad (12)$$

$$4ClO_2^- + 4H^+ \rightarrow 2Cl_2 + 3O_2 + 2H_2O \qquad (13)$$

Treated water is dosed with a solution containing chlorine dioxide, chlorine, hypochlorites formed during reaction of chlorine with water, chlorites and chlorates. Conversion of sodium chlorite to chlorine dioxide in reaction (11) generally approaches 80%, which is why the aqueous solution of chlorine dioxide injected into the water contains chlorite and chlorate ions [EPA… 1999].

Chlorine dioxide can also be obtained by dosing chlorine water with the sodium chlorite solution. Dosing the water being disinfected with gaseous chlorine produces a mixture of hydrochloric and hypochlorous acids (equation 1), which reacts with sodium chlorite as follows:

$$2NaClO_2 + HCl + HClO \rightarrow 2ClO_2 + 2NaCl + H_2O \tag{14}$$

This mode of chlorine dioxide production is characterised by 80–92% conversion of sodium chlorite. Reaction (14) is also accompanied by a secondary reaction which yields a chlorite ion:

$$ClO_2 + HClO + H_2O \rightarrow 2ClO_2^- + 2H^+ + HCl \tag{15}$$

To reduce the amounts of chlorite and chlorate ions in the solution injected into the water, a technology has recently been designed and implemented, which involves dosing the sodium chlorite solution with gaseous chlorine, and thus induces the following reaction:

$$Cl_2 + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl \tag{16}$$

In this case conversion ranges between 95 and 99%. In most instances chlorine is injected in excess of 2% in relation to the stoichiometric amounts of sodium chlorite.

Another method of chlorine dioxide production includes the reaction of sodium chlorate with H_2O_2 in the environment of sulphuric(VI) acid:

$$2NaClO_3 + H_2O_2 + H_2SO_4 \rightarrow 2ClO_2 + O_2 + Na_2SO_4 + 2H_2O \tag{17}$$

Reaction (17) is accompanied by a number of secondary reactions:

$$ClO_3^- + 2Cl^- + 2H^+ \rightarrow ClO_2^- + Cl_2 + H_2O \tag{18}$$

$$ClO_3^- + ClO_2^- + 2H^+ \rightarrow 2ClO_2 + H_2O \tag{19}$$

$$ClO_2^- + Cl^- \rightarrow 2ClO^- \tag{20}$$

$$ClO_2^- + Cl^- + 4H^+ \rightarrow Cl_2 + 2H_2O \tag{21}$$

$$ClO_3^- + 5Cl^- + 6H^+ \rightarrow 3Cl_2 + 3H_2O \tag{22}$$

Conversion, as well as chlorite and chlorate formation in the side reactions vary from 0.8 to 1.5% of the amount of ClO_2 produced [Burke et al. 1995]. The quantity of chlorites and chlorates formed during chlorine dioxide production *via* the reaction of sodium chlorite with H_2O_2 is strongly influenced by the presence of sodium chloride in the water [Crump et al. 1998]. The kinetics of the reaction of sodium chlorate with sodium chloride in the presence of the sulphuric acid solution was described by Deshwal and Lee [2004].

Chlorine dioxide can also be produced using the electrochemical reactions that occur on the anode in the presence of chlorides and chlorites [Bergmann, Koparal 2005, quoted after Pillai et al. 2009]. Electrochemical processes are used for the production of a mixture of strong oxidants from domestic salt by the patented commercial MIOX method [Nawrocki, Biłozor 2000]. Chlorine dioxide is produced using reaction (14) and 25% sodium chlorite [EPA… 1999].

2.2. Bactericidal properties of disinfectants

Microbiological quality of tap water is controlled using strong oxidants. Their choice depends primarily on the number of microorganisms undergoing deactivation during water disinfection, and also on the time over which they become deactivated. Until recently, when modelling the reduction in microbial number produced by the disinfectant, preference was given to the Chich-Watson equation [Cho et al. 2003]:

$$\ln\frac{N(t)}{N(0)} = -k_d C(0)^n t \tag{23}$$

where:

$N(0)$ – initial number of organisms, CFU·dm^{-3};
$N(t)$ – number of organisms at time t [h], CFU·dm^{-3};
$C(0)$ – initial concentration of disinfectant, mg·dm^{-3};
k_d – rate constant of microorganism decay, dm^3·(mg·h)$^{-1}$;
n – empirical constant.

From equation (23) it follows that the rate of reduction in the number of microorganisms is proportional to the concentration and the time of contact of the disinfectant with water. The empirical constant n takes values ranging between 0.7 and 1.2. The disinfecting properties of a reagent are most frequently assessed in terms of the CT factor, which is the product of the concentration of the disinfectant residual and the time of contact of this residual with water.

Chloramines, as well as trichloronitrogen, display poor disinfecting properties. Tables 1 and 2 show example CT values for different removal of *Giardia* cysts and viruses at water pH of 6 to 9. Table 3 relates the extent of virus inactivation obtained with chloramine to water temperature. According to Van der Kooij et al. [1999], water disinfection with chlorine can effectively destroy gram-negative bacteria and viruses at CT factor values of 10–25 g min·m^{-3}. The same values, however, fail to suffice for the destruction of protozoa cysts (Tab. 1).

Table 1

Values of CT factor (g·min·m^{-3}) for deactivation of *Giardia* cysts with various disinfectants at 10^{o}C and pH of 6 to 9 [EPA… 1999]

Disinfecting agent	Percent of *Giardia* cyst inactivation		
	99.0	99.9	99.99
Chlorine	3	4	6
Chloramines	643	1067	1491
Chlorine dioxide	4.2	12.8	25.1

Table 2

Values of CT factor (g·min·m^{-3}) for deactivation of viruses with various disinfectants at 10^{o}C and pH of 6 to 9 [EPA… 1999]

Disinfecting agent	Percent of virus inactivation				
	68.0	90.0	96.8	99.0	99.9
Chlorine	17	35	52	69	104
Chloramines	310	615	930	1230	1850
Chlorine dioxide	4	7.7	12	15	23

Table 3

Values of CT factor ($g \cdot min \cdot m^{-3}$) during water chloramination required for achieving a defined level of virus deactivation (AWWA and ASCE (American Society of Civil Engineers). (*Water Treatment Plant Design*, third edition. McGraw-Hill, Inc. New York, NY 1999)

Percent of virus inactivation	Temperature, ºC				
	5	10	15	20	25
99.00	857	643	428	321	214
99.90	1423	1067	712	534	356
99.99	1988	1491	994	746	497

Barbeau et al. [2005] and Cho et al. [2003] observed that the Chich-Watson equation (23) was not valid when the concentration of the disinfectant changed in contact with water. They proposed the following equation for describing the decay of microorganisms under the influence of various disinfecting agents (chlorine, chlorine dioxide, chloramines, ozone and hydroxyl radical):

$$\ln\frac{N(t)}{N(0)} = \begin{cases} 0 & t \le T_{lag} \\ -k_d\,\bar{C}(t - T_{lag}) & t \ge T_{lag} \end{cases} \tag{24}$$

where:

$$\bar{C} = \frac{1}{t}\int_0^t C(t)dt \tag{25}$$

and T_{lag} is the minimal time of contact between the microorganisms and the disinfectant to initiate the process of microbial decay. With times shorter than T_{lag} disinfection does not occur.

An important factor in maintaining biological stability of the water in the distribution system is the ability of the disinfectant to penetrate the interior of the biofilms growing on the internal surfaces of water-pipe networks. Biofilms are built from extracellular polymers produced by the bacteria that colonise the surfaces of the pipes. They contribute largely to pipe wall roughness, as well as to the corrosion of steel pipe systems, thus accounting for the increment in hydraulic loss over the time of pipeline service and, consequently, for the rise in pumping costs. What raises particular concern about the safety of water distribution is the risk that autotrophic sulphur bacteria may grow in the biofilm. Biofilms accumulating in fittings and plumbings may support the growth of such pathogens as *Legionella pneumoniae* (causing pneumonia, legionnaire's disease and Pontiac fever) or *Pseudomonas aeruginosa* (transmitting infections concomitant with severe inflammation, pneumonia, meningitis, as well as other acute diseases). The extent of penetration into the biofilm interior depends on the substance used for water disinfection, on the molecular diffusion of the disinfectant, on the density and chemical composition of the biofilm, on the rate of oxidation processes occurring in the biofilm, and also on the hydraulic regime at the pipe wall. The mechanism behind the penetration of the biofilm by strong oxidants has not been fully elucidated as yet. But information is available on the protective action of endogenous polymeric metabolites, EPS (Extracellular Polymeric Substances); they are produced by the microbial cells colonising the biofilm and proctect them against destruction. EPS readily react with the disinfectants and in this way weaken their disinfecting activity. Free chlorine, which displays a higher chemical reactivity, undergoes decay on the biofilm surface, and therefore limits biofilm growth and microbial proliferation to a smaller extent. It is assumed that the ability of the disinfectants to penetrate the biofilm is described by the following sequence:

$$ClO_2 > \text{chloramines} >> HOCl \tag{26}$$

During their study on the chlorine demand of biofilms growing on the internal walls of water pipes, Lu et al. [1999] made the following observation. At a constant biofilm thickness, chlorine demand increased linearly with the content of biodegradable dissolved organic carbon (BDOC) and with the surface-to-volume ratio of the biofilm. This was an indication that the chlorine demand of the biofilm increased with the decrease in the pipe diameter. Their study also revealed that chlorine demand during contact with the biofilm was correlated with the concentration of proteins and the number of heterotrophic bacteria in the biofilm. The pH of the water was without any significant effect on the rate of chlorine decay during contact with the biofilm.

Jang et al. [2006], who presented a method where use was made of microelectrodes for measuring the penetration and change of chlorine dioxide in pipe biofilms, demonstrated that ClO_2 penetrated the biofilm to the depth of 100 μm. The disinfecting efficacy of chlorine dioxide and chlorite ion (ClO_2^-) in the control of biofilm growth on pipe walls received the attention of Gagnon et al. [2005]. They found that the presence of chlorine dioxide was a contributing factor in the control of biofilm development in water distribution systems. They also observed that chlorite concentrations higher than 0.1 $mg \cdot dm^{-3}$ had an inhibiting effect on the growth of heterotrophic and nitrifying bacteria in the biofilm.

The focus of the studies reported by Ollos et al. [2003] was on the problem of how various factors affect biofilm accumulation in model distribution systems. Their experiments involved not only natural water, but also model systems with controlled chemical composition. Analyses were aimed at establishing the contribution of chlorine and chloramine content, pipe material, water temperature and flow velocity to biofilm formation; the measure of biofilm development being the number of bacteria identified in 1 cm^2 of surface area. Their research produced the following findings. Water temperature did not significantly affect biofilm growth, in contrast to the biodegradable organic matter (BOM) content of the water. When disinfectants were lacking, biofilms grew on plastic pipe samples at a rapid rate. The most efficacious factor in limiting the number of bacteria in the biofilm was the concentration of the disinfectant in the water. The increase in free chlorine concentration from 0 to 0.5 $mg \cdot dm^{-3}$ accounted for a fourfold decline in the number of bacteria colonising the biofilm. The same result was achieved with chloramine concentration maintained at the level of 2 $mg \cdot dm^{-3}$.

Zhang [2007] tested the efficacy of chlorine dioxide in controlling the growth of bacteria of the genus *Legionella* under conditions of a hospital water system. The findings of the study can be itemised as follows. ClO_2 is a good alternative to other disinfectants for the control of *Legionella* growth in internal water systems, provided that the pipes are not corroded, and that ClO_2 is supplied at the peripheries of the installation (the iron compounds washed away from the corrosion deposits affect the rate of ClO_2 decay in water). Combined ClO_2 and Cl_2 did not significantly limit biofilm development. The use of ClO_2 for water disinfection eliminated transmission of *Legionella*-related diseases to patients at that hospital. When ClO_2 was injected to cold water in the amount of 0.5 to 0.7 mg·dm^{-3}, average concentration of chlorites in cold and hot water samples did not exceed 0.8 and 1.0 mg·dm^{-3}, respectively. The distance from the disinfectant dosing point did not significantly affect the concentration of chlorine dioxide or chlorites.

The research reported by Dupuy et al. [2011] has demonstrated that the inactivation of *Legionella pneumophilia* depends on whether the bacterium lives independently or in symbiosis with *Acanthamoeba*. Chlorine and chlorine dioxide were found to be less efficacious when *Legionella* lived in symbiosis with an amoeba; the efficacy of monochloramine remained unchanged. This finding suggests that monochloramine may have a different mode of action on the microorganisms examined.

2.3. By-products of drinking water disinfection

Chlorination is associated with the formation of chlororganic compounds, which are responsible for the specific taste and odour of tap water. But they are also known to be carcinogenic and mutagenic. There is a general belief that the presence of pathogenic microorganisms in drinking water poses greater health hazards than does the increased amount of disinfection by-products [Craun 1993, Downs et al. 1999, quoted after Ashbolt 2004].

The problem of drinking water disinfection by-products came up in the 1970ies, owing to the advances in chromatographic methods, which enabled the determination of trace organic substances. Before that date, consideration was given solely to the formation of chlorophenols blamed for the unpleasant taste and odour of the tap water after chlorine disinfection. These days efforts are made to reduce the quantity of disinfection by-products to the lowest possible level. The problem, however, consists in controlling a very large number of different compounds that occur in disinfected water. In Israel, during eight-year research aimed at determining the drinking water disinfection by-products from the injection of chlorine, ozone, chlorine dioxide and chloramines, Richardson et al. [2000] were able to identify more than 200 compounds that had formed as a result of treating the water with powerful oxidants.

When the water being disinfected shows an increased bromide content, this induces additionally the formation of brominated disinfection by-products, which display a higher toxicity, carcinogenicity and genotoxicity than do chlorinated disinfection by-products [Richardson et al. 2007]. It is also essential to emphasise the importance of the sequence in which disinfectants should be injected. Narkis et al. [1995] demonstrated that when chlorine injection followed that of chlorine dioxide, the extent of reduction in the concentration of the undesired chlorite ion improved. They also observed that with the same sequence of disinfectant injection a higher efficiency of *Escherichia coli* destruction was achieved.

Figure 3 depicts the carcinogenicity of chlororganic compounds that form during water disinfection with chlorine. Relevant data were established based on epidemiological models [Bull 2003, quoted after Ashbolt].

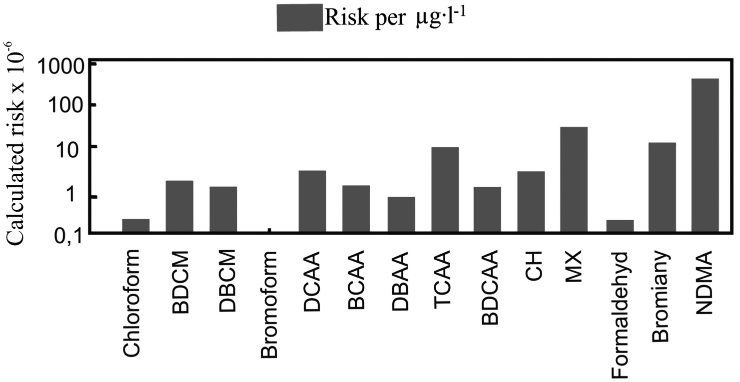

Fig. 3. Carcinogenic properties of chlorine disinfection by-products [Bull 2003, quoted after Ashbolt 2004] (DCA – dichloroacetic acid; BCA – bromochloroacetic acid; DBA – dibromoacetic acid; TCA – trichloroacetic acid; BDCA – bromodichloroacetic acid; Chloral – chloral hydrate; MX – 3-chloro-4-(dichloromethylo)-5-hydroxy-2(5h)-furanone; NDMA – nitrosodimethyloamine)

Table 4 includes the admissible concentrations of DBPs that are effective in different countries, whereas Table 5 presents major groups of DBPs that are formed during water disinfection with chlorine, chloramines and chlorine dioxide.

Chlororganic DBPs can induce neoplastic growth and genetic defects in newborns [King et al. 2000, quoted after Ashbolt 2004]. To assess the risk that chemical and microbiological factors will afflict human health, use can be made of the statistical models (given below), which describe the development of infections or toxaemia, but the mechanisms behind the symptoms differ considerably. When determining the risk of incidence induced by chemical factors, we can use the exponential model of the probability of infection [Teunis et al. 1996, Perz et al. 1998, quoted after Ashbolt 2004]:

$$P(D) = 1 - \exp(-rD) \tag{27}$$

or the model of probability of toxaemia:

$$P(D) = 1 - \left(1 + \left(\frac{D}{\beta}\right)\right)^{-\alpha} \tag{28}$$

where:

$P(D)$ – probability of occurrence of pathogenic symptoms;

D – dose of biological factor (equation 27) or dose of chemical factor (equation 28) inducing the pathogenic effect, $mg \cdot kg^{-1}$ of body;

r, α, β – experimental constants.

Table 4

Admissible DBPs concentration values decreed by WHO. US EPA and some governmental organisations [Sadiq, Rodriguez 2004; Richardson et al. 2007, Decree of Poland’s Health Minister of 29 March 2007 on the quality of water intended for human consumption. Dz.U. 2007 No. 61 item 417]

Component	Symbol	WHO (1993)	US EPA (2001a)	Canada (2001)	Australia – New Zealand (2000)	Great Britain (2000)	Poland (2007)
		mg·dm^{-3}					
Trichloromethane (chloroform)	TCM	0.200					0.03
Bromodichloromethane	BDCM	0.060	0.060				0.015
Dibromochloromethane	DBCM	0.100					
Tribromomethane (bromoform)	TBM	0.100					
Σ Trihalomethanes	TTHM		0.080	0.100	0.250	0.100	0.100[1]
Chloroacetic acid					0.150		
Dichloroacetic acid	DCAA	0.050			0.100		
Trichloroacetic acid	TCAA	0.100			0.100		
Haloacetic acid	HAA		0.060				
Dichloroacetonitriles	DCAN	0.090					
Trichloroacetonitriles	TCAN	0.001					
Dibromoacetonitriles	DBAN	0.100					
Chloral hydrate	CH	0.010			0.020		
Formaldehyde		0.900			0.500		0.050
Chlorites		0.200	1				0.700[2]
Chlorocyanate		0.070					
Bromates			0.010	0.010			0.010[1]
2-chlorophenol					0.300		
2,4-dichlorophenol					0.200		
2,4,6-trichlorophenol					0.020		0.200

Notation: [1] Generally without a negative effect on disinfection; attempts should be made to obtain a lower value; [2] sum of chlorite and chlorate ions.

Table 5

Major groups of disinfection by-products formed during application of different oxidants in the course of water treatment (plus sign (+) indicates formation of the compound) [based on Sadiq, Rodriguez 2004, Ashbolt 2004]

Group of disinfection by-products (DBPs)	Characteristic compound of the group	Chlorine	Chloramines	Chlorine dioxide
Trihalomethanes (THM)	Chloroform	+		
Other haloalkanes		+	+	
Haloalkenes		+		
Haloacetic acids (HAA)	Chloroacetic acid	+	+	
Haloaromatic acids		+		
Other halomonocarboxylic acids		+	+	
Unsaturated halocarboxylic acids		+	+	
Halodicarboxylic acids		+	+	
Halotricarboxylic acids		+		
MX and analogues		+	+	+
Other halofuranones		+		
Haloketones		+		+
Haloacetonitrile (HAN)	Chloroacetonitrile	+		
Other halonitrile	Cyanogen chloride	+		
Haloaldehyde	Chloral hydrate	+	+	
Haloalcohols		+	+	
Phenols	2-Chlorophenol	+	+	
Halonitromethane	Chloropicrin	+		
Inorganic compounds	Bromate, Hypobromite, Chlorite and Chlorate			+
Organic compounds				
Aliphatic aldehyde	Formaldehyde	+		+
Other aldehydes		+		+
Ketones (aliphatic and aromatic)	Acetone	+		+
Carboxylic acids	Acetic acid	+		+
Aromatic acids	Benzoic acid	+		+
Aldo and Ketoacids				+
Hydroxy acids		+		
Others		+	+	+

Formation of trihalomethanes (THM) during disinfection with chlorine water or sodium hypochlorite is associated with the reaction between the hypochlorite ion (OCl^-) and humic acids. When the water being chlorinated contains bromides, they are oxidised to the hypobromite ion (BrO^-) under the influence of OCl^- to form bromated THM with humic acids. The formation of THM is influenced by chlorine dose, time of water contact with chlorine, water pH and temperature, and also by the content of organic matter consisting predominantly of humus substances defined as THM precursors.

The discovery that water disinfection with chlorine induces chloroform formation gave a spur to extensive investigations into methods of predicting the concentrations of chlorination by-products. In a review paper about disinfection by-products found in drinking water, Sadiq and Rodriguez [2004] presented predictive models for their occurrence and concentrations, depending on the composition and the time of contact of the water with strong oxidants. The models are very useful when applied in water treatment plants with the aim to minimise the quantity of DBPs by controlling the composition of treated water and optimising disinfectant doses, with consideration of the time of water residence in the distribution system and exposure to free chlorine, chloramines or chlorine dioxide. These models contain some elements of empirical linear and nonlinear regression models, and in more recent times also of artificial neural networks (ANNs) and fuzzy models. Kulkarni and Chellam [2010] used artificial neural networks to predict the concentrations of such DBPs as the sum of THM, haloacetic acids (HAAs) and total organic halogenated compounds (TOX). The input data included concentration of dissolved organic carbon (DOC), measured value of UV_{254}, bromide concentrations (Br^-), chlorine dose, pH during chlorination, contact time and reaction temperature. The experiments involved four types of water samples: raw, after conventional treatment, after conventional treatment and filtration on activated carbon, after conventional treatment and nanofiltration. The results demonstrated that the analyses performed did not require many input data to provide reliable assessment of the quantity of DBPs formed either in untreated water samples or in those subjected to advanced treatment. Since the method is adaptable to changes in the treatment train, it can be used with success for the optimisation and control of the water treatment process. A direct advantage offered by this method is the reduction in the number of chemical analyses that have to be done, and consequently in the costs involved.

The presence of THM precursors in the water can be assessed in terms of total organic carbon (TOC), or electromagnetic wave absorbance at 254 nm length (UV_{254}). TOC indicates the mass of the organic substance whereas UV_{254} characterises the structure and functional groups of the organic compounds present in the water [Edzwald et al. 1985, Crocé et al. 1998, US EPA 2001b, quoted after Sadiq, Rodriguez 2004]. In assessing the potential of THM formation, the UV_{254} to TOC ratio indicates the reactivity of organic compounds with chlorine. Singer and Chang [1989] [quoted after Sadiq, Rodriguez 2004] revealed a linear relationship between UV_{254}, TOC, TOX and THM.

According to Clark [1998], the increment in the concentration of total trihalomethanes (TTHM) present in the water can be modelled using a linear function incorporating the total chlorine demand of the water:

$$[\mathrm{TTHM}](t) = \alpha Z_{\mathrm{Cl_2}}(t) + M \tag{29}$$

where:

$[\mathrm{TTHM}](t)$ – concentration of TTHM after time t [h], $mg \cdot dm^{-3}$;
$Z_{\mathrm{Cl_2}}(t)$ – total chlorine demand after time t [h], $mg\ Cl_2 \cdot dm^{-3}$;
M – initial concentration of TTHM, $mg \cdot dm^{-3}$;
α – coefficient determined experimentally.

When chlorine or chloramine is used as a disinfectant, TTHM concentrations in tap water are preferably determined with the following general model [Haestad Methods 2003–2004]:

$$[\mathrm{TTHM}](t) = M + \left(P_{\mathrm{TTHM}} - M\right)\left[1 - \exp(-k^{*}_{\mathrm{TTHM}}\, t)\right] \tag{30}$$

where:

P_{TTHM} – experimentally determined potential of TTHM formation in tap water, $\mathrm{mg \cdot dm^{-3}}$;

k^{*}_{TTHM} – experimentally determined rate constant of TTHM formation in tap water, $\mathrm{h^{-1}}$.

Boccelli et al. [2003], who investigated five water distribution systems for chlorine decay and THM formation under conditions of re-chlorination, demonstrated that the model of the kinetics of second-order reactions much better described the rate of TTHM formation when re-chlorination was applied. They found that the linear model was efficient when chlorination was applied only once. Another finding reported in their study was that under re-chlorination conditions two separate models should be used (Fig. 4) to depict the changes in TTHM concentrations, because the number of TTHM precursors at the stage of re-chlorination decreased as compared with their number observed at the stage of the first chlorination procedure.

Chloramination of drinking water reduces concentrations of chlorinated DBPs more efficiently than does disinfection with chlorine water or sodium hypochlorite. But chloramination fails to curb the increase in the TOX content of the tap water received by the user as compared with raw water subjected to treatment processes.

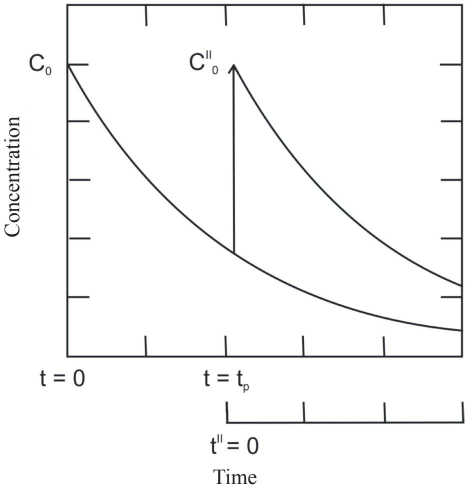

Fig. 4. Graphical interpretation of the kinetics of change in TTHM concentration during water disinfection with rechlorination (the arrow indicates the moment of rechlorination) [Boccelli et al. 2003]

These days, efforts are directed towards removing DBP precursors from the water mainly *via* treatment processes enhancing the removal of organic substances [Chen et al. 2007, 2008]. The idea of surface water pre-chlorination (a process during which DBPs are formed in large quantities) is being abandoned. Treatment trains are extended by the addition of biological processes, where water is purified by slow filtration, at infiltrative intakes, or by combining ozonation with filtration through biological filters involving activated carbon. When the water being treated contains great amounts of algae, mineral and organic suspended matter is removed by flotation instead of by conventional coagulation and sedimentation. Excess quantities of organic suspended matter are also removed *via* microfiltration [Gordon 2001].

Liu et al. [2006] demonstrated that pre-disinfection of the water by UV irradiation increases production of trihalomethanes after chlorination. To maintain high-quality water, free of microorganisms and hazardous disinfection by-products, it is necessary to reduce the number of precursors prior to the UV process [Choi, Choi 2010].

One of the methods for abating the formation of halogen organic compounds is to replace chlorine (sodium hypochlorite) disinfection with chlorine dioxide disinfection [Volk et al. 2002]. Chlorine dioxide as an oxidant is characterised by a high selectivity [Hoigné, Bader 1994]. This is attributable to the fact that in aqueous solutions with a pH lower than 8 chlorine dioxide occurs in a molecular form and practically does not undergo hydrolysis. It reacts with ions and molecules (compounds) which are electron donors. The kinetics of the oxidation reaction depends on the diffusion constants of the molecules taking part in the reaction [Hoigné, Bader 1994]. The study reported by Mielczarek [1995], which was carried out over the water pH range of 5 to 10, has revealed that the rate of chlorine dioxide decay increases with the rise in the pH level. This is associated with the occurrence of the dismutation reaction [Nawrocki, Biłozor 2000]:

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O \tag{31}$$

In their review paper on chlorine dioxide in drinking water treatment Aieta and Berg [1986] addressed a diversity of problems. They described the physicochemical properties of chlorine dioxide and the method of its production; they also provided a detailed discussion of the reactions of chlorine dioxide with inorganic and organic compounds (reactions between chlorine components, reactions of chlorine dioxide and chlorite from the reduction of inorganic components; reactions of chlorine dioxide with phenol, humus substances, with components responsible for the taste and odour of the water, with compounds other than phenols), as well as characterised the biological properties of chlorine dioxide.

Since chloride dioxide reacts with humic acids to a negligible extent, much lower quantities of THMs are formed in the water disinfected with this reagent, as can be seen from the data in Table 6 [Bruchet et al. 2004].

Table 6

Quantities of THMs formed and disinfectants used [Bruchet et al. 2004]

Compounds of THM group	Time of water contact with chlorine h		Time of water contact with chlorine dioxide h	
	2	24	2	24
	Concentration, µg·dm^{-3}			
$CHICl_2$	0.40	0.10	0.10	**0.00**
CHIBrCl	0.33	0.24	0.03	**0.00**
$CHIBr_2$	0.27	0.17	**0.00**	**0.00**
CHI_2Cl	0.08	0.03	**0.00**	**0.00**
CHI_2Br	0.19	0.03	**0.00**	**0.00**
CHI_3	0.09	**0.00**	0.07	0.08
Total	1.36	0.58	0.20	0.08

Hua and Reckhow [2007] focused their research on the formation of total organic halogen (TOX), total organic chlorine (TOCl), total organic iodine (TOI), total organic bromine (TOBr) and unknown total organic halogen (UTOX) induced by the injection of chlorine, chloramine, chlorine upon ozonation, chloramines upon ozonation, and chlorine dioxide. The results obtained from their studies show that ozonation performed prior to disinfection reduces the quantities of THM, TOX and HAA which form during chlorination. When water was disinfected with chloramines or chlorine dioxide, the amounts of UTOX produced were higher than when disinfection was carried out with free chlorine. During chlorination the quantities of TOCl, TOI and TOBr formed were substantially higher than during chloramination or disinfection with chlorine dioxide in the presence of iodides and bromides. Water ozonation at an earlier stage reduced UTOX formation after chlorination.

Chlorine dioxide reacts with diverse organic compounds that are present in the water, to form aldehydes and carboxylic acids but not saturated aliphatic hydrocarbons. In the reaction with alkenes, chlorine dioxide produces chlorohydrins, aldehydes, as well as α-chloro- and α-unsaturated ketones [Zbieć, Dojlido 1999]. The organic by-products that form during water disinfection with chlorine dioxide include the following compounds:

- **acids**: benzoic acid, butanoic acid, pentanoic acid, hexanoic acid, hexadecanoic acid, heptanoic acid, 2-ethylhexanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, tridecanoic acid, tetradecanoic acid, 2-tert-butylmaleic acid and 2-ethyl-3-methylmaleic acid;
- **esters**: hexanedioic acid, dioctyl ester;
- **ketones**: 2,3,4-trimethylcyclopent-2-en-1-one and 2,6,6-trimethyl-2-cyclohexene-1,4-dione;
- **aromatic compounds**: 3-ethyl styrene, 2-ethyl styrene, ethylbenzaldehyde, naphthalene, 2-methylnaphthalene, 1-methylnaphthalene;
- **chlorine-containing compounds**: (1-chloroethyl)dimethylbenzene and 1,1,3,3 tetrachloropropanone [Zbieć, Dojlido 1999, Richardson et al. 2000].

Dąbrowska et al. [2003] focused their interests on aldehyde formation induced by water disinfection with ClO_2 in the presence of humus substances. Their studies have demonstrated that the reactions of chlorine dioxide with natural organic matter (NOM) occur predominantly in the region of the aromatic parts of the humus compound's molecules. Total concentration of aldehydes increased significantly upon ClO_2 disinfection, and the main by-products of NOM oxidation by ClO_2 were formaldehyde and acetaldehyde. The formation of carbonyl compounds continued as long as chlorine dioxide was available in the water. The pH of the water was without any significant effect on the reaction between chlorine dioxide and organic matter. The extent of aldehydes formation in water disinfected with ClO_2 was comparable to the one observed during water ozonation.

A recurrent feature of water disinfection with chlorine dioxide is the rise in the concentrations of chlorites and chlorates [Condie 1986]. This is to be attributed to the presence of these speciation forms in the technological solutions of chlorine dioxide added into the water, as well as to the reaction of ClO_2 with the substances that are present in the water, specifically with the organic ones. In contact with inorganic matter, chlorine dioxide rapidly converts to chlorites (ClO_2^-), chlorates (ClO_3^-) and chlorides (Cl^-). Korn et al. [2002] developed models enabling prediction of chlorite and chlorate concentrations based on the ClO_2 dose, organic carbon content of the water, and UV_{254} absorbance.

The quantity of chlorite ions in the water subjected to ClO_2 disinfection varies between 60 and 70% of the ClO_2 dose, depending on the composition and temperature of the water, and also on the method used for the preparation of the ClO_2 solution injected into the water [Dojlido, 2002].

In the United States chlorite concentration in drinking water cannot be higher than 1 mg·dm^{-3}. Polish sanitary regulations [Decree of the Health Minister of March 29, 2007, on the quality of water for human consumption. Dz.U. 2007 No. 61 item 417) admit the presence of chlorites and chlorates, provided that the sum of their concentrations does not exceed 0.7 mg·dm^{-3}.

According to IARC [International Agency for Research on Cancer 1991], sodium chlorite is not classified as a substance with carcinogenic effects in humans; the same holds for chlorine dioxide [according to ATSDR – Agency for Toxic Substances and Disease Registry 2004]. Richardson et al. [2007] claim that as yet the genotoxicity and carcinogenicity of chlorites and chlorates have not been supported by any experimental evidence. Below presented are some interesting results obtained from pertinent studies demonstrating the negative influence of these compounds on living organisms. Table 7 includes data that characterise the toxic properties of, and the organoleptic thresholds for, ClO_2, ClO_2^- and ClO_3^-.

Table 7

Toxicity of chlorine dioxide, chlorites and chlorates [Michalski 2004, quoted after Nowack, Gunten 1999]

	Unit	ClO_2	ClO_2^-	ClO_3^-	Comments
Lowest concentration in water at which effects are observed	mg·dm^{-3}	12	1,2	1,2	Acute effect: 1000-15000 for ClO_3^-
	mg·(kg d)$^{-1}$	1 (rats)	1 (rats)	0.7-1 (rats)	No data
LD_{50}	mg·kg^{-1}	140 (rats)	140-200 (rats)	200 (humans)	–
Chronic toxicity	mg·(kg d)$^{-1}$	No effect till 5	No effect till 5	No effect till 5	5
	mg·dm^{-3}	No effect till 10	No data	No data	As a sum of three parameters (humans)
Teratogenic effect	mg·(kg d)$^{-1}$	1 (rats)	1 (rats)	1 (rats)	–
Carcinogenic effect	mg·(kg d)$^{-1}$	No data	No data	No effect till 10	–
Organoleptic threshold in water for humans	mg·dm^{-3}	0.4	0.3	5	–

Couri et al. [1982] examined the toxicological effects of ClO_2, ClO_2^- and ClO_3^- on experimental organisms (rats). The concentrations of ClO_2, ClO_2^- and ClO_3^- in the water administered to the rats varied between 1 and 1000 mg·dm^{-3}. With chlorite concentration of 100 mg·dm^{-3}and higher, they observed an increase in the number of thrombocytes, percentage of hemoglobin and volume of blood cells after 30 and 60 days of exposure. Those changes were also observable over 90 days after termination of the experiment. Similar effects were reported for experimental mice [Abel-Rachman et al. 1980, quoted after Couri et al. 1982]. Experiments on human subjects, who consumed water disinfected with chlorine and chlorine dioxide (where total concentration of ClO_2, ClO_2^- and ClO_3^- ranged from 5 to 7 $mg·dm^{-3}$), disclosed a significant decrease in hemoglobin and hematokrit only in one subject among the population of a small town [Michale et al. 1981, quoted after Couri et al. 1982]. As yet, the available data are insufficient for reliably assessing the toxicological effects of ClO_2 disinfection by-products on human health. In laboratory animals the final effect of exposure to chlorite and chlorate ions was damage of red blood cells. Some of the studies include mentions of the effect of chlorine dioxide on the thyroid gland. In general, researchers exclude chlorates from the list of mutagenic factors, but those exclusions are based predominantly on the lack of long-term investigations pertinent to this problem [Lipiak, Drouot 2000]. The question of why human subjects and experimental animals differ in vulnerability of their red blood cells to chlorite ions is still far from being well understood. According to one of the studies reported in the literature [Harrington et al. 1995, quoted after Lipiak, Drouot 2000], rat's blood was more vulnerable than human blood to the presence of chlorites when they occurred at lower concentrations; at higher concentrations, human blood was found to be more vulnerable to chlorite-related damage. In some human subjects the epithelium of the digestive-intestinal tract exhibited a higher vulnerability to ClO_2 and ClO_2^- in drinking water, but not to OCl^-.

Table 7 shows organoleptic levels for ClO_2, ClO_2^- and ClO_3^-. According to Hoehn et al. [2003], the customer may complain of the specific smell of the water even if the concentration of ClO_2 persisting in the distribution system is lower than 0.1 $mg·dm^{-3}$. They also observed that chlorite concentrations exceeding 0.4 $mg·dm^{-3}$ frequently caused the taste of the water to deteriorate.

Chlorite ions can be removed from the water by using an activated carbon filter [Collivignarelli et al. 2006]. Their removal involves a two-stage procedure. At the first stage, ClO_2^- is adsorbed onto the activated carbon; at the second stage, on the active sites of the activated carbon, ClO_2^- is reduced to chlorides. Adsorption of ClO_2^- is parallelled by the adsorption of the organic compounds that block the active sites of the sorbent. Experimental results have shown that sorption of ClO_2^- on activated carbon is also inhibited by the rise in nitrate concentrations. The adsorbing capacity of the carbon after thermal regeneration can be increased by rinsing with mineral acid.

Henderson et al. [2001], as well as Katz and Narkis [2001], reported on their attempts to remove chlorite and chlorate ions by means of iron(II) ions. Iron(II) ions effectively reduce chlorite ions to chloride ions (Cl^-) according to the following reaction:

$$4Fe^{2+} + ClO_2^- + 10H_2O \rightarrow 4Fe(OH)_{3(S)} + Cl^- + 8H^+ \tag{32}$$

However, the method is applicable only with a pre-oxidation step involving chlorine dioxide, when there is a need of adding Fe^{2+} into the water in order to remove ClO_2^- and the excess of chlorine dioxide:

$$Fe^{2+} + ClO_2 + 3H_2O \rightarrow Fe(OH)_{3(S)} + ClO_2^- + 3H^+ \tag{33}$$

2.4. Kinetics of chlorine (chlorine dioxide) decay in water distribution systems

When analysing the fate of the disinfectant in drinking water during distribution, it is necessary to consider the rate of its decay both in bulk water and at pipe wall (Fig. 5):

$$\frac{dC}{dt} = \left(\frac{dC}{dt}\right)_b + \left(\frac{dC}{dt}\right)_W \tag{34}$$

where subscript *b* denotes the rate of chlorine decay in bulk water and subscript *W* stands for the rate of chlorine decay at the pipe wall.

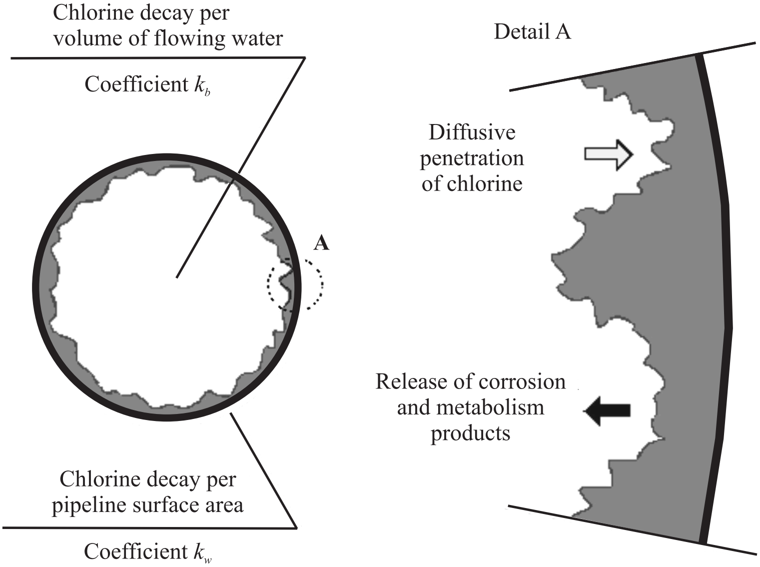

Fig. 5. Processes influencing the rate of chlorine decay during water flow in the pipes [Łomotowski 2007]

It is assumed that the rate constants of disinfectant decay under laboratory conditions are equal to the rate constants of disinfectant decay in bulk water flowing in the distribution system [Castro, Neves 2003]:

$$\left(\frac{dC}{dt}\right)_b = -k_b C = -kC \tag{35}$$

where:

k_b, k – real rate constant of disinfectant decay in bulk water, m·s^{-1}.

The rate of disinfectant decay at the pipe wall is described by the following relation:

$$\left(\frac{dC}{dt}\right)_W = -\frac{1}{R_h} k_W^* C_W \tag{36}$$

where:

k_W^* – real rate constant of disinfectant decay at the pipe wall, $m \cdot s^{-1}$;

C_W – disinfectant concentration at the pipe wall, $mg \cdot dm^{-3}$, whose value depends on the diffusive penetration of the mass of the disinfectant's molecules from water to the surface of the pipe walls;

R_h – hydraulic radius, m.

The rate of diffusive penetration of mass is defined as follows:

$$\left(\frac{dC}{dt}\right)_M = -\frac{1}{R_h} k_F \left(C - C_W\right) \tag{37}$$

where:

C – disinfectant concentration in water, $mg \cdot dm^{-3}$;

k_F – coefficient of diffusive penetration of mass, $m \cdot s^{-1}$.

The rate of disinfectant decay at the pipe wall must be equal to the rate of disinfectant penetration into the material accumulated at the pipe wall. Hence:

$$\left(\frac{dC}{dt}\right)_W = \left(\frac{dC}{dt}\right)_M \tag{38}$$

$$k_W^* C_W = k_F \left(C - C_W\right) \tag{39}$$

Using equation (39) we can calculate chlorine concentration at the pipe wall, C_W:

$$C_W = \frac{k_F}{(k_W^* + k_F)} C \tag{40}$$

Combining the relations of (40) with the relations of (37) and considering equation (38), we have:

$$\left(\frac{dC}{dt}\right)_W = -\frac{1}{R_h} \frac{k_W^* k_F}{(k_W^* + k_F)} C \tag{41}$$

The value obtained with the relation:

$$k_W = \frac{1}{R_h} \frac{k_W^* k_F}{(k_W^* + k_F)} \tag{42}$$

is the rate constant of disinfectant decay associated with the pipe wall.

Substituting the relations of (35), (41) and (42) into equation (34), we can write:

$$\frac{dC}{dt} = -kC - k_W C = -(k + k_W)C \tag{43}$$

The value of k_{Dez} taking the form of:

$$k_{Dez} = k + k_W \tag{44}$$

is the rate constant of disinfectant decay in the pipes. The rate constants of disinfectant decay in water distribution systems are expressed in h^{-1}.

The values of constants k are determined based on laboratory test results. Taking into account the changes observed in the disinfectant's concentrations, as well as the time of water retention in the distribution system (water age), the constants k_{Dez} are computed in terms of the relation obtained after integration of equation (43):

$$C(t_{WO}) = C_0 \exp(-k_{Dez}\, t_{WO}) \tag{45}$$

where:

C_0 – initial disinfectant concentration in water, mg·dm^{-3};

t_{WO} – time of water retention in the distribution system, min or h.

Knowing the values of k_{Dez} and k, we can determine the value of the constant k_W.

Chlorine decay occurs in two characteristic stages. At the first stage, which begins immediately upon chlorine addition and in most instances lasts several minutes, chlorine consumption is very quick. This stage is frequently defined as a stage of 'immediate chlorine decay'. At this stage, the rate of chlorine decay is described in terms of kinetic equations [Vieira et al. 2004]:

- for parallel reactions:

$$C(t) = C_0\, x \exp(-k_1 t) + C_0 (1 - x) \exp(-k_2 t) \tag{46}$$

- for limited first-order reactions:

$$C(t) = C^* + (C_0 - C^*) \exp(-k\, t) \tag{47}$$

- for second-order reactions:

$$C(t) = C_0 \frac{1 - R}{1 - R \exp(-k^* t)} \tag{48}$$

- for *n*th order reactions:

$$C(t) = \left(k^* t(n-1) + \left(\frac{1}{C_0}\right)^{n-1} \right)^{\frac{1}{n-1}} \tag{49}$$

where:

$C(t)$ – chlorine concentration in water at time t, mg $Cl_2 \cdot dm^{-3}$;
C^* – final concentration of chlorine, mg $Cl_2 \cdot dm^{-3}$;
t – time of water contact with chlorine, h;
n – order of reaction;
x – dimensionless empirical constant;
k^*, k_1, k_2 – empirical constants of chlorine decay in water, h^{-1}.

The first stage of change in chlorine concentration in the water being disinfected takes place at water treatment plants. A major contributory factor in preventing the water from re-contamination is the kinetics of change in chlorine concentration during water transmission to the user, namely the rate of chlorine decay characteristic for the second stage. Changes that occur at this stage are described by the equation of the kinetics of first-order reaction (35). Upon integration, the equation takes the following form [Vasconcelos et al. 1997, Kiéné et al. 1998]:

$$C(t) = C_0 \exp(-k\,t) \tag{50}$$

Kiéné et al. [1998] have demonstrated that the value of the rate constant of chlorine decay k is influenced by the organic matter content and the temperature of the water:

$$k = a\left[\mathrm{TOC}\right]\exp\left(\frac{-b}{T}\right) \tag{51}$$

where:
[TOC] – total organic carbon in water, mg $C \cdot dm^{-3}$;
T – water temperature, K;
a, b – empirical constants.

During their study on the pattern of change in chlorine concentrations in municipal water supply systems, Hua et al. [1999] observed that upon the first chlorine injection, chlorine decay was 3 to 10 times as rapid as in re-chlorinated water. They demonstrated that initial concentration, C_0, had a significant effect on the rate constants of chlorine decay, which were inversely proportional to the initial concentration of chlorine:

$$k = \frac{\alpha}{C_0}\exp(-\beta t) \tag{52}$$

In equation (52), α and β are empirical constants. Regression function (52) held true for the study conducted by Hua et al. [1999], which involved pre-chlorination of raw water, chlorination of treated water and re-chlorination. In the case of re-chlorination, the values of the constant α were lower compared with those defined for the initial disinfection process. Extension of the time of water contact with chlorine brought about a decline in the value of α during re-chlorination.

Vieira et al. [2004] generalised the relations of (51) and (52), and also verified empirically the expression:

$$k = a\left[\mathrm{TOC}\right]\frac{c}{C_0}\exp\left(\frac{-b}{T}\right) \tag{53}$$

where c is an empirical constant.

Powell et al. [2000] derived the constant k from the empirical functions of total organic carbon [TOC] and initial chlorine concentration C_0:

$$k = \frac{c_1}{C_0}([\mathrm{TOC}] - f)\exp\left(-\frac{E}{RT}\right) \tag{54}$$

or UV absorbance at the wavelength of 254 nm (UV_{254}) and initial chlorine concentration C_0:

$$k = \frac{c_2}{C_0}(\mathrm{UV}_{254} - h)\exp\left(-\frac{E}{RT}\right) \tag{55}$$

where:

E – experimentally established activation energy which depends on the type of compounds present in the water, $\mathrm{J \cdot mol^{-1}}$;

R – universal gas constant;

c_1, c_2, f, h – empirical constants.

To predict the rates of change for chlorine concentrations in water, Rossman [2000] made use of the following equation in the EpaNet software:

$$\frac{dC}{dt} = \frac{kC}{C_L - C} \tag{56}$$

where the constants k and C_L were determined as follows:

$$k = -0.32\,\mathrm{UV}^{1.365}\frac{100\mathrm{UV}}{[\mathrm{DOC}]} \tag{57}$$

$$C_L = 4.98\,\mathrm{UV}\text{-}1.91[\mathrm{DOC}] \tag{58}$$

where DOC stands for dissolved organic carbon, $\mathrm{mg\ C \cdot dm^{-3}}$.

Warton et al. [2006] showed that with a long contact time, up to 180 hours, the kinetics of chlorine decay at the second stage was well described by empirical models of the general formula:

$$C(t) = a + b\exp(-d\,t) \tag{59}$$

where a, b and d are determined *via* nonlinear estimation based on experimental results. Free chlorine concentration at time t, defined as C_t, depended on initial concentration C_0, and the relationship between the two quantities was found to be of a linear nature:

$$C_0 = e + fC_t \tag{60}$$

Models (59) and (60) held true for water of diverse composition. Using the relation of (60), we can establish the initial chlorine dose required for determining chlorine residual after time t.

When analysing the rates of change in the concentrations of chlorine, chloramines or chlorine dioxide, it is necessary to consider the material of which the pipes have been made. Experiments reported so far have revealed that the mode of disinfectant decay in unlined steel or cast-iron pipes differs from the one in plastic pipes and steel or cast-iron pipes with cement linings. The impact of the pipe wall on the rate of disinfectant decay in tap water depends on the ratio of pipe wall surface to the volume of the water accumulated in the pipe. In pipes with small diameters the impact of biofilms on the quality of the water being transported is greater than in pipes with large diameters. Biofilms may therefore have a major impact on water quality in small-diameter plumbings and fittings, where water stagnation is a recurrent phenomenon.

In plastic pipelines, the biofilms that develop on the pipe surface have a profound impact on chlorine decay; the rate of the decay, however, depends on the time the microorganisms take to colonise the internal surfaces of the pipes, but not on the length of the pipes' service life (pipe service age). While service age failed to significantly affect the rate of chlorine decay in PVC or MDPE pipelines, this was not so in the case of asbestos cement pipes, where service age accounted for a significant increase of the chlorine decay rate in the transported water [Al-Jasser 2007].

A major contributing factor in the biofilm's impact on chlorine decay is the presence of biodegradable dissolved organic carbon (BDOC). Kiéné et al. [1998] observed that the rate constant of chlorine decay in water staying in contact with biofilms displayed a linear dependence on the BDOC content of the biofilm. The BDOC content of the biofilm is influenced by the composition of the water transmitted in the pipes. A decisive factor in the microbiological composition of the biofilm is not only the quantity of organic compounds, but also the presence of the ammonium ion which supports growth of nitrifying bacteria.

The pipe service age effect should be taken into account when determining the rates of chlorine decay in cast-iron or steel pipes with and without cement linings. Al-Jasser [2007] found that in cast-iron pipes and steel pipes at a service age of 55 years the rates of chlorine decay were by 92 to 430% higher than in new pipes made from the same materials. The service age effect on the rate constants of chlorine decay was more pronounced in cast-iron than in steel pipes. Cement linings significantly inhibit the rate of chlorine decay at the pipe wall, regardless of the type of pipe material used.

In steel pipes and unlined cast-iron pipes, the rate of pipe wall decay of chlorine depends on the kinetics of corrosion on the internal surfaces. Assuming that this is the main factor affecting chlorine decay during water contact with corrosion-related deposits, we can describe chlorine decay in terms of the following equation [Kiéné et al. 1998]:

$$\frac{d[\mathrm{Cl_2}]}{dt} = \frac{4\times10^{-3}}{\tau}\frac{M_{\mathrm{Cl}}}{M_{\mathrm{Fe}}}\rho_{\mathrm{Fe}}\frac{C_r}{D} \tag{61}$$

where:

- $[\mathrm{Cl_2}]$ – chlorine concentration in water, mg·dm^{-3};
- C_r – annual rate of corrosion, µg·year^{-1};
- D – diameter of pipes undergoing corrosion, m;
- t – time of water contact with corrosion products, s;
- τ – seconds per year: $3.16\cdot10^7$ s·year^{-1};
- M_{Cl} – atomic weight of chlorine, 35.5 g·mol^{-1};
- M_{Fe} – atomic weight of iron, 55.8 g·mol^{-1};
- ρ_{Fe} – density of iron, 7.860 g·cm^{-3}.

For the conditions determined above, we can write:

$$\frac{d\left[\mathrm{Cl}_2\right]}{dt} = 6.33\times10^{-7}\frac{C_r}{D} \tag{62}$$

The experiment performed by Kiéné et al. [1998] on steel pipes in service has revealed that the rate of chlorine decay induced by the presence of corrosion products need not be modelled by the kinetics of a first-order reaction (equation 62), but by the following linear relation:

$$C(t) = C_0\left(1-1.36\times10^{-6}\frac{C_r}{D}t\right) \tag{63}$$

Hallam et al. [2002] examined different factors that affect the value of the rate constant k_W for chlorine decay. They divided the pipes being tested into reactive to corrosion (unlined metal pipes) and unreactive to corrosion (PVC, MDPE, lined cast-iron and steel pipes). The results summarised in Table 8 indicate that chlorine decay in cast-iron pipes is more rapid than in plastic pipes.

Table 8

Effect of pipe material on the rate constant of chlorine decay [Hallam et al. 2002]

Material	Variability of rate constant k_W h^{-1}	Average value of rate constant k_W h^{-1}
Investigations into a water-pipe network in service		
Grey cast iron pipes	0.035–2.5	0.67
Cast iron spun pipes	0.1–1.8	0.33
Spheroidal graphite iron pipes with cement lining	0.04–0.45	0.13
Medium density polyethylene (MDPE) pipes	0.009–0.25	0.05
Polyvinyl chloride (PVC) pipes	0.05–0.25	0.09
Laboratory investigations		
Spheroidal graphite iron pipes with cement lining	0.001–0.55	0.14
Medium density polyethylene (MDPE) pipes	0.001–0.18	0.05
Polyvinyl chloride (PVC) pipes	0.001–0.22	0.09

According to Nawrocki et al. [2010], a key factor in the decay of disinfectants at pipe wall with advanced corrosion is ammonia, which during water stagnation undergoes denitrification, to produce anaerobic conditions supporting microbial growth. This finding has been substantiated by Zhang and Edwards [2007], who observed that disinfectant decay was more rapid when the water contained nitrates.

Among the contributors to the rate of disinfectant decay is UV irradiation when used as a prior step to the chlorination process. Choi and Choi [2010] reported that low radiation doses, 40 mJ·cm^{-2}, had no significant effect on the characteristics of dissolved organic carbon

(DOC) or the concentration of assimilable organic carbon (AOC), which is an indicator of bacterial growth in the water distribution system. Small doses failed to mineralise DOC, but they might be responsible for breaking the chemical chain or changing the characteristics of the functional groups of DOC. UV-induced modification of the DOC structure did not stimulate microbial growth or biofilm formation in the water distribution system, but could adversely affect the quality of the water by increasing its chlorine demand or intensifying the formation of disinfection by-products during re-chlorination. Choi and Choi [2010] showed that UV radiation increased the rate of chlorine decay, but only at the first stage of disinfection.

Rossman [2006] examined the effect of the water treatment method on the decay of chlorine and chloramines in steel and cast-iron pipes under laboratory conditions. Prior to chlorination (chloramination), the model water solution was treated by ozonation, adsorption onto activated carbon, and reverse osmosis in order to control the quantities of organic compounds. The results obtained showed that the values of k_{Dez} constants were in every instance higher than those of k constants for chlorine (chloramine) determined in water staying in no contact with the pipe walls. The values of k_W obtained with water subjected to ozonation and filtration through a granular activated carbon bed were approximately twice as high as those achieved with water treated by reverse osmosis and by using a conventional treatment train involving coagulation. The k_W constants for chloramines took values by 40 to 70% higher compared with those for chlorine. The method of water treatment had a similar impact on the change in the values of the k_W constants for both chloramines and chlorine. The studies reported by Rossman also produced the finding that the DOC structure, which undergoes changes during ozonation, may contribute not only to the formation of complexes with iron(II) during corrosion of the metallic pipe walls, but also to the rise in the rate of chlorine (chloramine) decay in unlined metallic pipes. These findings undermine the statement (based on the results of other studies) that the reduction in TOC obtained with treatment trains involving ozonation and biologically active granular carbon beds hampers the rate of disinfectant decay in water distribution systems.

When examining the hospital water treatment system in Pittsburgh, Zhang [2007] found that TOC concentration in hot water was higher than in cold water. At 45ºC, the rise in TOC content was concomitant with a more rapid ClO_2 decay. Such phenomenon was not observed at the water temperature of 25ºC. This is an indication that both the temperature and the TOC content of the water exert a strong influence on the rate constants of chlorine dioxide decay in internal installations.

Raw water containing cyanobacterial cells is difficult to treat. Pre-oxidation causes algae to release toxins which are difficult to remove, and there is likelihood that they may become precursors to disinfection by-products. The use of chlorination at the end of the technological process may not provide the desired removal of bacteria. Zamyadi et al. [2011] observed that in the presence of algae chlorine decay proceeded at a more rapid rate and was similar for all the species examined (*Anabaena circinalis, Microcystis aeruginosa, Cylindrospermopsis raciborskii, Aphanizomenon issatsckenka*).

When modelling chlorine decay, Kohpaei and Sathasivan [2011], as well as Fisher et al. [2011], made use of very high initial disinfectant doses. Chlorine doses used in real water distribution systems are much lower, and the models presented fail to fully depict the conditions in the pipe interior.

2.5. Analytical problems dealt with during determination of chlorine, chlorine dioxide, chlorites and chlorates

Monitoring of the fate of disinfectants in water distribution systems is to a great extent influenced by the analytical potential of available laboratories. This becomes manifest primarily when measuring the concentrations of disinfectants used and disinfection by-products formed. Measurements of free chlorine and chloramine concentrations in tap water do not raise serious analytical problems, contrary to those of water chlorination by-products, which require the use of costly instrumental methods of analysis, such as gas or liquid chromatography. This is why the concentrations of water chlorination by-products in large distribution systems are monitored periodically. In the case of small-sized water distribution systems, use is made solely of rapid screening tests.

Attempts to extend the use of chlorine dioxide for water disinfection carry a real risk that no control will be provided either of the concentrations of ClO_2, or of those of the main by-products, ClO_2^- and ClO_3^-. This is attributable to the lack of low-cost and simple methods characterised by a suitable detectability threshold. The control of the above mentioned species in solutions is complicated; first, because ClO_2, ClO_2^- and ClO_3^- display similar properties, and second, because there may be an interaction among the components of the solution.

Cl_2, ClO_2, ClO_2^- and ClO_3^- concentrations can be measured by amperometry or potentiometry. These are iodometric methods utilising the release of iodine from potassium iodide by Cl_2, ClO_2, ClO_2^- and ClO_3^- at various pH. Titration of iodine is carried out with sodium thiosulphate or arsenobenzene (C_6H_5AsO). However, because of the analytical problems associated with the maintenance of the pH required and with the measurement of chlorine dioxide concentrations lower than 0.1 $mg \cdot dm^{-3}$, this method has not found wide acceptance [Aieta et al. 1984].

Hong and Rapson [1967] developed an analytical procedure for determining chlorine dioxide, chlorous acid, chlorites, chlorates and chloride ions in composite mixtures. In this procedure, they measured chlorine dioxide spectrophotometrically at the wavelength of 360 nm, taking advantage of the fact that at this length of electromagnetic waves molar absorption of chlorine dioxide equalled 1100 $1 \cdot (mol \cdot cm)^{-1}$, and that of ClO_2^- was 1.2 $1 \cdot (mol \cdot cm)^{-1}$. Then, after chlorine dioxide removal by passing air through the solution for 10 to 15 minutes, total concentrations of chlorous acid and chlorite ions in the solution were determined spectrophotometrically at the wavelength of 250 nm, as both the speciations of chlorine have the same molar absorption. Concentrations of chlorous acid, chlorite ion and chlorate ion were determined by the iodometric method described earlier. Chloride ion concentration was measured by the Mohr method, which in the case of the spectrophotometric approach has some weaknesses: it requires consideration of water-acidity-related changes in the molar absorption of chlorine dioxide, and permits the concentrations of chlorites and chlorates to be determined solely in inert solutions.

Puckett et al. [1999] analysed the possibility of measuring chlorine dioxide concentrations in tap water by colorimetric methods involving different dyes. They found that the most sensitive reagent to chlorine dioxide was lissamine green B, followed by Congo red and amaranth, and that the detection limit for lissamine green B was below 0.1 $mg \cdot dm^{-3}$. The usefulness of amaranth in determining ClO_2 concentration in water was the focus of the studies reported by Emmert et al. [2000]. They investigated the effect of water pH and temperature, as well as the influence of ClO_2^-, ClO_3^- and Fe^{3+} ions, manganese and monochloramine, on the error of free chlorine (Cl_2, HOCl, OCl^-) determination. The method is suitable for the determination of ClO_2 when its concentration in water ranges between 0.1 and 1 mg·dm^{-3}, in the presence of such interfering compounds as ClO_2^-, ClO_3^-, Fe^{3+} and NH_2Cl. In this method the effect of free chlorine on the determined concentration values is significant. Emmert et al. [2000] have demonstrated that amaranth reacts with ClO_2 at a faster rate than with the speciations defined as free chlorine.

Jiang et al. [2005] described a simple and selective method enabling measurements of chlorine dioxide concentration in tap water. The method consists in oxidising dyes of the rhodamine group (determined by fluorescence) with chlorine dioxide in an ammonium chloride buffer solution. They tested rhodamine S, rhodamine G, rhodamine B and butylrhodamine B, among which rhodamine S was found to be best suited for determining ClO_2 concentrations ranging between 0.0060 and 0.450 mg·dm^{-3}. The threshold of ClO_2 detection *via* this method amounted to 0.003 mg·dm^{-3}. The method proposed is selective, because chlorine, chloramines and OCl^-, OCl_2^- or OCl_3^- ions do not interfere.

Chlorine dioxide concentrations in drinking water can also be measured by biochemical methods, and these include the enzymatic one. In the enzymatic approach concentration is determined spectrophotometrically, and detectability ranges from 0.2 to 4.0 mgClO_2·dm^{-3}. The method utilises the ability of horseradish peroxidase to decolorise the dye Reactive Yellow 17, C.I. 18852 in the presence of chlorine dioxide. Tinoco et al. [1996] demonstrated that interference came only from OCl^- ions.

In Poland, chlorine residual in tap water samples is routinely analysed using the colorimetric method with N,N-diethyl-1,4-phenylenediamine specified in the Polish Standard PN--ISO 7393-2:1997 (Jakość wody – *Oznaczanie chloru wolnego i chloru ogólnego – Arkusz 2: Metoda kolorymetryczna z N,N-dietylo1,4-fenylenodiaminą, do celów kontrolnych*). Since the Polish Standard does not describe the method of analysing chlorine dioxide, in our study use was made also of the *Standard Methods for the Examination of Water and Wastewater* [19th Edition 1995].

The written abbreviation for N,N-diethyl-1,4-phenylenediamine is DPD, so the method is frequently referred to as the DPD method. It is used for determining free chlorine (Cl_2, HOCl, OCl^-), chloramines (also defined as combined chlorine), chlorine dioxide and chlorites. The DPD method is a spectrophotometric technique with a detection threshold of 0.01 mg Cl_2·dm^{-3} for free and combined chlorine; 0.04 mg ClO_2·dm^{-3} for chlorine dioxide, and 0.1 mg ClO_2^- ·dm^{-3}for chlorites. To assess its accuracy, extensive research was conducted throughout the USA in diverse Federal and State Laboratories. Pertinent results are shown in Table 9.

Table 9

Analytical parameters obtained from interlaboratory determinations of free chlorine residual carried out using the colorimetric DPD method (quoted after PN-ISO 7393-2:1997)

Real value mg·dm^{-3}	Number of laboratories (observations)	Average value mg·dm^{-3}	Standard deviation mg·dm^{-3}
0.50	7	0.48	0.13
0.80	14	0.79	0.29
1.10	14	1.15	0.39
1.29	7	1.41	0.38

Owing to the manifold benefits derived from its use, ion-exchange chromatography is a recommended analytical procedure for the determination of ClO_2^- and ClO_3^- concentrations in drinking water [Weinberg et al. 2003, quoted after Michalski 2004]. The advantages offered by this method can be itemised as follows: possibility of simultaneously determining a dozen ions; short duration of analysis; detection at the level of $\mu mol \cdot litre^{-1}$ or lower; only small quantities of sample are needed for analysis; possibility of using different detectors; simple preparation of sample for analysis; simultaneous determination of cations and anions, or organic and inorganic ions; high selectivity with respect to the substances being measured in samples with a complex matrix, and finally the possibility of analysing the same element at various levels of oxidation [Michalski 2005].

Watanabe et al. [1998] used high-resolution liquid chromatography to measure chlorine dioxide concentration in water where hypochlorite was present. Within three minutes they obtained highly effective separation of hypochlorite and chlorine dioxide. Some limitation to detectability may have come from the concentration of 0.2 and that of 10 $\mu g \cdot dm^{-3}$ for chlorine dioxide and hypochlorite, respectively. The method has been classified as suitable for routine analyses. A major impediment to a widespread use of ion chromatography is the insufficient number of, and limited access to, laboratories carrying out quantitative and qualitative determinations of both chlorites and chlorates (not to mention the costs incurred).

3. AIM AND SCOPE OF THE STUDY

Prior to the studies reported on here, the following hypotheses were put forward.

I *In the light of state-of-the-art knowledge, the values of the rate constants of free chlorine decay in tap water are influenced primarily by the concentrations of waterborne organic substances. The assumption was made that the investigations will confirm or reject the hypothesis about the significance of the influence of organic substance concentrations on the rate constants of chlorine dioxide decay in tap water.*

II *The rate constants of chlorine dioxide decay depend on the rate constants of free chlorine decay and on the five-minute chlorine demand of the water defined as the difference between chlorine dose and chlorine concentration after five-minute contact of water with chlorine. Five-minute chlorine demand is an indirect measure of the quantity of organic and mineral compounds occurring in the water, which are readily oxidised with chlorine.*

III *The quantity of chlorites and chlorates that form in the water being disinfected with chlorine dioxide depends on the mode of chlorine dioxide production in generators*.

IV *The rates of chlorine and chlorine dioxide decay are influenced by the deposits accumulating in the pipes.*

To verify these hypotheses, investigations were carried out with the aim of determining:

- the composition of 43 untreated and 33 treated water samples under laboratory conditions; for these samples determined were the rate constants of chlorine and chlorine dioxide decay, five-minute chlorine demand and five-minute chlorine dioxide demand (the results obtained being subjected to analysis);
- the rate constants of chlorine and chlorine dioxide decay in the water samples collected along the main conduit supplying water from WTP Wrocław Mokry Dwór to the municipality of Oława;
- the effect of water-pipe deposits (collected from the the main conduit supplying water from WTP Wrocław Mokry Dwór to the municipality of Oława) on the rates of chlorine and chlorine dioxide decay;
- the effect of the mole ratio of the reagents used for chlorine dioxide generation on the quantity of disinfection by-products formed;
- the effect of chlorine dioxide dose on the quantity of chlorites and chlorates formed (relevant full-scale tests were conducted in cold and hot water installations of the groundwater treatment plant operated at one of Wrocław's hospitals).

4. EXPERIMENTAL

4.1. RESEARCH METHODS

4.1.1. Methods for determining the physicochemical composition of the water

Physicochemical parameters were analysed using the methods summarised in Table 10.

Table 10

Analytical methods used for determining the physicochemical parameters of the water

Parameter	Method	Procedure (symbol of standard or procedure)
Turbidity	Nephelometry	PN-EN ISO 7027:2003
Conductivity	Electrometry	PN-EN 27888:1999
pH	Electrometry	PN-C-04540-01:1990
Absorbance	Spectrophotometry	At 254 nm, after passage of the sample through a membrane filter, 0.45 µm
Manganese	Formaldoxime method	PN-C-04590-03:1992
Iron	Spectrophotometry, 1.10-phenanthroline	PN-ISO 6332:2001
Permanganate COD	In acidic medium, with $KMnO_4$	PN-EN ISO 8467:2001
Total alkalinity	In the presence of phenolphthaleine	PN-EN ISO 9963-1:2001
Ammonium ion	Direct nesslerization method	PN-C-04576-4:1994
Total hardness	Versenate method	PN-ISO 6059: 1999
Chlorides	Titration (Mohr's method)	PN-ISO 9297:1994
Nitrates	Colorimetry	PN-82 C-04576.08

Turbidity was measured using an Eutech Instruments TB 1000 nephelometer with a measuring accuracy of ± 2% (± 0.01 NTU). For conductivity and pH measurements, use was made of an Elmetron CPC-501 electrometer with a measuring accuracy of 0.1% and ± 0.002 for conductivity and pH, respectively. Absorbance was determined using a WTW SpectroFlex 6600 spectrophotometer.

Water was collected in PE containers, which had been carefully rinsed with distilled water before use. After being brought to the laboratory, the water was kept in a thermostat at temperature set to the one that occurs in the pipe interior. Water samples for physicochemical analyses were not preserved during transport to the laboratory.

4.1.2. Determination of chlorine and chlorine dioxide

Chlorine and chlorine dioxide concentrations in the water samples were determined using the DPD method according to the Polish standard PN-ISO 7393-2:1997 *Jakość wody – Oznaczanie chloru wolnego i chloru ogólnego – Arkusz 2: Metoda kolorymetryczna z N,N-dietylo1, 4-fenylenodiaminą, do rutynowych celów kontrolnych*. The method involved colour depth measurements performed by comparison with the colorimetric scale. The use of the colorimetric scale is suitable when free chlorine concentrations range between 0.03 and 5 mg $Cl_2 \cdot dm^{-3}$. Measurements were carried out with WTW SpectroFlex 6600 at 510 and 515 nm for chlorine and chlorine dioxide, respectively. The cuvette used in the study was made of quartz glass and had an optic path length of 10 mm. The measurement was conducted immediately after sample collection, to avoid exposure to daylight and shakes. In the time span between measurements, the samples were maintained in a heat-insulating chamber with temperature set to 11°C, which is close to the temperature of the water in distribution systems. Chlorine (chlorine dioxide) concentration was read off from the calibrated curve plotted for the two disinfectants separately.

4.1.3. Determination of chlorites and chlorates

Initially (in July 2008), analysis of water samples for chlorite and chlorate concentrations was performed at the laboratory operated by the Water Treatment Plant (WTP) Mokry Dwór, Wrocław. Measurements were carried out using the DIONEX ion-exchange chromatograph involving an AS9HC column with conductivity detection. The eluent (sodium bicarbonate, $NaHCO_3$) passed through the column with a velocity of 1.2 $ml \cdot min^{-1}$. Injection loop volume and suppressor current amounted to 100 µl and 50 mA, respectively. The samples being analysed contained tap water and did not need pretreatment. Analyses were performed in compliance with the Polish standard PN-EN ISO 10304-4:2002 (*Jakość wody – Oznaczanie rozpuszczonych anionów za pomocą chromatografii jonowej. Część 4: Oznaczanie chloranów, chlorków i chlorynów w wodach mało zanieczyszczonych*).

Further analyses were conducted at the laboratory of the Institute of Environmental Engineering Zabrze (Polish Academy of Sciences), using Metrohm apparatus (Herisau Metrohm AG, Switzerland, connected with an 818 IC pump, 819 IC detector and 830 IC interface) and the software Metrodata 2.3.

Before being placed in the chromatographic column, the water sample was made subject to filtration through a 0.2 µm ceramic microfilter.

Analyses were carried out under the following conditions:

• column	Metrohm A Supp 5 (250 x 4.6);
• eluent	3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$;
• flow rate of eluent	0.7 $ml \cdot min^{-1}$;
• injection volume of sample	100 µl;
• detection mode	suppressed conductivity.

Solutions for plotting calibration curves were prepared from reference materials *via* the following route: 2 ml of reference solution, equivalent to 2 mg of the ion being analysed, were placed in class A measuring flasks (each of a 1000 ml volume) and made up to 1 litre. The solution prepared in this way was the calibration solution referred to as Number 5 (Tab. 11) and characterised by the highest concentration. Solution no. 5 served for the preparation of the other four solutions (numbered 4, 3, 2 and 1, respectively), which displayed lower concentrations. These solutions were prepared by transferring appropriate volumes to the 100 ml volume measuring flasks of class A, and upon dilution the desired number of calibration solutions was obtained. Their titres are shown in Table 11.

Table 11

Solutions of chlorites and chlorates used for determining the calibration curve

Ion	Concentration in calibration solution, $mg \cdot dm^{-3}$				
	Number 1	Number 2	Number 3	Number 4	Number 5
ClO_2^-	0.1	0.25	0.5	1	2
ClO_3^-	0.1	0.25	0.5	1	2

Figure 6 shows an example chromatogram obtained during determination of chlorite and chlorate concentrations in the water samples.

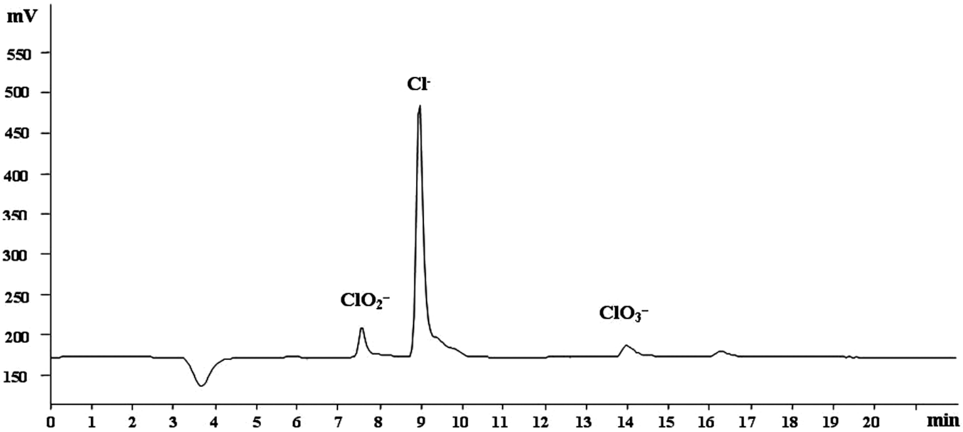

Fig. 6. Chromatogram depicting the presence of chlorites and chlorates in the water sample

4.1.4. Method for determining five-minute disinfectant demand (PZD) and rate constants of chlorine (chlorine dioxide) decay

Untreated and treated water was collected in opaque plastic containers of 1- and 1.5-litre volume. The doses of disinfectants added depended on the composition of the water. Treated water samples received lower disinfectant doses than did raw water samples. Disinfectant doses were chosen randomly from a defined range of values to comply with the rule of principal component analysis, which is that the data sets introduced should be uncorrelated. Concentrations were determined using the method described in Subsection 4.1.2.

Five-minute chlorine (chlorine dioxide) demand was calculated by subtracting the disinfectant concentration determined after 5 minutes from the initial concentration (dose) applied. The adoption of the five-minute time span was dictated by the analytical methods used, but there were also practical reasons behind it. Only in the case of on-line measurements can the initial concentration be determined immediately upon disinfectant addition. When use is made of colorimetric methods, a certain time span is required for the conversion of the solution. Vieira et al. [2004] described immediate chlorine consumption as one of the two stages of disinfectant decay. My supervisor Prof. J. Łomotowski proposed a 5-minute time span. Five-minute chlorine demand (PZD_Cl_2) and 5-minute chlorine dioxide demand (PZD_ClO_2) were established in order to ascertain whether or not the two parameters are of significance for the modelling of changes that occur in the disinfectant, as well as to establish how they influence the disinfectant dose.

Based on the experimental data describing how chlorine (chlorine dioxide) concentrations changed over time, the rate constants of chlorine decay, k_{Cl}, and chlorine dioxide decay, k_{ClO_2}, were estimated in terms of the equation of first-order reaction (equation (50)), assuming that C_0 stands for the concentration of chlorine (chlorine dioxide) after 5-minute contact of the water sample with the disinfectant. Comparison with the equations already mentioned, which describe the kinetics of change in chlorine and chlorine dioxide concentrations, has demonstrated that the equation for the kinetics of first-order reaction provides the best fitting of the data obtained. The poor correlations observed in some instances do not result from an inadequate choice of the kinetic equation; they are inherent in the concentration measurements performed. During the experiments some of the disinfectant concentration values failed to change even with long time spans.

The duration of the experiments was influenced by the rate of change in chlorine (chlorine dioxide) concentration. They were discontinued when the concentrations of the disinfectants reached values lower than those of the detection limit.

4.1.5. Statistical processing of the data obtained

To find the relationship between the independent variables and the dependent variable, use was made of the nonlinear estimation module incorporated in the STATISTICA 8 Pl software. Computations were carried out with the least squares method, which consists in minimising the sum of the squares of deviations of the observed dependent variable value from the values predicted by the model. The parameters were estimated using the quasi-Newtonian optimising algorithm based on the asymptotic convergence of the derivative of the second-order loss function defined in particular iterations.

To obtain a reliable description of the phenomenon of disinfectant decay, it is necessary to identify the largest possible number of deterministic factors in the compositions of both untreated and treated water. It is essential to note, however, that if the number of the factors being considered is excessively high, this will certainly complicate analysis, which in many instances also becomes difficult to interpret. On the other hand, a reduction in the sets of data being analysed may be concomitant with a loss of meaningful information. Among the available statistical methods offering procedures for reducing the number of variables is Principal Component Analysis (PCA).

Using the PCA method it is possible to disclose the structure of the relationship among the variables of a randomly extracted data set. PCA reveals the variance in the observed variables, as well as the correlations between them. In PCA the observed variables are considered as a set of uncorrelated components, and this enables the mathematical models to be formulated as sets of linear equations for the observed variables being analysed. Total variance in the observed variables is the sum of variance in the principal components, and the structure of the relations between the properties examined is a set of statistical procedures transforming the initial variables into new, orthogonal variables.

In the PCA approach multidimensional data are projected onto a two-dimensional space defined by two variables. The choice of the plane relates to the projection for which the sum of the squares of the differences between the data points and their projections onto this plane is smaller than for any other plane that might have been chosen. The PCA method is graphically shown in Figure 7.

All initial variables are standardised to have a variance of one (circles representing the initial variables have the same diameters). The new variable is supposed to explain the maximal amount of variance in the initial variables (in the figure the variance in the new variable is indicated by the shadowed space). The variance in the new variable explaining a certain amount of the variance in the initial variables is defined as eigenvalue.

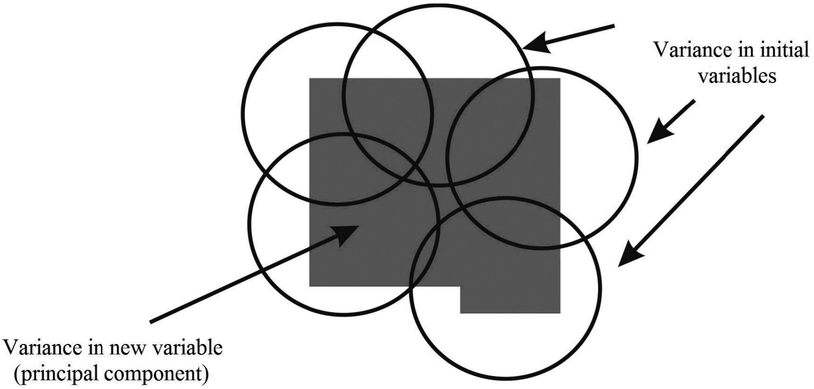

Fig. 7. Graphical interpretation of principal component analysis [Ciecielak 2009]

The object of PCA is a set of results that constitute a matrix (*X*) with dimensions $n \times p$, where *n* denotes rows, *i.e.* cases, and *p* stands for columns, *i.e.* variables (water quality parameters). Rows are vectors of data x_i; however, considering the fact that data vectors are treated as column vectors, the *i*th row of the matrix is a transposition x^T of the *i*th data vector $x(i)$.

The data matrix containing *n* realisations of *p* variables can be described iteratively as follows:

$$X = [x_{ij}] \qquad x_{ij} \geq 0; \quad i = 1,2,.....,n; \quad j = 1,2,.....,p \tag{64}$$

Upon standardisation, the variables have expected values of zero, and the following unit standard deviations:

$$Z = [z_{ij}] \tag{65}$$

In the PCA method it is assumed that variables x_i display such relations whose strength and directions are defined by the coefficients of Pearson's linear correlation. They form a correlation matrix, which is built of the values of the coefficients of the correlations between particular variables.

The basic equation of the PCA method can take the form of the following set of linear equations:

$$Z^T = AG^T \tag{66}$$

$$G = A^T Z \tag{67}$$

where:

Z – matrix of j standardised initial variables;
A – matrix of factor loadings of principal components;
G – matrix of principal components.

Each of the extracted principal components G_l is a linear combination of the observed variables Z:

$$G_l = \sum_{i=1}^{k} \sum_{j=1}^{m} a_{ij} Z_j \tag{68}$$

where:

m – number of initial variables;
k – number of principal components (which equals the number of initial variables);
Z_j – jth standardised variable (initial variable);
G_l – lth principal component;
a_{jt} – factor loadings.

The solution consists in determining the factor loadings a_{jl} in such a way that the principal component explains the maximal amount of variance in the initial variables. Each lth principal component is a linear combination of initial variables and explains the ith amount of total variability.

The first principal component is an eigenvector which corresponds with the highest eigenvalue of the covariance matrix (variance matrix for multidimensional data) under the assumption that:

$$a_1^T a_1 = 1 \tag{69}$$

The second principal component (direction perpendicular to the first component, with the highest projected variance) is an eigenvector corresponding with the second highest eigenvalue. It is a linear combination of initial variables, which maximises the variance under the following conditions:

$$a_1^T a_1 = 1 \text{ and } a_1^T a_2 = 0 \tag{70}$$

In the PCA method use is made of three criteria that enable the number of components to be reduced. The first one involves the percentage of variance explained by a component. If the sum of variance in the first few components accounts for most of the variance in all of the components being analysed, the other ones can be discarded. Generally, the sum of variance should range higher than between 75 and 80%. The second criterion is the Kaiser criterion based on the rule that solely components with eigenvalues higher than 1 should be retained. The third criterion involves the so-called Cattell scree plot, which is a line that shows the eigenvalues associated with each component. It is necessary to find such a point (break) that separates meaningful eigenvalues from those less important, indicating where the increment in information begins to level off. Before that point (on the left-hand side of the break), the plot displays an obviously gentle slope. This is why the values for analysis should be taken from among those appearing before the break [Stanisz 2007].

The suitability of the PCA method is measured by the amount of total variance explained. If in a set of dozen variables the first component explains 85% of the variance for example, this is an indication that almost all of the variance in this set can be shown by a straight line instead of by dozen dimensions. As a result, there are as many principal components as were initial variables. We still have an *m*-dimensional set, but in fact we limit ourselves to the first few principal components that explain the amount of *a priori* defined variance.

Principal component analysis has found wide acceptance as a tool for reducing the dimensions of the vectors of experimental results in various fields of science and technology. In Environmental Engineering, for example, PCA was used for assessing surface water quality [Boyacioglu 2006, Boyacioglu, Boyacioglu 2008] and determining the chemical composition of groundwater [Kotowski, Kachnic 2007].

4.2. Effect of chlorine dioxide dose on chlorite and chlorate concentrations

4.2.1. Effect of the mole ratio of hydrochloric acid to sodium chlorite

Our first study on the disinfection by-products (DBPs) that form in the water being disinfected with chlorine dioxide was conducted in July 2008. In that study, tap water subjected to disinfection with chlorine dioxide was analysed for the presence of chlorites and chlorates. Chlorine dioxide was obtained from WTP Mokry Dwór in Wrocław, where it was produced using sodium chlorite and gaseous chlorine. During chlorine dioxide production, chlorine water was generated by dissolving chlorine in 1.5 m^3 of water at a rate of 4.5 $kg \cdot h^{-1}$, followed by mixing with 25% sodium chlorite at a rate of 26.5 $l \cdot h^{-1}$. The mole ratio of chlorine to sodium chlorite was 0.72. Prior to disinfection, the water samples were treated by coagulation and filtration, and did not contain a disinfectant.

The influence of the chlorine dioxide dose on the sum of chlorite and chlorate ions determined chromatographically is depicted in Figure 8, which has revealed a proportional relation between them. The plot in Figure 8 has furthermore disclosed that the sum of chlorite and chlorate ions accounts for more than 77% of the chlorine dioxide dose applied. This value is much higher than the one reported in the literature [Dojlido 2002]. With the chlorine dioxide dose of 0.4 $mg \cdot dm^{-3}$, the sum of chlorite and chlorate ions formed is 0.7 mg, which accounts for 175% of the ClO_2 dose applied.

These findings prompted us to perform additional analyses with the aim to ascertain why the amounts of chlorite and chlorate ions that form during water disinfection with chlorine dioxide are so high. To eliminate the impact of water composition on their formation when use is made of chlorine dioxide as a disinfectant, our investigations were carried out with deionised water. Their objective was to demonstrate to what extent the concentration of the sum of chlorites and chlorates is influenced by the mole ratio of hydrochloric acid to sodium chlorite that was used for the production of chlorine dioxide. For this purpose, one-mole hydrochloric acid solutions and one-mole sodium chlorite solutions were prepared and then mixed in appropriate proportions (Tab. 12). After 20 minutes, the deionised water was treated with the chlorine dioxide solution in amounts of 1 mg·dm^{-3}. Chlorine dioxide concentration was measured by the DPD method, and the concentrations of chlorites and chlorates were determined by ion chromatography. The results are summarised in Table 12 and plotted in Figures 9 to 11.

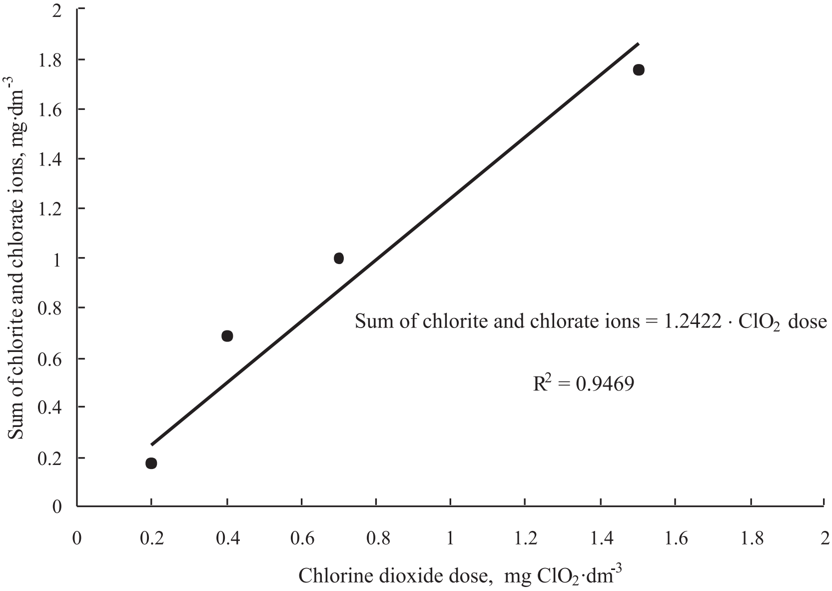

Fig. 8. Effect of chlorine dioxide dose on the sum of chlorite and chlorate concentrations in tap water, as determined by chromatography during studies at WTP Mokry Dwór, Wrocław, on 7 to 8 July 2008

Table 12

Effect of the ratio of hydrochloric acid to sodium chlorite on the increment in the concentration of the sum of chlorite and chlorate ions

Ratio of hydrochloric acid to sodium chlorite	Sum of chlorite and chlorate ion concentrations in water at the chlorine dioxide dose of 1 mg·dm^{-3}
0.25	7.46
0.50	3.36
1.00	1.17
2.00	0.92
4.00	0.75

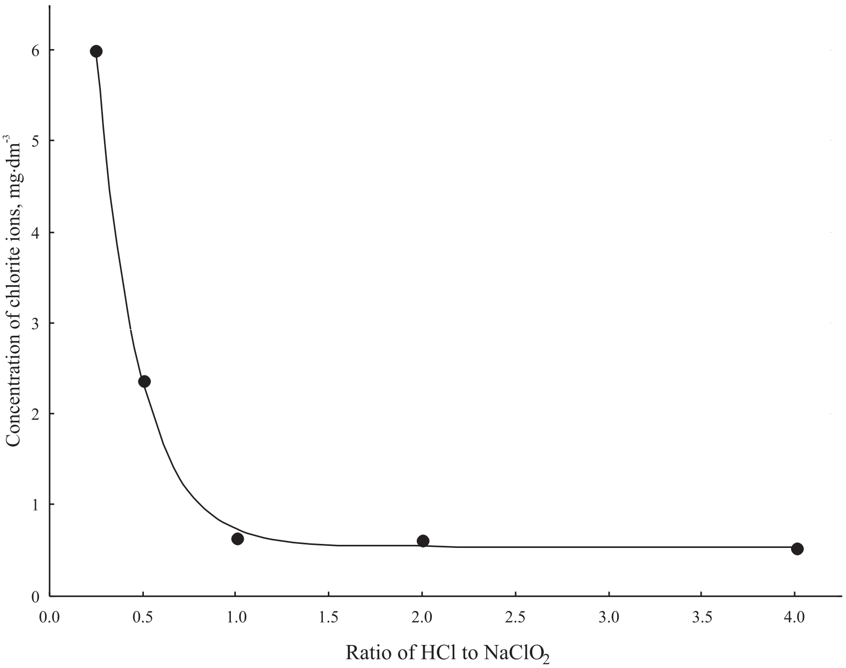

Fig. 9. Concentration of chlorite ions related to the ratio of hydrochloric acid to sodium chlorite

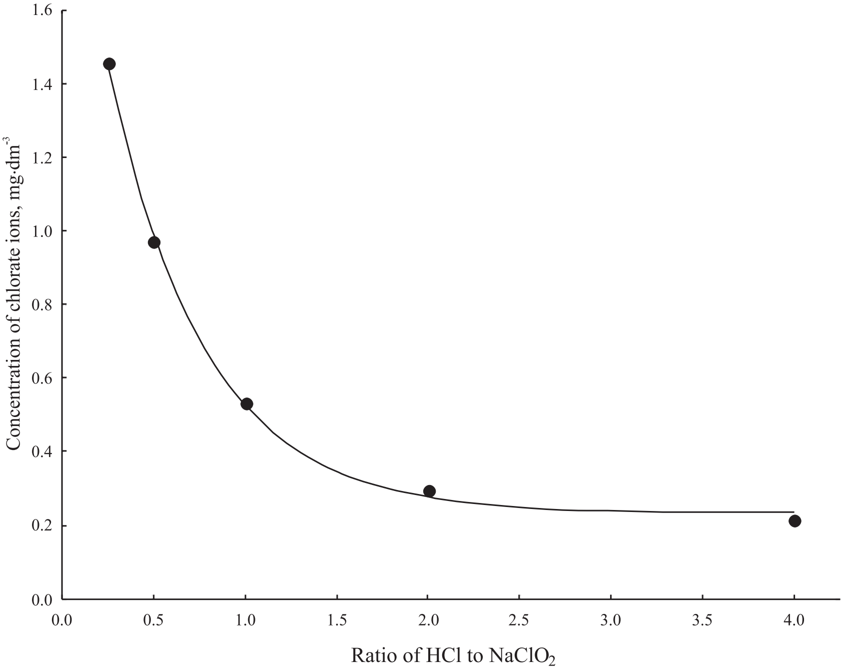

Fig. 10. Concentration of chlorate ions related to the ratio of hydrochloric acid to sodium chlorite

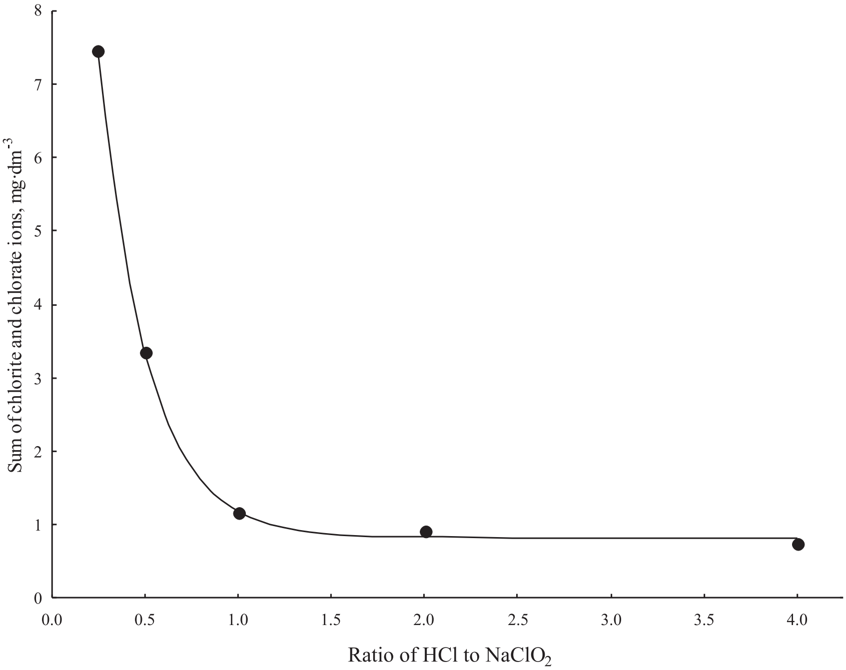

Fig. 11. Concentration of the sum of chlorite and chlorate ions related to the ratio of hydrochloric acid to sodium chlorite

With a chlorine dioxide dose of 1 mg·dm^{-3}, the increase in the ratio of hydrochloric acid to sodium chlorite was paralleled by a decrease in the concentrations of chlorites and chlorates. The lowest concentrations of chlorites and chlorates were obtained when the molar ratio of hydrochloric acid to sodium chlorite amounted to 4. Upon addition of chlorine dioxide, the pH of the water varied from 4 to 5, the lowest values being measured at the hydrochloric acid/sodium chlorite ratio of 4. With a chlorine dioxide dose of 1 mg·dm^{-3} and a 1:1 molar ratio of hydrochloric acid to sodium chlorite (most frequently used for the production of chlorine dioxide in generators), the concentrations of chlorites and chlorates were 0.64 and 0.53 mg·dm^{-3}, respectively, whereas the sum of the concentrations of the sum of these ions greatly exceeded the admissible value of 0.7 mg·dm^{-3}.

The experiment has shown that the sum of chlorite and chlorate ions in water disinfected with chlorine dioxide can be determined using simple proportional relations. When the excess of hydrochloric acid in relation to sodium chlorite increases, the concentrations of chlorites and chlorates decrease (Tab. 12). The increment in the concentrations of these ions is strongly influenced by the decrease in the molar ratio of hydrochloric acid to sodium chlorite to a level lower than 1.

In the experiments performed at the chlorine dioxide dosing station operated at WTP Mokry Dwór, the factor of proportionality between the increment in the concentration of the sum of chlorites and chlorates and the dose of chlorine dioxide applied was 1.2422 mg·mg^{-1} (Fig. 8). This value does not very much differ from the proportionality factor value of 1.17 mg·mg^{-1} obtained under laboratory conditions with a 1:1 ratio of hydrochloric acid to sodium chlorite.

The results obtained make it clear that either the conversion of chlorine dioxide components has to be brought under control, or the existing standards for the admissible chlorine dioxide dose have to be tightened. In the light of these findings, it is not surprising that in Germany the admissible chlorine dioxide dose cannot be higher than 0.4 mg·dm^{-3} (DIN EN--12671:2000).

Although the use of chlorine dioxide under such conditions does not raise technological problems, it necessitates controlling the fate of this disinfectant, as well as the concentrations of chlorites and chlorates, in the water distribution system. The point is that only few laboratories possess ion-exchange chromatographs and are ready to carry out relevant analyses. In Lower Silesia, for example, only two laboratories are sufficiently well prepared for performing costly analyses of the sum of chlorite and chlorate ions.

4.2.2. Formation of chlorites and chlorates in cold and hot water installations of a hospital water system

A major advantage of using chlorine dioxide as a disinfectant in hospital water systems is the inhibition of *Legionella* growth in hot water installations. To reduce *Legionella*-related infections inside the hospital, chlorine dioxide is preferentially added to the water that feeds these installations. In the framework of the study reported on here, one of Wrocław's hospitals was selected as a test object. In this hospital 80% of the water feeding the internal installations comes from the local water treatment station, and 20% is derived from the municipal water supply system. The water coming from the hospital's treatment station is purified using a treatment train that involves pre-aeration and pressure filtration through a DEFEMAN catalytic bed. After treatment, the water is disinfected with chlorine dioxide. The flow diagram for the local treatment station is shown in Photo 1.

Chlorine dioxide is generated from hydrochloric acid and sodium chlorite. The generator of chlorine dioxide is shown in Photo 2.

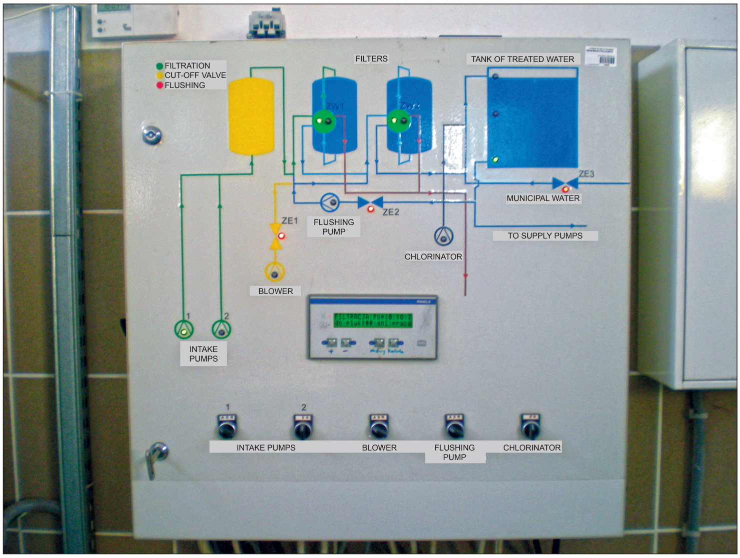

Photo 1. Control cabinet of the groundwater treatment station operated by the hospital

Investigations into the hospital water system were aimed at demonstrating that the concentrations of the disinfection by-products found in both cold and hot water installations undergo changes. The points of water sampling are shown in Figure 12. The composition of the water determined over the period of the study is characterised in Table 13.

Photo 2. Chlorine dioxide generator installed at the water treatment station in one of Wrocław's hospitals

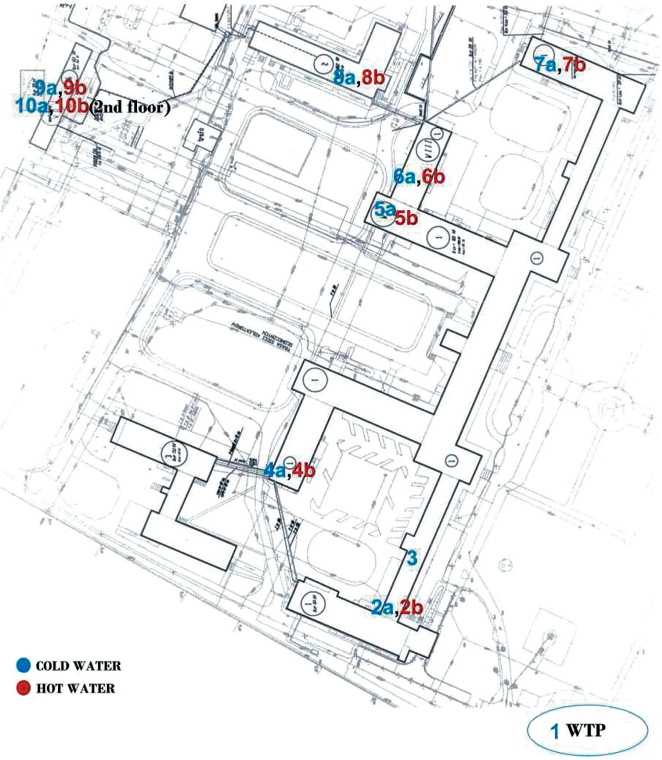

Fig. 12. Sampling points within the area of the hospital

Table 13

Results obtained from analysis of water collected at different sampling points located within the area of the water treatment plant operated by the hospital

Water quality parameter	Unit	Raw water drawn from the well	Treated water (after aeration and filtration)	Municipal water	Treated water + municipal water + ClO_2*
Turbidity	NTU	9	3	0.19	3
Colour	mg Pt·dm^{-3}	30	20	5	10
Smell		Specific H_2S	Acceptable	Acceptable	Acceptable
pH	pH	6.7	7.0	6.8	6.8
Alkalinity	mval·dm^{-3}	4.8	3.6	3	4.4
Total hardness	mg $CaCO_3$·dm^{-3}	640	528.5	285.7	589.2
Iron	mg Fe·dm^{-3}	12.8	0.85	0.05	0.45
Manganese	mg Mn·dm^{-3}	1.1	0.02	0.05	0.05
Chlorides	mg Cl^-·dm^{-3}	72	56	54	56
Ammonia	mg NH_4·dm^{-3}	0.2	<0.05	<0.05	<0.05
Nitrites	mg NO_2·dm^{-3}	0.03	0.056	0.03	0.04
Nitrates	mg NO_3·dm^{-3}	1.7	9.6	15	3.5
Permanganate COD	mg O_2·dm^{-3}	6.5	3.6	3.3	3.4
Calcium	mg Ca·dm^{-3}	211	158.6	80	187.1
Magnesium	mg Mg·dm^{-3}	25	25	19	19
Conductivity	µScm^{-1}	1033	931	563	994

Nonation: *Water feeding the hospital's cold and hot water installations.

Tap water samples were collected twice, on 18 February and 15 March 2010. During the study performed on 18 February, use was made of a chlorine dioxide dose amounting to 0.8 mg·dm^{-3}, which was reduced to 0.4 mg·dm^{-3} in the study of 15 March. In both instances, the disinfectant was produced using the local generator. Over the period of the two studies, no chlorine dioxide was detected at any of the sampling points. The temperature of cold water was approximately 8ºC, and that of hot water approached 40ºC. Chlorite and chlorate concentrations were determined by chromatography, 24 h after sample collection. During transport, the temperature of the water samples did not exceed 10ºC. Water was also analysed for turbidity and UV_{254}. The results of analysis are summarised in Table 14.

Table 14

Concentrations of chlorates, chlorites and turbidity measured in the hospital water system on 18 February and 15 March 2010

Sampling point	Analyses performed on 18 February 2010				Analyses performed on 15 March 2010			
	Turbidity	Chlorite ions	Chlorate ions	$ClO_2^- + ClO_3^-$	Turbidity	Chlorite ions	Chlorate ions	$ClO_2^- + ClO_3^-$
	NTU	mg·dm^{-3}			NTU	mg·dm^{-3}		
1	0.28	1.22	0.05	1.27	0.98	0.41	0.24	0.65
2a	0.23	1.07	0.16	1.23	0.23	0.18	0.07	0.25
2b	0.28	1.27	–	1.27	0.27	0.14	0.09	0.23
3	0.27	1.18	0.15	1.33	0.25	0.15	0.09	0.24
4a	0.20	0.77	–	0.77	0.26	0.17	0.09	0.26
4b	0.60	1.21	0.21	1.42	0.32	0.13	0.07	0.2
5a	0.22	0.85	0.26	1.11	0.25	0.17	0.09	0.26
5b	1.26	1.03	0.23	1.26	0.31	0.13	0.07	0.2
6a	0.33	1.08	0.22	1.3	0.34	0.13	<0.01	0.13
6b	0.32	1.01	0.13	1.14	0.4	0.14	<0.01	0.14
7a	0.41	1.13	0.14	1.27	0.25	0.17	0.07	0.24
7b	0.54	0.97	–	0.97	0.33	0.12	0.06	0.18
8a	0.50	2.18	0.28	2.46	0.34	0.14	0.07	0.21
8b	0.95	0.86	0.22	1.08	0.3	0.13	0.08	0.21
9a	0.28	2.17	0.31	2.48	0.27	0.16	0.07	0.23
9b	0.75	1.24	0.11	1.35	0.27	0.09	<0.01	0.09
10a	0.53	–	–	–	0.28	0.14	0.08	0.22
10b	1.83	0.54	0.31	0.85	0.31	0.08	<0.01	0.08

Figure 13 shows the concentrations of the sum of chlorite and chlorate ions in the samples collected from the hospital's cold water installation. The red line indicates the admissible concentration value specified in the Polish standard for the sum of chlorites and chlorates in water. The data in Figure 13 make it clear that with the dose of 0.8 mg dm^{-3}, the admissible concentration value for the sum of the two ions has been exceeded in every instance. When the chlorine dioxide dose was reduced to 0.4 mg·dm^{-3}, the concentration of the sum of chlorites and chlorates decreased significantly.

Figures 14 and 15 show the differences between chlorite concentrations obtained with the two chlorine dioxide doses both in cold and hot water installations; Figures 16 and 17 depict the differences observed in chlorate concentrations, whereas Figures 18 and 19 illustrate those noted in the concentration of the sum of chlorite and chlorate ions.

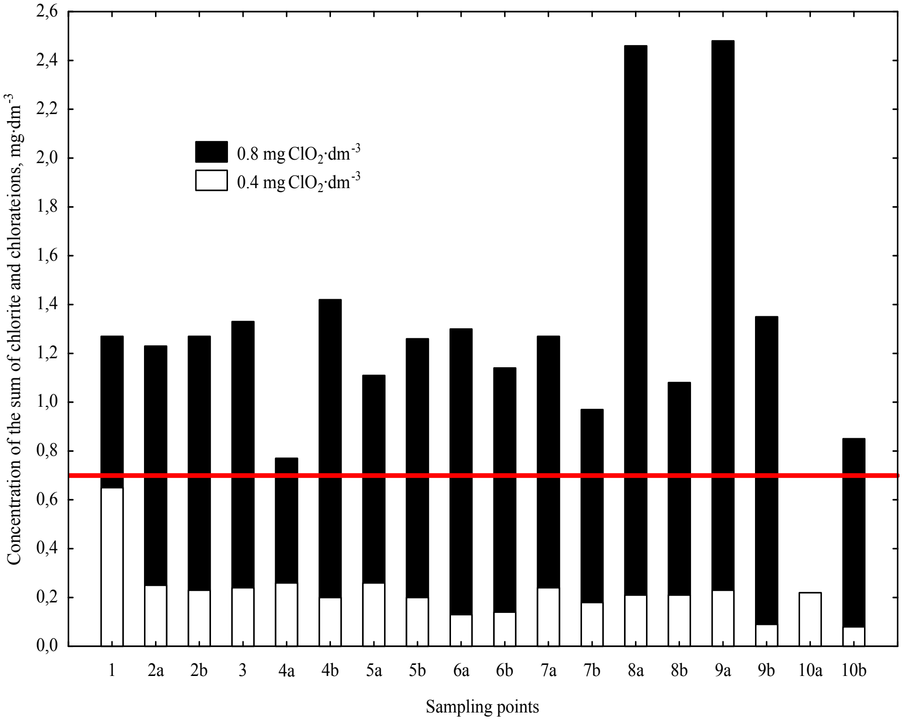

Fig. 13. Concentration of the sum of chlorite and chlorate ions in samples of hospital water collected on 18 February and 15 March 2010 (red line indicates admissible concentration of the sum of chlorite and chlorate ions in cold water)

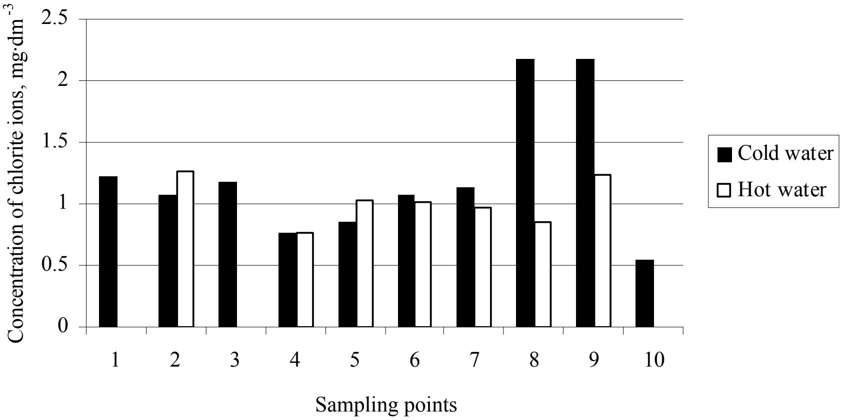

Fig. 14. Concentrations of chlorite ions in hospital water samples collected on 18 February 2010

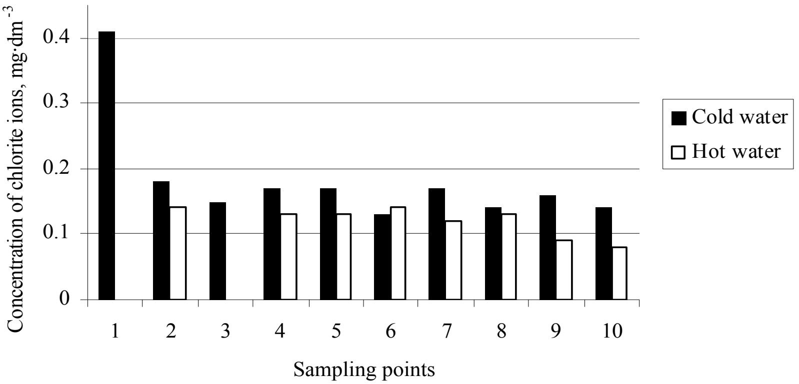

Fig. 15. Concentration of chlorite ions in hospital water samples collected on 15 March 2010

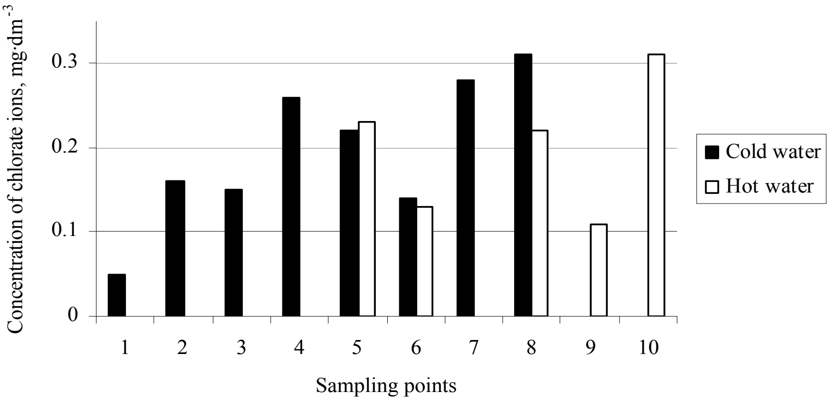

Fig. 16. Concentration of chlorate ions in hospital water samples collected on 18 February 2010

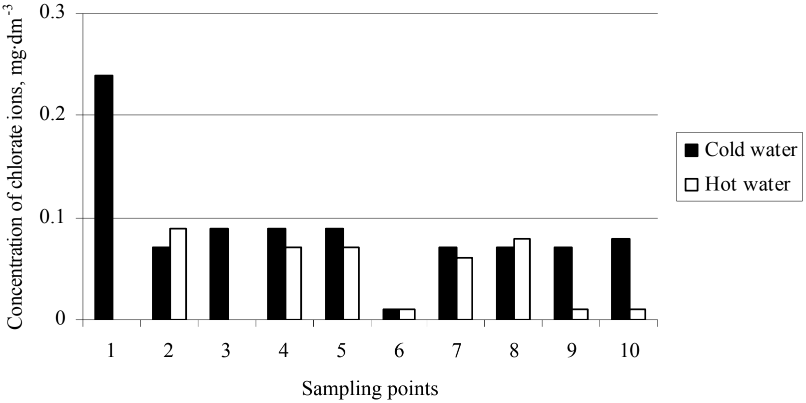

Fig. 17. Concentration of chlorate ions in hospital water samples collected on 15 March 2010

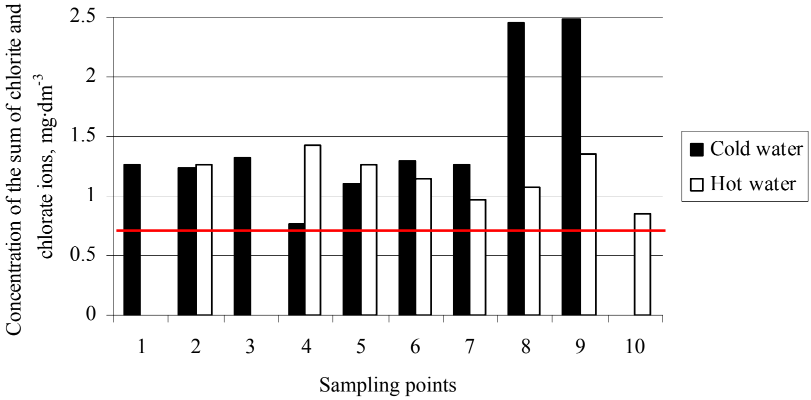

Fig. 18. Concentration of the sum of chlorite and chlorate ions in hospital water samples collected on 18 February 2010

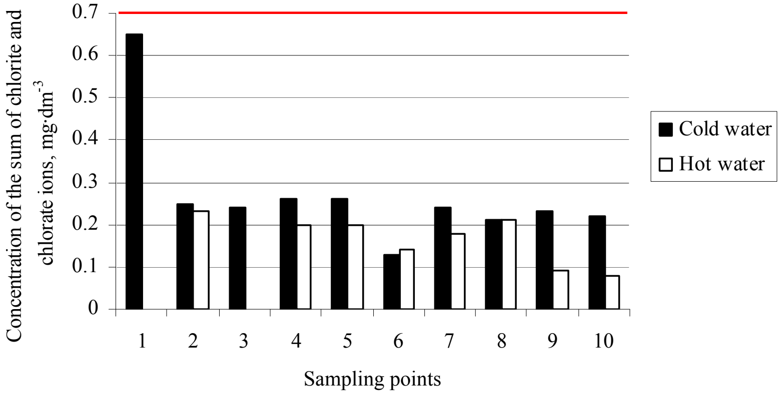

Fig. 19. Concentration of the sum of chlorite and chlorate ions in hospital water samples collected on 15 March 2010

The tests of 18 February were conducted one month after the start-up of the chlorine dioxide generator. In those days various chlorine dioxide doses were applied, and the concentrations of chlorites and chlorates at the sampling points were characterised by high variability. Upon reduction of the chlorine dioxide dose and after adjustment of the generator, chlorite and chlorate concentrations both in cold and hot water were found to decrease (Figs. 15, 17 and 19) with increasing distance from the hospital water treatment system.

Zhang [2007], who tested two hospital water systems in Pittsburgh, found that chlorite and chlorate concentrations were higher in hot water than cold water installations. This finding was not confirmed by the study of the hospital water system in Wrocław. Our study demonstrated that UV_{254} absorbance increased with increasing distance from the hospital water treatment plant (Fig. 20). This finding provides indirect evidence for biofilm growth in the hospital water system examined. No relationship was found to occur between UV_{254} absorbance and the concentrations of chlorites and chlorates.

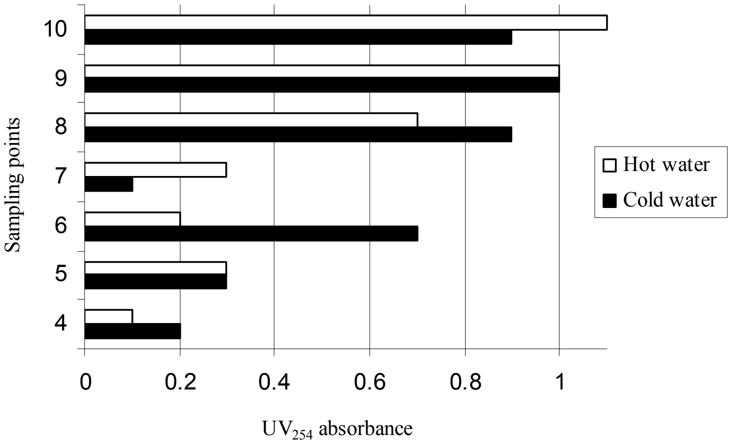

Fig. 20 Comparison of UV_{254} absorbance in cold and hot hospital water samples collected on 15 March 2010

The results obtained show that the application of chlorine dioxide as a disinfectant requires analytical control of chlorites and chlorates, as well as of the ratio of the reagents used for chlorine dioxide generation. Lack of analytical control may cause the concentrations of chlorites and chlorates in tap water to significantly exceed the admissible levels.

4.3. Effect of water composition on the rate of chlorine and chlorine dioxide decay

4.3.1. Sampling points

In order to establish how the composition of the water affects the rate of chlorine and chlorine dioxide decay, samples of treated and untreated water were collected from different water treatment plants. The majority of them, however, are located in the Lower Silesia District (Województwo Dolnośląskie). Surface water samples were collected at WTP Mokry Dwór in Wrocław, and also at the intakes in Polanica-Zdrój and Ostroszowice. The other samples were taken at groundwater treatment plants. Two water samples were taken from a well located in Kajakowa Street, Warsaw. The groundwater examined in the framework of this work was drawn from Tertiary and Quaternary formations. The locations of the sampling points were chosen so as to provide sufficient variance in the composition of the water. Figure 21 shows the sampling points located in Lower Silesia.

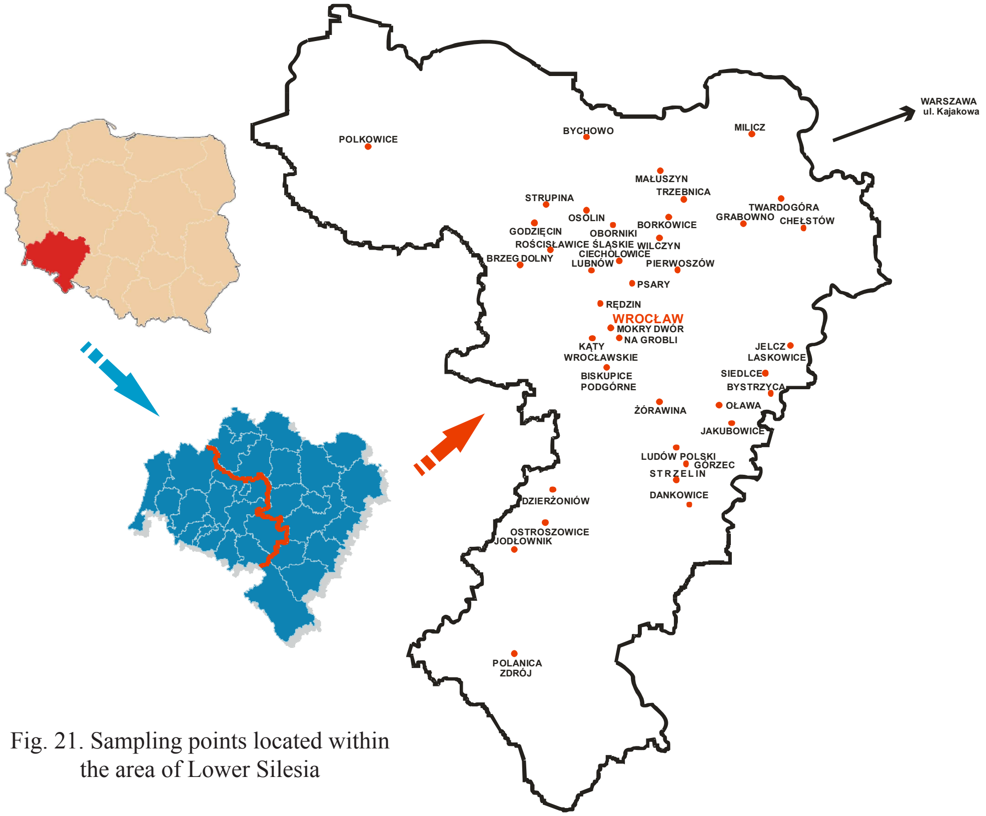

Fig. 21. Sampling points located within the area of Lower Silesia

The study involved 43 raw water and 33 treated water samples. The groundwater and surface water intakes are characterised in Tables 15 and 16, respectively.

Table 15

Characteristics of groundwater intakes

Sampling point	Date of sampling	Number of well / Depth of well in m	Treatment train	Type of disinfectant
1	2	3	4	5
Polkowice	November 2007	8/44-76	PA-PF-D	SH
Strzelin (Brzegowa)	January 2008	4/12-15	PA-PF-O-CF-D	SH
Biskupice Podgórne		5/90-125	PA-PF-D	SH
Strzelin (Górzec)	February 2008	2/40	PA-PF-D	SH
Strzelin (Dankowice)		2/45	PA-PF-D	SH
Żórawina		2/80	PA-PF-D	SH
Brzeg Dolny		2/41,48	PA-PF-D	SH
Jodłownik		1/149,5	O-PA-PF-D	SH
Dzierżoniów		18/18-57	O-PA-PF-D	SH

Table 15 cont.

1	2	3	4	5
Polanica-Zdrój (BS1, BS6, Nowa Sokołówka, Stara Sokołówka)	April 2008	2/no data	D	SH
Polanica-Zdrój (BS4, Wojska Polskiego, Zbiornik Piastowski 7 and 13)	May 2008	No data	D	SH
Kąty Wrocławskie	June 2008	17/no data	PA-PF-D	SH
Oborniki Śląskie	August 2008	12/22-100	PA-PF-D	SH
Godzięcin		2/no data	PA-PF-D	SH
Jelcz-Laskowice		6/30	LW-PLA-PF-D	SH
Strzelin (Ludów Polski)	September 2008	2/8	PA-PF-D	SH
Trzebnica	February 2009	5/74-94	PA-PF-D	JS
Warszawa	February 2009	2/40-50	PA-PF-D	SH
Psary	March 2009	3/40	PA-PF-D	SH
Rościsławice		1/50	PA-PF-D	JS
Bychowo	April 2009	6/60-80	PA-PF-PLA-PF-D	SH
Rędzin	June 2009	1/10	PA-PF-D	SH
Borkowice		2/50	PA-PF-D	JS
Wilczyn		2/40	PA-PF-D	SH
Lubnów		3/30-35	PA-PF-PLA-D	SH
Ciecholowice		1/50	PA-PF-D	LB
Pierwoszów	July 2009	1/30	PA-PF-D	LB
Osolin		2/38,43	PA-PF-D	SH
Milicz		1/60	PA-PF-D	SH
Twardogóra		4/25-38	PA-PF-D	SH
Chełstów		1/39	PA-PF-D	SH
Grabowno Wielkie		3/50	PA-PF-D	SH
Jakubowice	August 2009	1/30	PA-PF-D	SH
Bystrzyca		1/100	PA-PF-D	SH
Siedlce near Oława		1/70	PA-PF-D	SH

Notation: PA – pressure aeration, PLA – pressureless aeration, PF – pressure filters (mainly mineral, for iron and manganese removal, single- and multilayer), CF – carbon filters, O – oxidation, LW – limewater, D – disinfection, SH – sodium hypochlorite, SL – sterilamp, JS – Jasol-Solid

Table 16

Characteristics of surface water intakes

Sampling point	Date of sampling	Type of intake	Treatment train	Type of disinfectant
Wrocław Mokry Dwór	February 2008	Nysa Kłodzka River – Oława River	RMT-SMT-ST-SF-O-FW-D	O_3 Cl_2 ClO_2
Wrocław Na Grobli		Infiltrative water	AT-SF-O-CF-D	O_3 Cl_2
Ostroszowice		7 surface intakes in the Owl Mountains (Góry Sowie)	PF-D	SH
Polanica-Zdrój (Polna)	May 2008	Natural outflow	D	SH
Polanica-Zdrój (Polna)		Drainage intake	D	SH

Notation: RMT – rapid mix tank, SMT – slow mix tank, ST – settling tanks, SF – sand filters, CF – carbon filters, AT – aeration tower, D – disinfection, PF – pressure filters, SH – sodium hypochlorite

4.3.1. Physicochemical composition

The physicochemical composition of the water samples examined is characterised in Tables 17 to 20. Table 20 summarises the minimal and maximal values of the parameters describing the quality of the sets of raw and treated water.

Turbidity of raw water samples was highly variable, ranging from 0.14 NTU for the intakes in Polanica-Zdrój to 57 NTU for the intake in Jodłownik. Treated water samples displayed turbidities lower than 1 NTU (the admissible limit value for drinking water) in the majority of instances. There were a few exceptions, and among them a notable one, the intake in Godzięcin, where turbidity amounted to 7.2 NTU. Total iron concentration varied from 0.2 to 15 mg Fe·dm^{-3} in raw water, and reached 1.5 mg Fe·dm^{-3} in treated water samples. The pH of raw water ranged between 5.6 and 8.10, whereas that of treated water varied from 6.2 to 8.7. Manganese concentration in treated samples fell between 0 and 0.11 mg Mn·dm^{-3} for water collected from the Bystrzyca River near Oława. Raw water samples were characterised by a manganese content ranging from 0.01 mg Mn·dm^{-3} for an intake in Polanica-Zdrój to 0.89 mg Mn·dm^{-3} for the intake in Twardogóra. The admissible conductivity value, which is 2500 μS·cm^{-1}, was not exceeded in any of the water samples examined. Raw water samples collected in Strzelin, Rędzin, Borkowice and Siedlce exhibited high conductivity, which varied between 1118 and 2006 μS·cm^{-1}, whereas that measured in the water samples from Polanica-Zdrój was lower than 100 μS·cm^{-1}. Permanganate COD ranged from 1 to 10.40 mg O_2·dm^{-3} in raw water samples. In treated water, it was found to be lower than the admissible value 5 mg O_2·dm^{-3} in all samples but one. The only exception was in the sample from Strzelin (Górzec), where permanganate COD reached the limit value. Alkalinity ranged from 0.4 to 7.6 mval·dm^{-3}, and hardness from 39.20 to 557.14 mg $CaCO_3$·dm^{-3}, both in treated and untreated water. Ammonium ion content of all the samples examined was between 0.03 to 0.77 mg NH_4·dm^{-3}, and chloride content fell in the range of 1.5 to 108 mg Cl^-·dm^{-3}. The presence of nitrates was detected in the majority of both raw and treated water samples, the maximal concentration value, 26.4 mg NO_3^-·dm^{-3}, being measured in the treated water sample collected at WTP Jelcz-Laskowice.

UV_{254}, which ranged between 0.2 and 17.4 m^{-1}, was generally lower in treated than in untreated water.

Table 17

Physicochemical parameters of raw water samples

Sampling point	Turbidity	Total iron	Fe^{2+}	Fe^{3+}	pH	Manganese	Conductivity	Permanganate COD	Alkalinity	Hardness	Ammonium ion	Chlorides	Nitrates
	NTU	mg Fe·dm^{-3}			pH	mg Mn·dm^{-3}	µS·cm	mg O_2·dm^{-3}	mval	mg $CaCO_3$·dm^{-3}	mg NH_4^+·dm^{-3}	mg Cl^-·dm^{-3}	mg NO_3^-·dm^{-3}
Strzelin (Brzegowa)	28.00	15.00	0.00	15.00	6.30	0.85	1300.00	5.10	5.20	557.14	0.20	80.00	22.00
Strzelin (Górzec)	7.30	1.70	0.00	1.70	6.30	0.12	552.40	4.90	4.40	235.71	0.26	14.00	0.00
Biskupice Podgórne	11.80	1.60	0.00	1.60	6.20	0.10	504.00	1.70	4.80	228.57	0.28	10.00	0.00
Żórawina	7.40	1.50	0.00	1.50	8.10	0.13	594.00	1.80	5.60	225.00	0.26	14.00	22.00
Ostroszowice	0.27	0.20	0.05	0.15	7.20	0.02	158.00	1.60	1.20	92.85	0.03	2.00	5.28
Dzierżoniów	1.90	8.00	1.30	6.70	7.20	0.68	879.00	1.00	5.20	457.14	0.13	30.00	0.88
Strzelin (Dankowice)	10.40	2.30	0.50	1.80	7.40	0.13	581.40	1.00	5.80	332.14	0.05	10.00	0.00
Strzelin (Ludów Polski)	21.50	3.30	0.20	3.10	7.40	0.11	605.00	1.70	5.20	260.71	0.26	6.00	0.88
Trzebnica	–	0.10	0.00	0.10	7.30	0.06	861.80	1.50	6.20	403.57	0.03	34.00	0.88
Wrocław Mokry Dwór	6.60	0.30	0.05	0.25	8.00	0.03	525.90	4.50	3.00	267.85	0.10	36.00	17.60
Brzeg Dolny	40.00	11.60	11.50	0.10	7.50	0.23	519.60	1.00	4.00	239.28	0.33	4.00	0.88
Jodłownik	57.10	0.55	0.00	0.55	7.60	0.03	325.50	10.40	0.60	64.28	0.05	8.00	6.16
Wrocław Na Grobli	20.00	3.10	0.00	3.10	7.90	0.34	526.00	5.00	2.60	242.80	0.26	36.00	1.76
Kąty Wrocławskie	15.00	2.80	2.10	0.70	7.20	0.11	315.00	2.00	3.20	132.14	0.15	6.00	0.88
Bychowo	52.00	11.00	0.00	11.0	7.30	0.16	613.00	5.20	5.80	285.70	0.77	34.00	1.76
Polanica (BS1)	0.20	0.05	–	–	7.20	0.01	338.00	1.10	3.80	189.20	0.10	6.00	1.70
Polanica (BS6)	0.20	0.05	–	–	6.60	0.01	147.00	1.00	1.20	75.00	0.07	6.00	6.10
Polanica (Stara Sokołówka)	2.90	0.10	–	–	6.50	0.01	130.00	4.20	0.80	53.50	0.13	6.00	3.50
Polanica (Nowa Sokołówka)	0.55	0.10	–	–	6.70	0.02	86.10	6.00	0.60	39.20	0.15	8.00	3.50
Polanica (Wojska Polskiego)	0.80	0.15	–	–	6.20	0.02	140.00	1.50	0.40	60.70	0.05	6.00	2.20

Table 17 cont.

Sampling point	Turbidity	Total iron	Fe^{2+}	Fe^{3+}	pH	Manganese	Conductivity	Permanganate COD	Alkalinity	Hardness	Ammonium ion	Chlorides	Nitrates
	NTU	mg Fe·dm^{-3}			pH	mg Mn·dm^{-3}	µS·cm	mg O_2·dm^{-3}	mval	mg $CaCO_3$·dm^{-3}	mg NH_4^+·dm^{-3}	mg Cl^-·dm^{-3}	mg NO_3^-·dm^{-3}
Polanica (BS4)	0.55	0.10	–	–	5.60	0.02	178.00	1.50	1.60	78.50	0.05	4.00	0.88
Polanica (drainage)	0.25	0.05	–	–	5.90	0.02	289.00	1.30	0.80	96.40	0.05	54.00	26.00
Polanica (Zbiornik Piastowski 13)	0.14	0.05	–	–	6.70	0.01	240.00	1.00	1.60	121.40	0.05	2.00	13.00
Polanica (Zbiornik Piastowski 7)	0.40	0.05	–	–	7.20	0.02	502.00	1.80	4.60	278.50	0.05	12.00	8.80
Polanica (outflow)	0.26	0.05	–	–	6.40	0.01	611.00	2.80	1.80	164.20	0.05	18.00	17.60
Warszawa (Kajakowa 2)	0.23	2.40	–	–	7.10	0.28	514.00	1.00	3.20	250.00	0.15	44.00	0.88
Warszawa (Kajakowa 3)	0.15	2.50	–	–	7.30	0.08	640.00	1.50	5.40	157.00	0.43	70.00	0.88
Psary	16.70	1.80	–	–	7.40	0.18	717.00	2.20	7.00	314.20	0.25	26.00	0.88
Rościsławice	9.50	1.70	–	–	7.20	0.23	434.00	2.10	3.80	214.20	0.10	12.00	0.88
Rędzin	6.40	1.50	0.00	1.50	7.10	0.80	2006.00	7.80	3.20	303.60	0.48	12.50	0.00
Borkowice	24.10	2.00	0.40	1.60	6.90	0.30	1226.00	2.50	5.40	410.70	0.25	2.20	0.00
Wilczyn	6.60	4.20	3.30	0.90	7.20	0.10	661.00	1.60	6.00	375.00	0.03	1.50	0.00
Lubnów	0.40	0.05	0.00	0.05	6.90	0.50	564.00	2.40	3.40	307.10	0.51	2.10	0.02
Ciecholowice	17.00	3.00	1.00	2.00	7.30	0.37	468.00	2.40	3.20	271.40	0.15	24.00	0.88
Pierwoszów	15.10	2.20	0.80	1.40	7.90	0.17	744.00	1.30	7.60	407.10	0.04	24.00	4.40
Osolin	32.00	2.50	1.20	1.30	7.20	0.16	340.00	2.00	3.00	175.00	0.05	22.00	3.50
Milicz	0.27	0.10	0.10	0.00	7.30	0.10	352.00	2.20	2.00	150.00	0.03	18.00	11.40
Twardogóra	2.90	0.80	0.45	0.35	7.30	0.25	224.00	2.30	2.40	178.57	0.03	12.00	0.88
Chełstów	17.50	7.30	4.70	2.60	7.50	0.89	275.50	2.10	2.40	196.43	0.05	18.00	7.04
Grabowno Wielkie	1.10	0.60	0.40	0.20	6.90	0.13	235.50	2.10	1.00	132.14	0.03	16.00	8.80
Jakubowice	14.80	2.30	0.70	1.60	7.50	0.26	476.10	1.50	4.40	325.00	0.10	38.00	0.88
Bystrzyca	5.30	1.40	0.40	1.00	7.50	0.12	322.80	3.10	3.80	153.57	0.31	8.00	0.88
Siedlce near Oława	12.80	1.50	0.30	1.20	7.40	0.35	1118.00	2.40	5.60	482.14	0.64	108.00	1.76

Table 18

Physicochemical parameters of treated water samples

Sampling point	Turbidity	Total iron	Fe^{2+}	Fe^{3+}	pH	Manganese	Conductivity	Permanganate COD	Alkalinity	Hardness	Ammonium ion	Chlorides	Nitrates
	NTU	mg Fe·dm^{-3}			pH	mg Mn·dm^{-3}	µS·cm	mg O_2·dm^{-3}	mval	mg $CaCO_3$·dm^{-3}	mg NH_4^+·dm^{-3}	mg Cl^-·dm^{-3}	mg NO_3^-·dm^{-3}
Strzelin (Brzegowa)	0.70	0.05	0.00	0.05	6.30	0.02	534.7	5.00	4.20	242.85	0.03	20.00	0.88
Strzelin (Górzec)	0.70	0.05	0.00	0.05	6.30	0.02	534.7	5.00	4.20	242.85	0.03	20.00	0.88
Biskupice Podgórne	0.20	0.05	0.00	0.05	6.20	0.07	509.0	1.40	5.20	275.00	0.77	6.00	0.00
Żórawina	0.80	0.15	0.00	0.15	8.20	0.06	599.0	1.10	5.40	217.85	0.077	14.00	1.76
Ostroszowice	0.90	0.30	0.10	0.20	7.30	0.02	162.0	0.60	1.00	92.85	0.03	4.00	4.40
Dzierżoniów	0.36	0.20	0.00	0.20	7.60	0.03	579.0	1.20	3.20	307.14	0.03	18.00	1.76
Strzelin (Dankowice)	0.30	0.05	0.00	0.05	7.60	0.02	620.3	0.60	5.60	314.28	0.03	10.00	1.46
Strzelin (Ludów Polski)	0.35	0.05	0.00	0.05	7.50	0.03	538.4	1.20	5.80	275.00	0.03	8.00	0.88
Trzebnica	–	0.50	0.00	0.50	7.30	0.06	820.6	1.10	6.60	407.141	0.03	34.00	0.88
Wrocław Mokry Dwór	0.45	0.05	0.00	0.05	8.00	0.01	536.1	2.00	2.80	271.42	0.03	52.00	17.60
Brzeg Dolny	1.00	0.10	0.00	0.10	7.60	0.01	404.9	1.10	4.20	232.14	0.03	6.00	0.88
Jodłownik	3.60	0.10	0.00	0.10	7.60	0.01	144.7	1.80	0.60	67.85	0.03	8.00	6.16
Wrocław Na Grobli	0.18	0.05	0.00	0.05	8.10	0.01	533.0	3.20	3.00	250.00	0.03	34.00	2.64
Kąty Wrocławskie	0.65	0.10	0.05	0.05	7.50	0.01	310.0	1.00	3.00	142.85	0.03	6.00	0.88
Bychowo	0.90	0.10	0.05	0.05	7.30	0.02	580.0	3.90	5.20	275.00	0.05	30.00	7.04
Oborniki Śląskie	0.45	0.50	0.00	0.50	7.20	0.01	460.0	2.60	3.60	232.10	0.02	14.00	3.50
Godzięcin	7.20	0.05	0.00	0.05	7.00	0.01	152.7	2.50	1.80	75.00	0.05	6.00	0.80
Jelcz-Laskowice	2.10	0.37	0.02	0.35	6.90	0.10	584.6	2.90	2.20	114.20	0.02	36.00	26.40
Psary	0.15	0.05	–	–	7.50	0.07	715.0	1.60	6.40	303.50	0.10	26.00	0.88

Table 18 cont.

Sampling point	Turbidity	Total iron	Fe^{2+}	Fe^{3+}	pH	Manganese	Conductivity	Permanganate COD	Alkalinity	Hardness	Ammonium ion	Chlorides	Nitrates
	NTU	mg Fe·dm^{-3}			pH	mg Mn·dm^{-3}	µS·cm	mg O_2·dm^{-3}	mval	mg $CaCO_3$·dm^{-3}	mg NH_4^+·dm^{-3}	mg Cl^-·dm^{-3}	mg NO_3^-·dm^{-3}
Rościsławice	0.12	0.05	–	–	7.10	0.005	437.0	0.90	4.00	225.00	0.02	10.00	0.88
Rędzin	0.20	0.07	0.02	0.05	7.20	0.025	1155.0	3.10	2.80	100.00	0.13	12.20	0.001
Borkowice	0.50	0.05	0.00	0.00	6.90	0.03	715.2	0.70	5.60	375.00	0.03	2.00	0.001
Wilczyn	0.60	0.05	0.00	0.05	7.30	0.025	662.0	1.40	4.20	303.60	0.03	1.50	0.013
Lubnów	0.30	0.05	0.00	0.05	7.00	0.02	571.0	1.00	3.20	289.20	0.03	2.50	0.014
Ciecholowice	2.70	0.20	0.00	0.20	7.30	0.11	624.0	1.50	3.40	285.70	0.05	26.00	0.88
Pierwoszów	0.18	0.00	0.00	0.00	8.70	0.02	665.0	2.00	7.00	17.80	0.03	20.00	2.60
Milicz	0.95	0.60	0.20	0.40	7.10	0.03	272.0	2.00	2.20	164.20	0.26	20.00	11.40
Twardogóra	0.90	0.05	0.00	0.05	7.50	0.02	304.5	1.30	2.00	160.71	0.03	10.00	0.88
Chełstów	2.0	1.50	1.30	0.20	7.50	0.025	125.6	1.00	2.80	210.71	0.03	18.00	7.04
Grabowno Wielkie	2.8	0.40	0.30	0.10	6.70	0.055	181.5	1.50	1.00	128.57	0.03	14.00	9.68
Jakubowice	0.45	0.05	0.00	0.05	7.60	0.04	649.0	1.60	4.00	371.43	0.03	36.00	14.08
Bystrzyca	1.00	0.05	0.00	0.05	7.70	0.11	328.5	2.80	4.00	175.00	0.15	10.00	1.76
Siedlce near Oława	0.25	0.05	0.00	0.05	7.50	0.08	1240.0	1.60	5.80	482.14	0.64	108.00	1.76

Table 19

Values of UV_{254} absorbance for raw and treated water samples

Sampling point	UV_{254} m^{-1}	
	Raw water	Treated water
Strzelin (Brzegowa)	12.03	8.72
Strzelin (Górzec)	11.26	8.72
Biskupice Podgórne	3.86	3.51
Żórawina	5.20	2.82
Ostroszowice	2.67	2.29
Dzierżoniów	2.89	2.14
Strzelin (Dankowice)	4.86	1.46
Strzelin (Ludów Polski)	4.99	2.80
Trzebnica	2.34	1.89
Wrocław Mokry Dwór	8.80	4.43
Brzeg Dolny	3.22	1.77
Jodłownik	5.06	4.49
Wrocław Na Grobli	6.07	2.70
Bychowo	5.00	–
Polanica (BS1)	3.40	–
Polanica (BS6)	17.40	–
Polanica (Stara Sokołówka)	15.90	–
Polanica (Nowa Sokołówka)	1.70	–
Polanica (Wojska Polskiego)	7.00	–
Polanica (BS4)	16.50	–
Polanica (drainage)	3.90	–
Polanica (Zbiornik Piastowski 13)	1.10	–
Polanica (Zbiornik Piastowski 7)	12.90	–
Polanica (outflow)	3.50	–
Warszawa (Kajakowa 2)	0.80	–
Warszawa (Kajakowa 3)	0.40	–
Psary	0.40	1.10
Rościsławice	0.20	0.80
Rędzin	5.70	6.40
Borkowice	6.30	1.50
Wilczyn	6.90	6.70
Lubnów	6.90	6.70
Ciecholowice	0.50	0.20
Pierwoszów	0.40	0.60
Osolin	0.20	–
Milicz	0.30	0.40
Twardogóra	5.00	4.00
Chełstów	4.00	3.80
Grabowno Wielkie	3.70	4.20
Jakubowice	6.50	7.00
Bystrzyca	6.70	6.50
Siedlce near Oława	6.30	6.40

Table 20

Minimal and maximal values of the parameters describing the quality of the sets of raw and treated water samples

Parameter	Unit	Set of raw water samples		Set of treated water samples	
		Minimal value	Maximal value	Minimal value	Maximal value
Turbidity	NTU	0.14	57.10	0.12	7.20
Toatal iron	$mg\ Fe\cdot dm^{-3}$	0.05	15.00	0.00	1.50
Fe^{2+}		0.00	11.50	0.00	1.30
Fe^{3+}		0.00	15.00	0.00	0.50
pH	pH	5.60	8.10	6.20	8.70
Manganese	$mg\ Mn\cdot dm^{-3}$	0.01	0.89	0.01	0.11
Conductivity	$\mu S\cdot cm^{-1}$	86.10	2006.00	125.60	1240.00
Permanganate COD	$mg\ O_2\cdot dm^{-3}$	1.00	10.40	0.60	5.00
Alkalinity	Mval	0.40	7.60	0.60	7.00
Hardness	$mg\ CaCO_3\cdot dm^{-3}$	39.20	557.14	17.80	482.14
Ammonium ion	$mg\ NH_4^+\cdot dm^{-3}$	0.03	0.77	0.02	0.77
Chlorides	$mg\ Cl^-\cdot dm^{-3}$	1.50	108.00	1.50	108.00
Nitrates	$mg\ NO_3\cdot dm^{-3}$	0.00	26.00	0.00	26.40
UV_{254}	m^{-1}	0.20	17.40	0.20	8.72

4.3.3. Rate constants of chlorine and chlorine dioxide decay

The estimated values for the rate constants of chlorine and chlorine dioxide decay are summarised in Tables 21 to 24. Values printed in bold are insignificant at the adopted significance level $\alpha = 0.05$, so they were neglected in further analyses. Detailed results of the study on the rate of chlorine and chlorine dioxide decay are not shown because of the large number of data obtained from about 1300 measurements.

Table 21

Five-minute chlorine demand of raw water, estimated rate constants of chlorine decay, as well as correlation and determination coefficients of regression functions describing the kinetics of first-order reaction

Sampling point	PZD_Cl_2	k_Cl_2	R	R^2
	$mg\ Cl_2$	h^{-1}		
1	2	3	4	5
Strzelin (Brzegowa)	2.740	0.209	0.9965	0.9930
Strzelin (Górzec)	4.010	0.270	0.9932	0.9864
Biskupice Podgórne	3.710	0.620	0.8334	0.6946
Żórawina	3.930	0.740	0.9760	0.9526
Ostroszowice	1.190	0.255	0.9941	0.9882

Table 21 cont.

1	2	3	4	5
Dzierżoniów	1.780	0.190	0.9931	0.9862
Strzelin (Dankowice)	1.510	0.068	0.9387	0.8812
Strzelin (Ludów Polski)	2.820	0.133	0.8923	0.7962
Trzebnica	1.250	0.164	0.9912	0.9825
Wrocław Mokry Dwór	2.000	1.061	0.9844	0.9690
Brzeg Dolny	2.920	0.155	0.8629	0.7446
Jodłownik	2.080	0.756	0.9485	0.8997
Wrocław Na Grobli	1.190	0.255	0.9941	0.9882
Kąty Wrocławskie	1.910	0.236	0.8530	0.7276
Bychowo	3.720	**0.072**	0.8075	0.6521
Polanica (BS1)	1.380	0.125	0.9967	0.9934
Polanica (BS6)	1.330	0.090	0.9978	0.9956
Polanica (Stara Sokołówka)	1.940	1.068	0.9970	0.9940
Polanica (Nowa Sokołówka)	2.050	2.455	0.9887	0.9775
Polanica (Wojska Polskiego)	0.670	0.065	0.9577	0.9172
Polanica (BS4)	0.810	0.159	0.7515	0.5648
Polanica (drainage)	0.770	0.212	0.8652	0.7486
Polanica (Zbiornik Piastowski 13)	0.740	0.161	0.7314	0.5349
Polanica (Zbiornik Piastowski 7)	0.990	0.157	0.9938	0.9876
Polanica (outflow)	1.620	**1.992**	0.9214	0.8490
Warszawa (Kajakowa 2)	3.050	0.067	0.9417	0.8868
Warszawa (Kajakowa 3)	4.080	0.104	0.9302	0.8653
Psary	3.250	0.011	0.8289	0.6871
Rościsławice	2.410	0.013	0.9316	0.8679
Rędzin	0.530	0.291	0.9507	0.9038
Borkowice	0.550	0.333	0.9400	0.8836
Wilczyn	0.230	0.319	0.9750	0.9506
Lubnów	0.860	1.052	0.9806	0.9616
Ciecholowice	0.770	**0.357**	0.7146	0.5107
Pierwoszów	0.500	0.051	0.9432	0.8896
Osolin	0.030	0.027	0.9324	0.8694
Milicz	0.150	0.143	0.9542	0.9105
Twardogóra	0.300	0.057	0.9241	0.8540
Chełstów	0.520	0.314	0.9458	0.8945
Grabowno Wielkie	0.620	0.254	0.9720	0.9448
Jakubowice	0.510	0.166	0.9176	0.8420
Bystrzyca	0.910	**0.024**	0.5176	0.2679
Siedlce near Oława	0.870	0.000	–	–

Table 22

Five-minute chlorine demand of raw water, estimated rate constants of chlorine decay, as well as correlation and determination coefficients of regression functions describing the kinetics of first-order reaction

Sampling point	PZD_ClO_2	k_ClO_2	R	R^2
	mg ClO_2	h^{-1}		
Strzelin (Brzegowa)	1.560	0.148	0.6868	0.4717
Strzelin (Górzec)	0.580	0.396	0.9723	0.9454
Biskupice Podgórne	0.600	0.270	0.9660	0.9331
Żórawina	0.580	0.291	0.9623	0.9260
Ostroszowice	0.000	0.228	0.9946	0.9892
Dzierżoniów	1.920	0.598	0.9212	0.8486
Strzelin (Dankowice)	0.000	0.192	0.9589	0.9195
Strzelin (Ludów Polski)	0.210	0.268	0.9349	0.8740
Trzebnica	0.000	0.324	0.9905	0.9811
Wrocław Mokry Dwór	0.350	0.387	0.9402	0.8840
Brzeg Dolny	0.000	0.131	0.9882	0.9765
Jodłownik	0.000	0.193	0.9917	0.9835
Wrocław Na Grobli	0.000	0.228	0.9946	0.9892
Kąty Wrocławskie	0.640	0.099	0.8781	0.7711
Bychowo	0.000	0.131	0.8977	0.8059
Polanica (BS1)	0.000	0.629	0.9887	0.9775
Polanica (BS6)	0.000	0.297	0.9926	0.9853
Polanica (Stara Sokołówka)	0.280	1.631	0.9728	0.9463
Polanica (Nowa Sokołówka)	0.310	1.924	0.9877	0.9756
Polanica (Wojska Polskiego)	0.000	0.218	0.9907	0.9815
Polanica (BS4)	0.000	0.231	0.9804	0.9612
Polanica (drainage)	0.000	0.161	0.9854	0.9710
Polanica (Zbiornik Piastowski 13)	0.000	0.164	0.9805	0.9614
Polanica (Zbiornik Piastowski 7)	0.000	0.290	0.9957	0.9914
Polanica (outflow)	0.000	0.174	0.9897	0.9795
Warszawa (Kajakowa 2)	0.000	0.100	0.9882	0.9765
Warszawa (Kajakowa 3)	0.490	0.180	0.9446	0.8923
Psary	0.000	0.020	0.9457	0.8943
Rościsławice	0.000	0.015	0.9396	0.8828
Rędzin	0.100	0.034	0.9429	0.8891
Borkowice	0.000	0.019	0.9859	0.9720
Wilczyn	0.000	0.029	0.9699	0.9407
Lubnów	0.000	0.014	0.8154	0.6649
Ciecholowice	0.000	0.041	0.9567	0.9153
Pierwoszów	0.000	0.016	0.8592	0.7382
Osolin	0.000	0.006	0.7742	0.5994
Milicz	0.000	**0.052**	0.5667	0.3211
Twardogóra	0.000	**0.015**	0.6040	0.3648
Chełstów	0.000	0.014	0.7812	0.6103
Grabowno Wielkie	0.000	0.046	0.6179	0.3818
Jakubowice	0.000	0.037	0.7508	0.5637
Bystrzyca	0.020	0.056	0.8953	0.8016
Siedlce near Oława	0.240	0.062	0.9227	0.8514

Table 23

Five-minute chlorine demand of treated water, estimated rate constants of chlorine decay, as well as correlation and determination coefficients of regression functions describing the kinetics of first-order reaction

Sampling point	PZD_Cl_2	k_Cl_2	R	R^2
	mg Cl_2	h^{-1}		
Strzelin (Brzegowa)	1.980	0.030	0.9871	0.9744
Strzelin (Górzec)	1.980	0.030	0.9871	0.9744
Biskupice Podgórne	2.560	0.121	0.9616	0.9247
Żórawina	2.730	0.099	0.9225	0.8510
Ostroszowice	0.650	0.060	0.9078	0.8241
Dzierżoniów	0.160	0.019	0.9452	0.8934
Strzelin (Dankowice)	1.180	0.398	0.9978	0.9956
Strzelin (Ludów Polski)	1.270	0.243	0.9974	0.9948
Trzebnica	1.220	0.072	0.9745	0.9497
Wrocław Mokry Dwór	0.990	0.398	0.9948	0.9896
Brzeg Dolny	1.420	0.038	0.9763	0.9532
Jodłownik	1.070	0.192	0.9958	0.9916
Wrocław Na Grobli	0.590	0.080	0.9969	0.9938
Kąty Wrocławskie	1.250	0.200	0.8958	0.8025
Bychowo	3.640	5.147	0.9968	0.9936
Oborniki Śląskie	1.190	0.301	0.9823	0.9649
Godzięcin	0.940	0.184	0.9738	0.9483
Jelcz-Laskowice	0.130	0.054	0.9741	0.9489
Psary	2.180	0.083	0.8697	0.7564
Rościsławice	2.030	0.018	0.8598	0.7393
Rędzin	0.800	2.173	0.9814	0.9631
Borkowice	0.000	0.271	0.9811	0.9626
Wilczyn	0.010	0.358	0.9916	0.9833
Lubnów	0.130	0.874	0.9758	0.9522
Ciecholowice	0.190	2.020	0.9716	0.9440
Pierwoszów	0.060	0.181	0.9809	0.9621
Milicz	0.050	0.247	0.9540	0.9101
Twardogóra	0.070	0.158	0.9794	0.9592
Chełstów	0.080	0.245	0.9601	0.9218
Grabowno Wielkie	0.090	0.295	0.9447	0.8925
Jakubowice	0.100	0.307	0.9676	0.9362
Bystrzyca	0.250	**0.034**	0.5374	0.2888
Siedlce near Oława	0.270	0.000	–	–

Table 24

Five-minute chlorine demand of treated water, estimated rate constants of chlorine decay, as well as correlation and determination coefficients of regression functions describing the kinetics of first-order reaction

Sampling point	PZD_ClO$_2$	k_ClO$_2$	R	R^2
	mg ClO$_2$	h^{-1}		
Strzelin (Brzegowa)	0.040	0.526	0.9933	0.9866
Strzelin (Górzec)	0.040	0.526	0.9933	0.9866
Biskupice Podgórne	0.360	0.696	0.9936	0.9872
Żórawina	0.320	0.471	0.9960	0.9920
Ostroszowice	0.000	0.154	0.9830	0.9663
Dzierżoniów	0.000	0.435	0.9986	0.9972
Strzelin (Dankowice)	0.210	0.408	0.9865	0.9732
Strzelin (Ludów Polski)	0.000	0.329	0.9569	0.9157
Trzebnica	0.000	0.219	0.9854	0.9710
Wrocław Mokry Dwór	0.000	0.153	0.9990	0.9980
Brzeg Dolny	0.000	0.271	0.9903	0.9807
Jodłownik	0.000	0.208	0.9933	0.9866
Wrocław Na Grobli	0.000	0.154	0.9830	0.9663
Kąty Wrocławskie	0.000	0.217	0.9712	0.9432
Bychowo	0.230	1.355	0.9493	0.9012
Oborniki Śląskie	0.000	0.587	0.9934	0.9868
Godzięcin	0.000	0.408	0.9835	0.9672
Jelcz-Laskowice	0.000	0.092	0.9663	0.9337
Psary	0.000	0.010	0.6929	0.4801
Rościsławice	0.000	0.036	0.8758	0.7670
Rędzin	0.000	0.028	0.8111	0.6579
Borkowice	0.000	0.086	0.9759	0.9524
Wilczyn	0.000	0.079	0.9588	0.9193
Lubnów	0.000	0.098	0.9532	0.9086
Ciecholowice	0.000	0.048	0.8492	0.7211
Pierwoszów	0.000	**0.029**	0.6043	0.3652
Milicz	0.000	0.051	0.8719	0.7602
Twardogóra	0.000	0.055	0.9063	0.8214
Chełstów	0.000	0.061	0.9703	0.9415
Grabowno Wielkie	0.000	0.054	0.8272	0.6843
Jakubowice	0.000	0.053	0.9500	0.9025
Bystrzyca	0.000	0.023	0.6184	0.3824
Siedlce near Oława	0.000	0.049	0.7665	0.5875

Figures 22 to 27 show examples of change in chlorine (chlorine dioxide) concentrations after 5-minute contact of water with chlorine (chlorine dioxide).

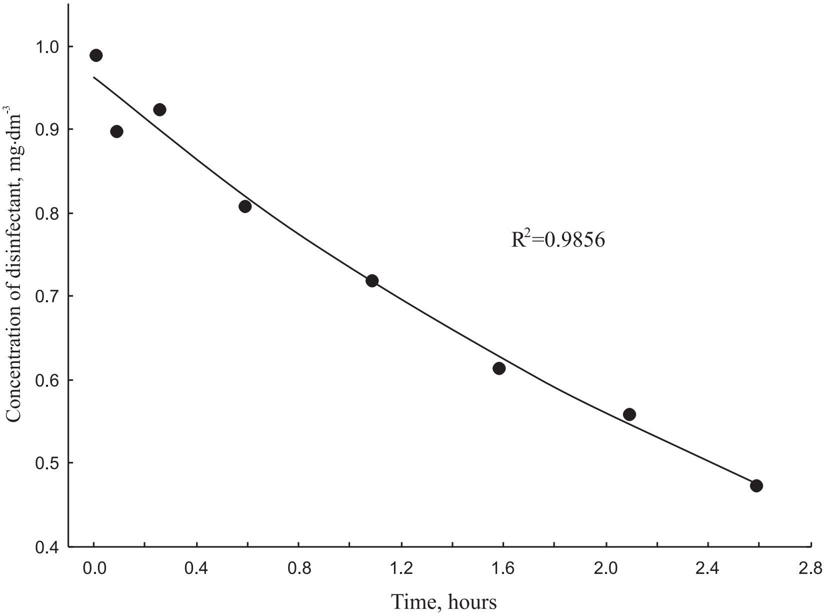

Fig. 22. Change in chlorine concentration with contact time in raw water samples collected at Strzelin (Górzec)

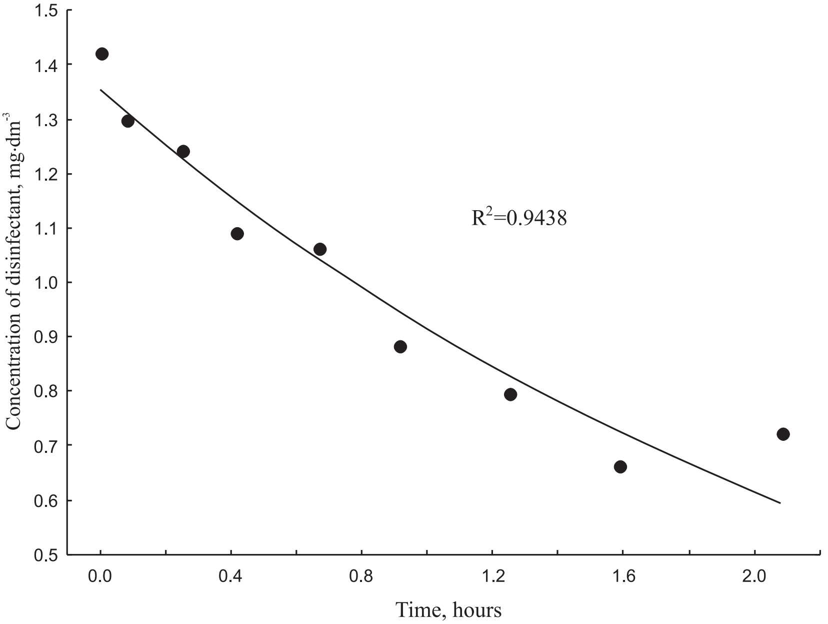

Fig. 23. Change in chlorine dioxide concentration with contact time observed in raw water samples collected in Strzelin (Górzec)

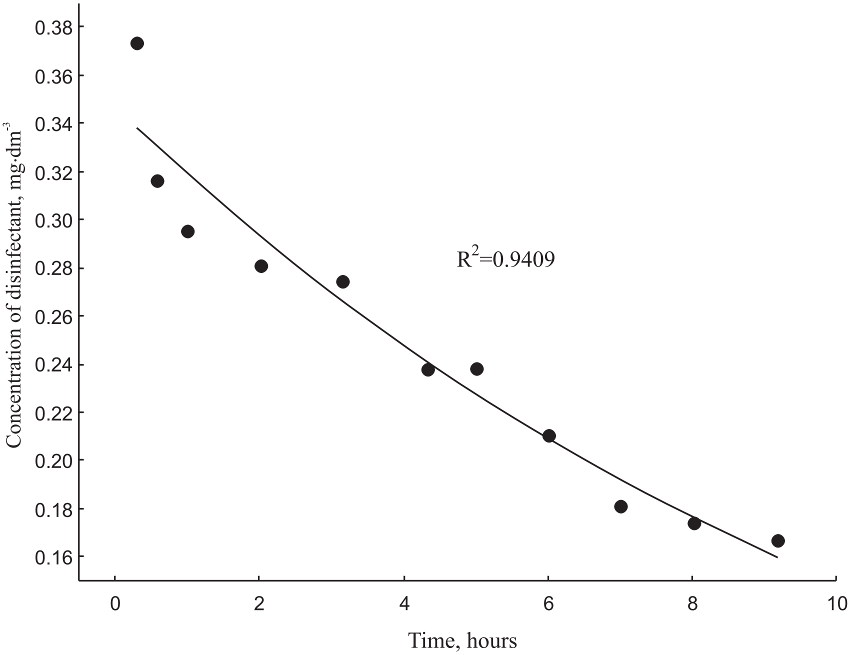

Fig. 24. Change in chlorine dioxide concentration with contact time observed in treated water samples collected in Borkowice

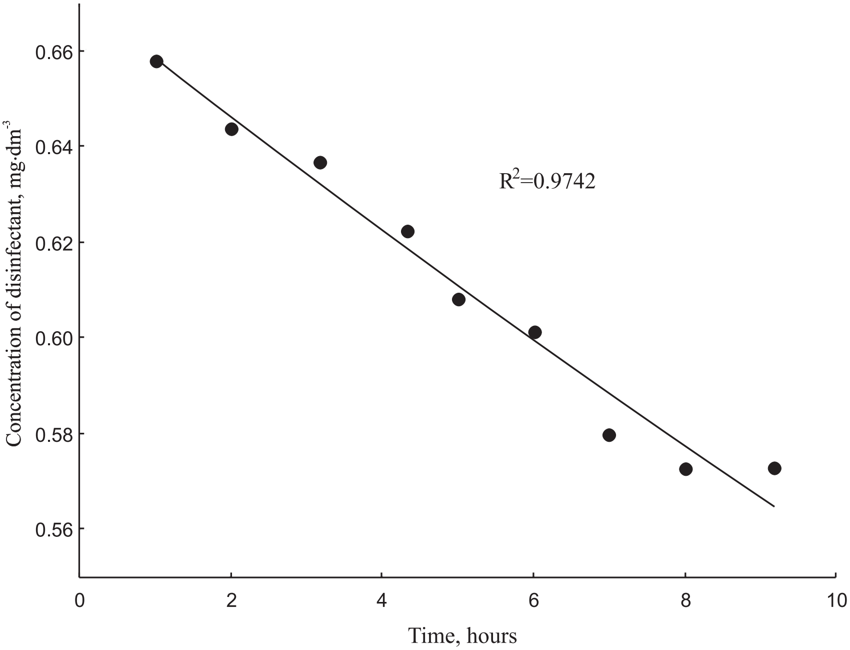

Fig. 25. Change in chlorine dioxide concentration with contact time observed in raw water samples collected in Borkowice

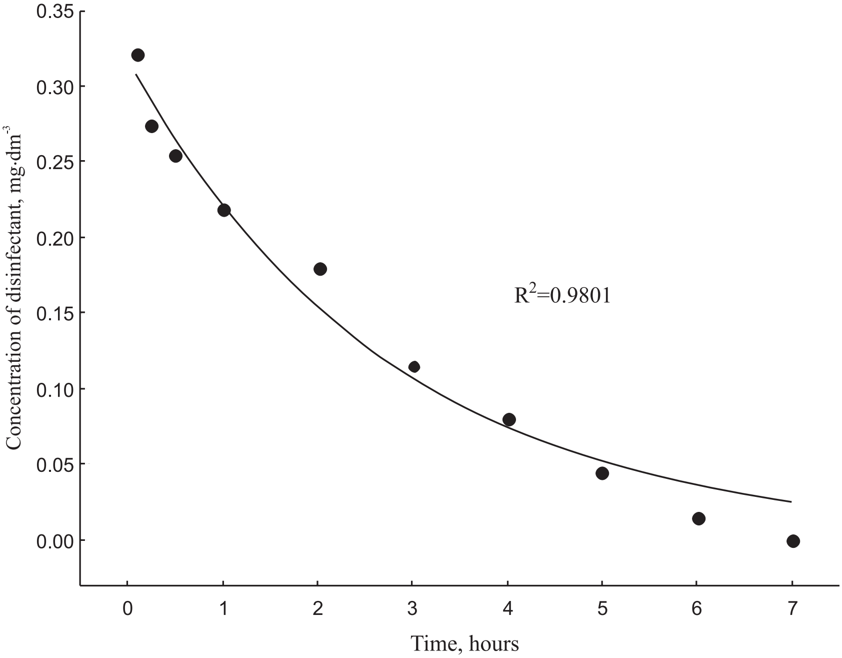

Fig. 26. Change in chlorine concentration with contact time observed in treated water samples collected in Wilczyn

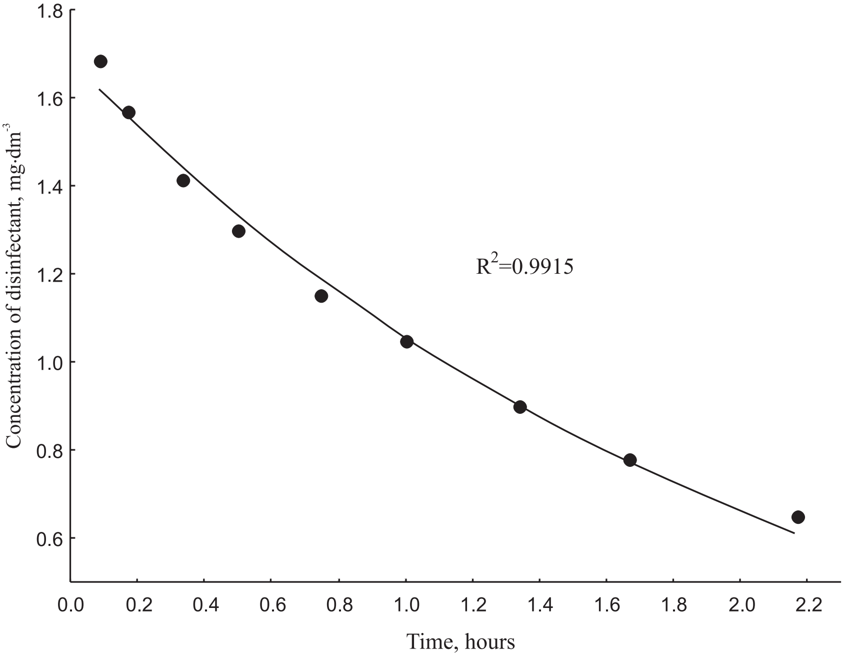

Fig. 27. Change in chlorine dioxide concentration with contact time observed in treated water samples collected in Żórawina

Figure 28 illustrates the scatter of the values of $k_{\mathrm{Cl_2}}$ and $k_{\mathrm{ClO_2}}$ determined experimentally for the same water samples. As can be seen, there is no correlation between them. Pearson's linear correlation coefficient R for the set of pairs of experimental data was 0.3986. From this scatter can also be inferred that there is no linear or nonlinear trend between $k_{\mathrm{Cl_2}}$ and $k_{\mathrm{ClO_2}}$.

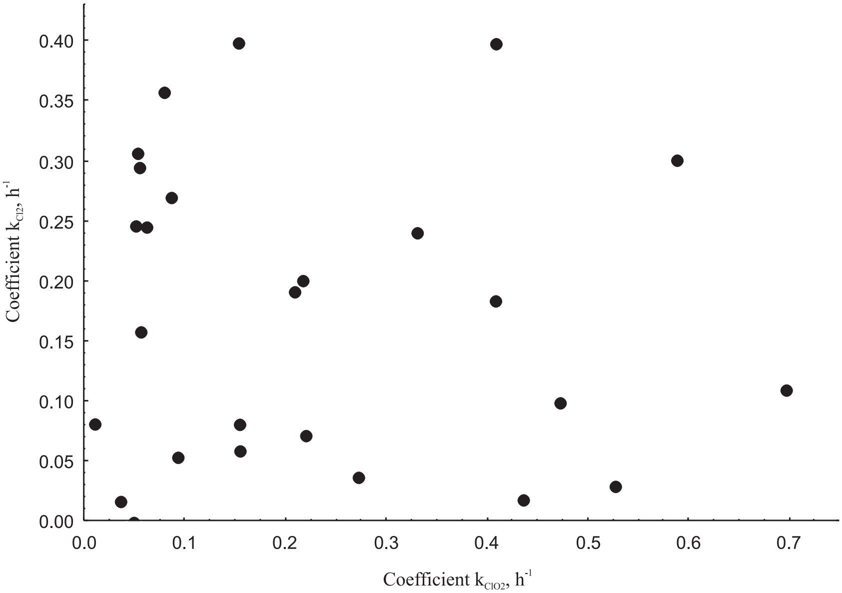

Fig. 28. Relation between particular rates of chlorine decay and chlorine dioxide decay in treated water

Five-minute chlorine dioxide demand (PZD_ClO$_2$) was generally close to zero. Only in some water samples, namely those characterised by elevated UV$_{254}$ values, (PZD_ClO$_2$) was higher than 0.

Five-minute chlorine demand (PZD_Cl$_2$) was a recurrent feature of almost all the water samples examined, but the values of PZD_Cl$_2$ were higher in untreated than treated water collected at the same water treatment plants (Fig. 29). These values follow a linear trend described as:

$$\mathrm{PZD\_Cl_2}^{treated\_water} = 0.6331\,\mathrm{PZD\_Cl_2}^{raw\_water} \tag{71}$$

the value of the determination coefficient being 0.8102.

A significant relation was found to occur between PZD_ClO$_2$ and PZD_Cl$_2$. The relation is described by a segmented regression defined by the following function:

$$\mathrm{PZD\_ClO_2} = \begin{cases} 0 & 0 \le \mathrm{PZD\_Cl_2} \le 1.87 \\ -0.24 + 0.13\,\mathrm{PZD\_Cl_2}, & \mathrm{PZD\_Cl_2} > 1.87 \end{cases} \tag{72}$$

The determination coefficient obtained for this regression function is 0.9366, which indicates that approximately 94% of the cases being analysed can be modelled using the relation of (72).

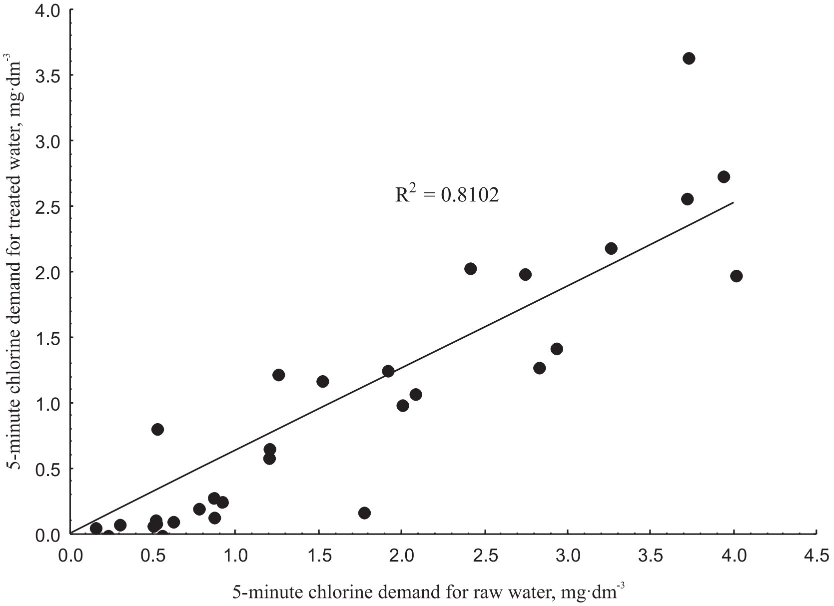

Fig. 29. Relation between 5-minute chlorine demand for raw water samples and that for treated water samples collected from the same water treatment plants

The relation of (72) shows that up to the threshold value of 5-minute chlorine demand, which amounts to 1.87 mg Cl_2·dm^{-3}, the 5-minute chlorine dioxide demand is zero. At a higher chlorine demand, a linear increment in PZD_ClO_2 with respect to PZD_Cl_2 was observed (Fig. 30).

High disinfectant doses are not applied in water treatment plants, because with a high dose, disinfection by-products are formed in large quantities. That is why the number of data sets obtained with high disinfectant doses was insufficiently high to allow drawing reliable conclusions.

Figure 31 shows the scatter of the $\mathrm{PZD\_Cl_2}$ and $k_{\mathrm{ClO_2}}$ values determined for treated water. For the two variables it has been established that the regression described by equation:

$$k_{\mathrm{ClO_2}} = 0.0564 + 0.0550 \exp\left(0.8573\,\mathrm{PZD\_Cl_2}\right) \tag{73}$$

is a significant one, and that the determination coefficient equals 0.6763 (Fig. 31). This demonstrates that in the absence of iron(II) compounds which readily undergo oxidation with chlorine (chlorine dioxide), water samples display a deterministic exponential relation between 5-minute chlorine demand and the rate constants of chlorine dioxide decay. Thus, as PZD_Cl_2 increased, so did the rate constant $k_{\mathrm{ClO_2}}$. The existence of a relation between the two variables is of great practical meaning, because based on the 5-minute chlorine demand it is possible to predict the value of the rate constant of chlorine dioxide decay in the water. While the determination of PZD_Cl_2 is very simple in analytical terms, the determination of $k_{\mathrm{ClO_2}}$ requires several hours of laboratory tests and analytical interpretation of the results obtained. Knowledge of the regression function that relates the values of PZD_Cl_2 to those of $k_{\mathrm{ClO_2}}$ facilitates the determination of chlorine dioxide doses for treated water disinfection or for post-disinfection.

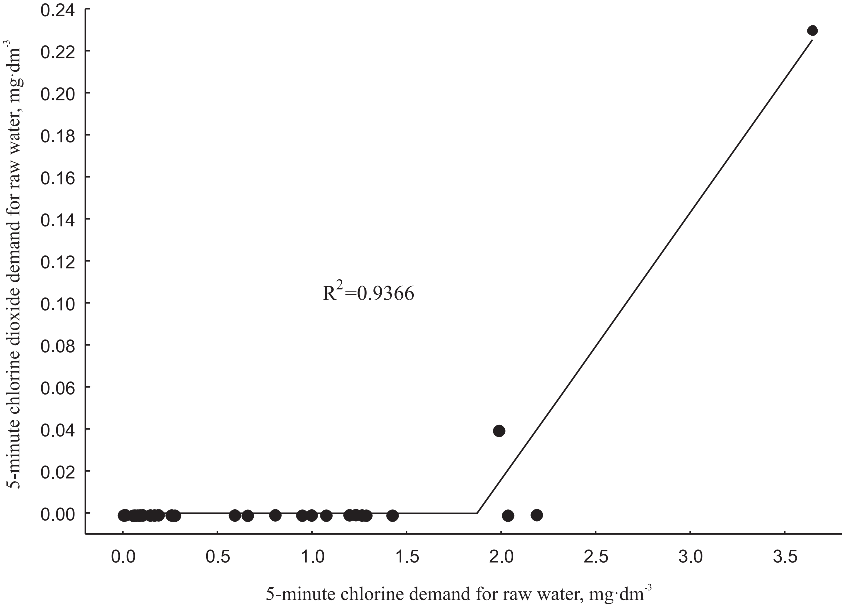

Fig. 30. Relation between 5-minute chlorine demand and 5-minute chlorine dioxide demand for raw water samples

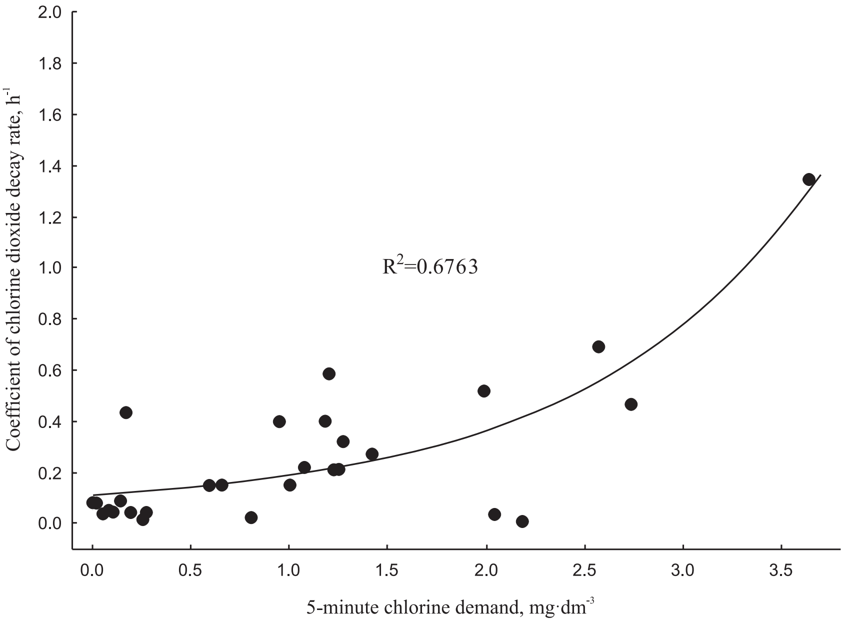

Fig. 31. Relation between 5-minute chlorine demand and the coefficients of chlorine dioxide decay rate for treated water samples

4.3.4. Principal component analysis

To establish the interaction between the variables defining water quality (UV_{254}, pH, Fe_{tot}, Mn, NH_4^+, Cl) and those characterising the disinfectant decay rates (k_Cl_2, k_ClO_2, PZD_Cl_2, PZD_ClO_2), use was made of principal component analysis (PCA). Using this method, it is possible to reduce the number of correlated variables and explain the same amount of variance with fewer variables (principal components). A matrix of 11 variables was analysed separately for the sets of data obtained with raw water samples (Tab. 25), treated water samples (Tab. 26), and all of the water samples tested (Tab. 27).

Table 25

Matrix of correlation coefficients of particular variables for the set of raw water samples

Variable	UV_{254}	pH	Fe_{tot}	Mn	Permanganate COD	Ammonium ion	Chlorides	PZD_Cl_2	k_Cl_2	PZD_ClO_2	k_ClO_2
UV_{254}	1.000	-0.417	-0.033	-0.051	0.162	-0.035	-0.091	-0.078	0.081	0.102	0.206
pH	-0.417	1.000	0.094	0.118	0.064	0.108	0.092	0.046	-0.039	-0.115	-0.200
Fe_{tot}	-0.033	0.094	1.000	0.650	-0.009	0.134	0.287	0.208	-0.199	0.560	-0.176
Mn	-0.051	0.118	0.650	1.000	0.194	0.373	0.300	-0.098	-0.115	0.435	-0.269
Permanganate COD	0.162	0.064	-0.009	0.194	1.000	0.182	0.013	0.092	0.476	0.101	0.256
Ammonium ion	-0.035	0.108	0.134	0.373	0.182	1.000	0.390	0.321	0.067	0.174	-0.103
Chlorides	-0.091	0.092	0.287	0.300	0.013	0.390	1.000	0.133	-0.221	0.351	-0.172
PZD_Cl_2	-0.078	0.046	0.208	-0.098	0.092	0.321	0.133	1.000	0.131	0.413	0.182
k_Cl_2	0.081	-0.039	-0.199	-0.115	0.476	0.067	-0.221	0.131	1.000	0.101	0.739
PZD_ClO_2	0.102	-0.115	0.560	0.435	0.101	0.174	0.351	0.413	0.101	1.000	0.221
k_ClO_2	0.206	-0.200	-0.176	-0.269	0.256	-0.103	-0.172	0.182	0.739	0.221	1.000

Table 26

Matrix of correlation coefficients of particular variables for the set of treated water samples

Variable	UV_{254}	pH	Fe_{tot}	Mn	Permanganate COD	Ammonium ion	Chlorides	PZD_Cl_2	k_Cl_2	PZD_ClO_2	k_ClO_2
UV_{254}	1.000	-0.187	-0.339	-0.196	0.613	0.060	0.187	-0.023	0.027	-0.072	0.163
pH	-0.187	1.000	0.034	0.041	-0.188	-0.078	-0.025	-0.285	-0.047	-0.134	-0.205
Fe_{tot}	-0.339	0.034	1.000	-0.092	-0.390	-0.291	0.252	-0.160	-0.021	-0.099	-0.310
Mn	-0.196	0.041	-0.092	1.000	-0.162	0.471	0.377	0.051	0.276	0.256	-0.026
Permanganate COD	0.613	-0.188	-0.390	-0.162	1.000	-0.024	0.160	0.253	0.059	-0.098	0.299
Ammonium ion	0.060	-0.078	-0.291	0.471	-0.024	1.000	0.424	0.187	-0.078	0.467	0.241
Chlorides	0.187	-0.025	0.252	0.377	0.160	0.424	1.000	-0.119	-0.095	-0.169	-0.198
PZD_Cl_2	-0.023	-0.285	-0.160	0.051	0.253	0.187	-0.119	1.000	-0.267	0.609	0.635
k_Cl_2	0.027	-0.047	-0.021	0.276	0.059	-0.078	-0.095	-0.267	1.000	-0.124	-0.322
PZD_ClO_2	-0.072	-0.134	-0.099	0.256	-0.098	0.467	-0.169	0.609	-0.124	1.000	0.696
k_ClO_2	0.163	-0.205	-0.310	-0.026	0.299	0.241	-0.198	0.635	-0.322	0.696	1.000

Table 27

Matrix of correlation coefficients of particular variables for the set of all the water samples tested

Variable	UV_{254}	pH	Fe_{tot}	Mn	Permanganate COD	Ammonium ion	Chlorides	PZD_Cl$_2$	k_Cl$_2$	PZD_ClO$_2$	k_ClO$_2$
UV_{254}	1.000	0.180	-0.198	0.049	0.283	0.042	-0.009	0.018	0.059	0.137	0.217
pH	0.180	1.000	-0.687	0.423	0.240	0.204	0.047	0.326	-0.001	0.222	0.076
Fe_{tot}	-0.198	-0.687	1.000	0.125	-0.188	-0.094	0.148	-0.123	-0.104	0.207	-0.199
Mn	0.049	0.423	0.125	1.000	0.249	0.342	0.251	0.068	-0.056	0.479	-0.182
Permanganate COD	0.283	0.240	-0.188	0.249	1.000	0.152	0.058	0.196	0.315	0.135	0.278
Ammonium ion	0.042	0.204	-0.094	0.342	0.152	1.000	0.400	0.308	-0.005	0.223	0.019
Chlorides	-0.009	0.047	0.148	0.251	0.058	0.400	1.000	0.061	-0.165	0.256	-0.167
PZD_Cl$_2$	0.018	0.326	-0.123	0.068	0.196	0.308	0.061	1.000	-0.019	0.451	0.288
k_Cl$_2$	0.059	-0.001	-0.104	-0.056	0.315	-0.005	-0.165	-0.019	1.000	0.053	0.399
PZD_ClO$_2$	0.137	0.222	0.207	0.479	0.135	0.223	0.256	0.451	0.053	1.000	0.267
k_ClO$_2$	0.217	0.076	-0.199	-0.182	0.278	0.019	-0.167	0.288	0.399	0.267	1.000

From the correlation matrix for the set of water quality parameters and experimental parameters of chlorine and chlorine dioxide decay in raw water samples it can be inferred that PZD_ClO_2 is more strongly correlated than PZD_Cl_2 with the concentrations of iron and manganese compounds. This finding implies that chlorine dioxide oxidises iron(II) and manganese(II) at a faster rate than chlorine does. As for the ammonium ion, chlorine dioxide and chlorine follow a reverse pattern. The correlation of the PZD_Cl_2 values with ammonium ion content of the water is stronger than that of the PZD_ClO_2 values.

In the case of raw water, there is no significant correlation between permanganate COD and UV_{254}, but there is a significant correlation between the two parameters in the case of treated water. This should be attributed to the presence of colloidal particles, which absorb electromagnetic waves of 254 nm length. Colloids are removed from the water during treatment processes. In the case of treated water, neither the rate constants of chlorine and chlorine dioxide decay, k_Cl_2 and k_ClO_2, nor the values of 5-minute chlorine and chlorine dioxide demand, PZD_Cl_2 and PZD_ClO_2, show a correlation with the water quality parameters being analysed. This is an indication that chlorine decay in treated water is influenced by many different factors.

The average result of the absolute values of the correlation coefficients for the set of raw water samples was 0.1996, for the set of treated water samples amounted to 0.2120, and for all the water samples tested totalled 0.2058. This indicates that the variables being analysed are characterised by nonlinearity. Principal component analysis is regarded as suitable for variables displaying some linearity; and this is why it is believed that if the average absolute value of the correlation coefficient is lower than 0.3, the results of factor analysis fail to adequately describe the relations between particular variables [Sagan 1998]. In spite of such belief, in this work here the sets of data were made subject to factor analysis in order to find the water quality parameters, as well as the parameters describing the chlorine (chlorine dioxide) demand of the water, which affect the demand for the disinfectant and the rate of its decay in the water distribution system. Table 28 summarises the calculated eigenvalues of 11 factors established based on the correlation matrix. The factors were ordered according to the increasing eigenvalues and the variance explained. In the case of the set of results for raw water samples, the first factor explained 24.545% and the second factor more than 20% of the total variance in the data set. The cumulative eigenvalue of variance taken up by the first two factors was 45.212%. Similar values were obtained for the set of treated water samples and for the set of all the water samples tested.

The number of initial variables was reduced using Kaiser's criterion, which requires that the factors being analysed have eigenvalues higher than 1. As for the water samples, both raw and treated, there were 5 factors satisfying the Kaiser criterion, and their cumulative eigenvalues amounted to 78.128 and 81.222%, respectively. As for all the samples tested, there were 4 factors that fulfilled the Kaiser criterion, but the cumulative eigenvalue for these factors was only 65.635%. As many as 6 factors were needed to explain more than 80% of variance.

Table 28

Eigenvalues of the correlation matrix

Factor	Raw water samples		Treated water samples		All the water samples tested	
	Eigen-value	Cumulative eigenvalue %	Eigen-value	Cumulative eigenvalue %	Eigen-value	Cumulative eigenvalue %
1	2.700	24.545	2.879	26.173	2.676	24.330
2	2.273	45.212	1.992	44.279	1.985	42.373
3	1.432	58.234	1.798	60.623	1.457	55.619
4	1.168	68.856	1.225	71.757	1.102	65.635
5	1.020	78.128	1.041	81.222	0.942	74.196
6	0.699	84.484	0.678	87.384	0.902	82.398
7	0.603	89.963	0.558	92.456	0.637	88.188
8	0.499	94.495	0.341	95.554	0.569	93.359
9	0.289	97.124	0.278	98.082	0.424	97.210
10	0.175	98.714	0.128	99.243	0.212	99.141
11	0.142	100.000	0.083	100.000	0.094	100.000

Tables 29 to 31 show the eigenvectors of the first five factors with the highest proportion in the cumulative eigenvalue. Figures 32 to 34 depict the configuration of the loading vectors with respect to the first two principal components obtained for the analyses of raw water samples, treated water samples and all the samples tested. The data in Tables 29 to 31 demonstrate that particular factors are related with other water quality parameters and with the parameters describing the rate of chlorine (chlorine dioxide) decay.

Table 29

Eigenvectors of the first five factors for the set of raw water samples

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
UV_{254}	-0.1642	-0.3420	-0.6650	-0.2133	0.3102
pH	0.2211	0.2401	0.7441	-0.1121	-0.2477
Fe_{tot}	0.7803	-0.0424	-0.2392	-0.0174	-0.4183
Manganese	0.7759	-0.0225	-0.1051	-0.4856	-0.1615
Permanganate COD	0.0607	-0.5941	0.2567	-0.5473	0.1053
NH_4^+	0.5370	-0.2088	0.2995	-0.0459	0.6198
Chlorides	0.6422	0.0266	0.0284	0.1140	0.3852
PZD_Cl_2	0.3140	-0.4228	0.2197	0.6753	0.0920
k_Cl_2	-0.2910	-0.8044	0.2904	-0.1507	-0.1262
PZD_ClO_2	0.6358	-0.4836	-0.2811	0.2476	-0.2473
k_ClO_2	-0.3482	-0.7997	0.0172	0.1394	-0.1796

Table 30

Eigenvectors of the first five factors for the set of treated water samples

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
UV_{254}	-0.2800	-0.6786	-0.4542	-0.0814	0.0527
pH	0.3533	0.1833	0.0668	0.0907	0.7801
Fe_{tot}	0.4778	0.3230	0.2104	-0.5124	-0.4200
Manganese	-0.1408	0.6506	-0.5301	0.2779	-0.0546
Permanganate COD	-0.3978	-0.7011	-0.3624	-0.0318	-0.0252
NH_4^+	-0.5055	0.4802	-0.5176	-0.0337	0.1883
Chlorides	0.0505	0.2143	-0.7531	-0.5718	-0.0429
PZD_Cl_2	-0.7798	0.0786	0.2723	-0.1032	-0.1880
k_Cl_2	0.2765	-0.0153	-0.3250	0.7196	-0.4127
PZD_ClO_2	-0.7597	0.4404	0.2193	0.1066	-0.0542
k_ClO_2	-0.8658	-0.0411	0.2597	-0.0344	0.0625

Table 31

Eigenvalues of the first five factors for the set of all the water samples tested

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Variable
UV_{254}	-0.3586	0.2840	-0.0023	-0.4117	0.2901	0.6818
pH	-0.7027	0.1353	0.5860	0.0695	0.1706	-0.1870
Fe_{tot}	0.3849	-0.5635	-0.6512	-0.1033	0.1539	-0.0073
Manganese	-0.5453	-0.5239	0.0770	-0.3521	0.2955	-0.3577
Permanganate COD	-0.5647	0.2658	-0.1637	-0.4491	-0.1257	-0.0661
NH_4^+	-0.5389	-0.3764	0.0585	0.0413	-0.5529	0.0924
Chlorides	-0.2712	-0.6233	-0.0086	-0.1405	-0.4185	0.2831
PZD_Cl_2	-0.5962	-0.0217	-0.1519	0.6457	0.0065	0.0616
k_Cl_2	-0.2002	0.5074	-0.4447	-0.2740	-0.2858	-0.4031
PZD_ClO_2	-0.6174	-0.3438	-0.4414	0.1707	0.3700	-0.0204
k_ClO_2	-0.3860	0.5630	-0.4875	0.2201	-0.0482	0.1205

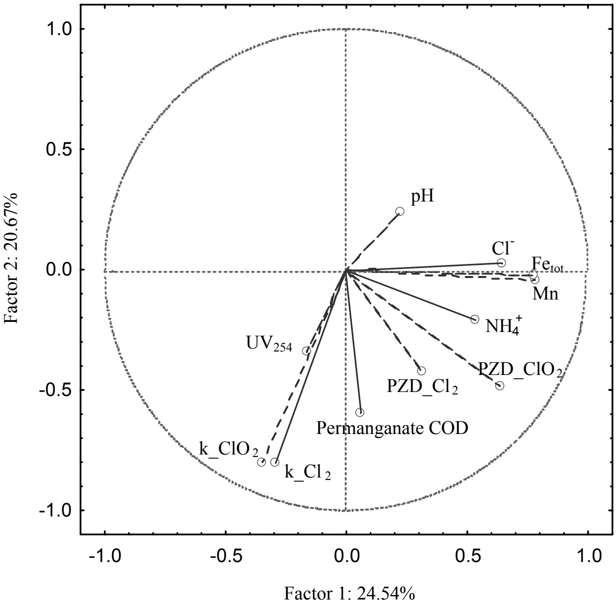

Fig. 32. Configuration of loading vectors with respect to the first two principal components for the set of raw water samples

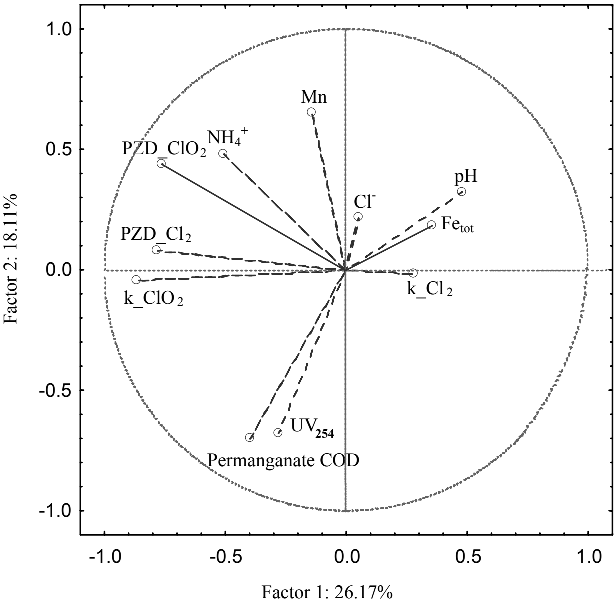

Fig. 33. Configuration of loading vectors with respect to the first two principal components for the set of treated water samples

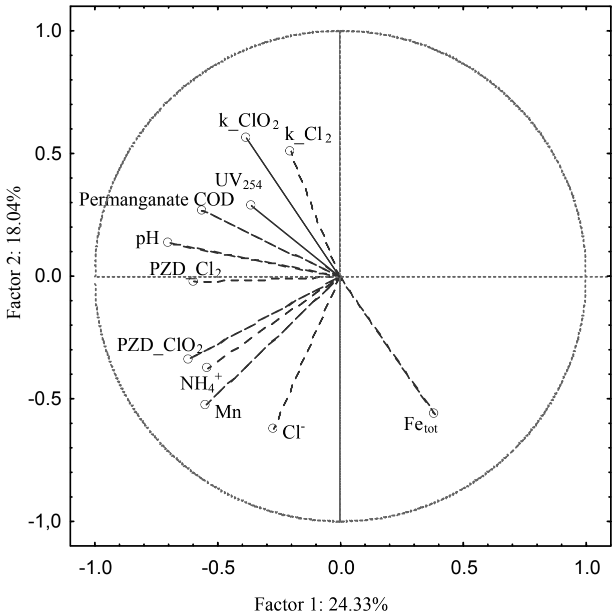

Fig. 34. Configuration of loading vectors with respect to the first two principal components for the set of all water samples tested

In the case of raw water, factor 1 was strongly influenced by the concentrations of iron, manganese, ammonium ion, chlorides and 5-minute chlorine dioxide demand (PZD_ClO_2). Factor 2 was affected by permanganate COD, as well as by the rate constants of chlorine and chlorine dioxide decay (k_ClO_2, k_Cl_2). Factor 3 was under the influence of UV_{254} absorbance and the pH of the water, and factor 4 under the influence of permanganate COD and 5-minute chlorine demand (PZD_Cl_2). Factor 5 depended primarily on the concentration of NH_4^+. The results obtained indicate that the decisive contributory factor in the rate of chlorine (chlorine dioxide) decay in raw water is the content of reduced compounds: the presence of iron(II), manganese(II) and organic matter, the level of pH and the concentration of chlorides. So far, chlorides have not been analysed in the literature as a factor that may influence the rate of chlorine (chlorine dioxide) decay in water.

The influence of chloride concentration was also observed with treated water samples, where chlorides exerted an influence on factor 3 and factor 4. Both the factors explained altogether 27.478% of the variance in the cases being analysed in this work here.

The explanation for the effect of chlorine concentration in the water on PZD_Cl_2 and PZD_ClO_2, as well as on k_Cl_2 and k_ClO_2, lies in the kinetics of the oxidation reactions that occur in the presence of chlorine (chlorine dioxide). As a result of this oxidation reaction, chlorides are formed. By virtue of Le Châtelier-Braun's principle, it can be concluded that with increasing concentration of the products, the rate of chemical change decreases. The effect of chlorides on the rate of chlorine (chlorine dioxide) decay in water distribution systems deserves further studies.

In the case of treated water, where iron and manganese compounds were removed and the quantity of organic compounds was reduced in the course of the treatment process, the value of factor 1 was influenced by the 5-minute chlorine dioxide demand (PZD_ClO_2), the

5-minute chlorine demand (PZD_Cl_2), the rate constant of chloride dioxide decay (k_ClO_2) and the concentration of ammonium ion. The value of factor 2 depended on permanganate COD (as in the case of raw water), as well as on UV_{254} absorbance and manganese concentration. Factor 3 was strongly influenced not only by the chlorides content of the water, but also by the concentrations of manganese and ammonium ion.The value of factor 4 depended on the coefficient of the rate of chlorine decay in the water, as well as on the concentrations of iron and chlorides. Factor 5 was strongly correlated with the pH of the water.

4.4. Chlorine (chlorine dioxide) decay in the main conduit supplying water from WTP Wrocław Mokry Dwór to the municipality of Oława

The pipeline chosen for the investigations into chlorine and chlorine dioxide decay transfers drinking water from WTP Wrocław Mokry Dwór to Oława and is one of the available tap water sources for this municipality. The pipes are made of steel and have a diameter of 500 mm; the water main is 19.49 km long. The aim of the study was to determine the change in chlorine concentration during passage through the WTP Mokry Dwór–Oława pipeline and to establish the constants of chlorine and chlorine dioxide decay. At the first stage of the investigations, water for analysis was taken from sampling points located at different distance from WTP Mokry Dwór on 6 November 2008. The results obtained are plotted in Figure 35 and summarised in Table 32. Chlorine concentration in the water pumped into the WTP Mokry Dwór–Oława main conduit was 0.4 $mgCl_2 \cdot dm^{-3}$.

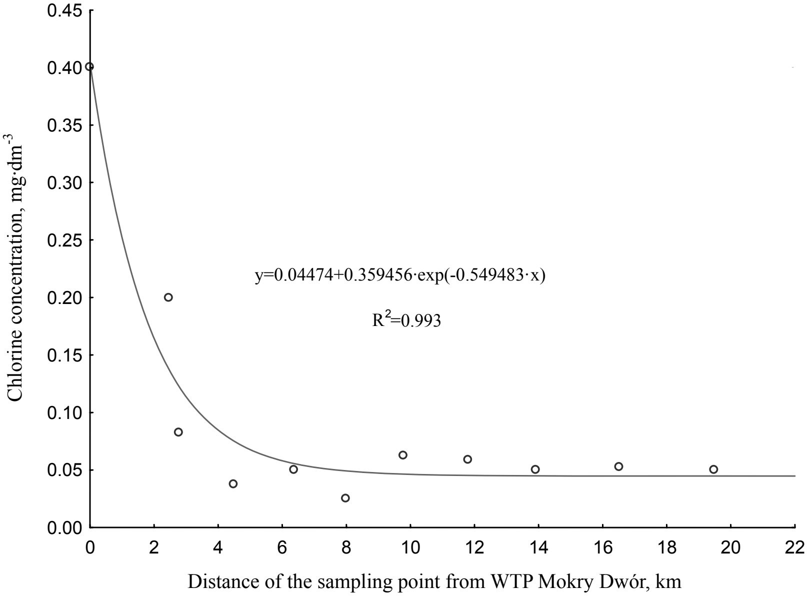

Fig. 35. Chlorine concentration variations in water collected at different sampling points along the WTP Mokry Dwór–Oława main conduit

Table 32

Chlorine concentrations in the WTP Mokry Dwór–Oława main conduit analysed on 6 November 2008

Distance from WTP Mokry Dwór km	Hour of sampling	Water temperature °C	Free chlorine concentration mg $Cl_2 \cdot dm^{-3}$	Average free chlorine concentration mg $Cl_2 \cdot dm^{-3}$
2.49	8.04	10.6	0.14	0.2
	8.09		0.22	
	8.12		0.41	
	8.28		0.07	
	8.42		0.16	
2.80	9.05	10.8	0.1	0.082
	9.10		0.09	
	9.14		0.08	
	9.19		0.06	
	9.23		0.08	
4.51	9.47	11	0.04	0.0375
	9.51		0.03	
	9.55		0.03	
	9.58		0.05	
6.40	10.10	11.3	0.04	0.025
	10.14		0.01	
7.98	10.35	11.4	0.08	0.062
	10.39		0.06	
	10.44		0.07	
	10.51		0.05	
	10.58		0.05	
9.81	11.11	11.6	0.08	0.0575
	11.16		0.05	
	11.21		0.03	
	11.26		0.07	
11.79	11.47	11.8	0.06	0.05
	11.51		0.06	
	11.56		0.03	
13.92	12.07	12	0.06	0.053
	12.12		0.08	
	12.17		0.02	
16.54	12.37	12.1	0.06	0.055
	12.57		0.02	
	12.41		0.05	
	12.46		0.09	
19.49	13.00	12.2	0.07	0.05
	13.03		0.07	
	13.10		0.01	
	13.16		0.05	

With increasing distance from WTP Mokry Dwór, chlorine concentration decreased gradually as far as approximately to the 8th km, and thereafter changed only slightly. Assuming that the time of water residence in the pipeline can be defined from the relation:

$$t = \frac{L}{v_{avg}} \tag{74}$$

where:

L – distance from WTP Mokry Dwór, km;
v_{avg} – average velocity of water flow, km·h^{-1};

equation (59) proposed by Warton et al. [2006] can be written as:

$$C(L) = a + b\exp(-d\frac{L}{v_{avg}}) \tag{75}$$

and after incorporation of the constant:

$$d^* = \frac{d}{v_{avg}} \tag{76}$$

into equation (75), we obtain:

$$C(L) = a + b\exp(-d^* L) \tag{77}$$

where:

a, b and d are constants determined *via* nonlinear estimation on the basis of experimental results.

Consistency between the model and experimental results is good (Fig. 35). The results obtained have demonstrated that in water mains chlorine decay can be modelled using the generalised relation of (77). To substantiate this conclusion, it is necessary to carry out investigations into other main conduits.

Table 33 shows the values of UV$_{254}$ absorbance measured in the water collected at the sampling points along the WTP Mokry Dwór–Oława main conduit. As can be seen from these data, UV$_{254}$ absorbance increased with the increase in both distance from WTP Mokry Dwór and the time of water residence in the pipeline. These changes were described by a linear function (Fig. 36). The increment in UV$_{254}$ adsorbance with the increase in residence time substantiates the increment in the organic matter content of the tap water. The increment in UV$_{254}$ absorbance has probably been induced by the activity of the biofilm grown on the pipe surface.

At the second stage of the study, the water collected at the sampling points along the WTP Mokry Dwór–Oława main conduit was tested for the rate constants of chlorine and chlorine dioxide decay. The samples were treated with chlorine doses or chlorine dioxide doses amounting to 0.36 mg Cl$_2$·dm^{-3} and 0.44 mg ClO$_2$·dm^{-3}, respectively. The results are summarised in Table 34.

Table 33

Results of investigations into UV_{254} absorbance in water collected at sampling points along the WTP Mokry Dwór–Oława main conduit on 6 November 2008

Distance from WTP Mokry Dwór	UV_{254} absorbance
km	m^{-1}
2.49	0.80
2.80	1.20
4.51	1.20
6.40	1.30
7.98	1.40
9.81	3.20
11.79	3.40
13.92	3.70
16.54	3.70
19.49	4.10

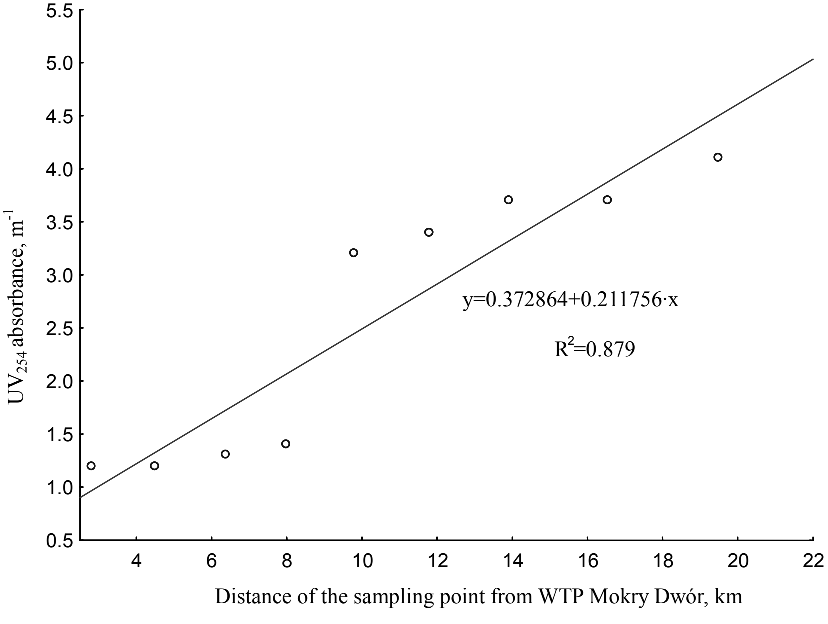

Fig. 36. Change in UV_{254} absorbance in tap water with distance of the sampling point from WTP Mokry Dwór

Table 34

Kinetics of chlorine (chlorine dioxide) decay involving post-disinfection of water collected at different sampling points along the WTP Mokry Dwór–Oława main conduit on 6 November 2008

Time of water contact with chlorine (chlorine dioxide)	Distance from WTP Mokry Dwór	Chlorine concentration	Chlorine dioxide concentration	Distance from WTP Mokry Dwór	Chlorine concentration	Chlorine dioxide concentration
minutes	km	mg·dm^{-3}		km	mg·dm^{-3}	
5	2.49	0.34	0.44	9.81	0.17	0.39
120		0.19	0.25		0.06	0.32
240		0.15	0.23		0.05	0.28
360		0.09	0.19		0.06	0.20
1230		0.04	0.07		0.06	0.18
5	2.80	0.35	0.44	11.79	0.32	0.39
120		0.23	0.30		0.20	0.32
240		0.20	0.24		0.16	0.23
360		0.13	0.21		0.13	0.19
1230		0.08	0.05		0.07	0.17
5	4.51	0.30	0.41	13.92	0.29	0.39
120		0.13	0.31		0.12	0.29
240		0.09	0.27		0.11	0.27
360		0.06	0.21		0.05	0.23
1230		0.05	0.07		0.04	0.17
5	6.40	0.33	0.44	16.54	0.31	0.42
120		0.19	0.40		0.19	0.34
240		0.15	0.32		0.15	0.29
360		0.12	0.28		0.04	0.26
1230		0.05	0.11		0.10	0.20
5	7.98	0.33	0.39	19.49	0.31	0.39
120		0.22	0.32		0.23	0.32
240		0.18	0.26		0.19	0.27
360		0.13	0.20		0.06	0.24
1230		0.06	0.09		0.09	0.16

The kinetics of chlorine (chlorine dioxide decay) was modelled using the following equation:

$$C(t) = a\exp(-k\,t) \tag{78}$$

where:

a – estimated initial concentration of the disinfectant, mg·dm^{-3};
k – rate constant of disinfectant decay in water, h^{-1}.

The values of the rate constants k of disinfectant decay for the water collected at particular sampling points are shown in Table 35.

Table 35

Rate constants of chlorine and chlorine dioxide decay
in water collected at the sampling points along the WTP Mokry Dwór–Oława main conduit
on 6 November 2008

Distance from WTP Mokry Dwór, km	Rate constant, *k*, of chlorine decay, h^{-1}, and determination coefficients of the model described by the generalised equation (78)		Rate constant, *k*, of chlorine dioxide decay, h^{-1}, and determination coefficients of the model described by the generalised equation (78)	
	k	R^2	*k*	R^2
2.49	0.22	0.96	0.137	0.89
2.80	0.13	0.88	0.128	0.98
4.51	0.33	0.91	0.100	0.99
6.40	0.18	0.93	0.072	0.99
7.98	0.15	0.95	0.091	0.97
9.81	0.21	0.64	0.092	0.97
11.79	0.16	0.97	0.101	0.95
13.92	0.30	0.94	0.083	0.95
16.54	0.21	0.86	0.077	0.99
19.49	0.17	0.88	0.091	0.99
Average values of decay constant	0.21	–	0.097	–

As for chlorine, the decay constants were characterised by a high variability, which remained at a similar level; in the case of chlorine dioxide, the decay constants followed a downward trend with the increase in the distance from WTP Mokry Dwór.

On 22 April 2009, water flowing through the WTP Mokry Dwór–Oława main conduit was collected again but only at the sampling points located at the distance of 2.8; 7.98; 16.54 and 19.49 km from WTP Mokry Dwór. All the them contained trace amounts of chlorine. Under laboratory conditions, the water samples were made subject to post-disinfection with chlorine (chlorine dioxide) at the same temperature as that in the pipe interior. The process was conducted with three chlorine doses: 0.3; 0.6 and 0.9 mg·dm^{-3}, and three chlorine dioxide doses: 0.2; 0.4 and 0.6 mg·dm^{-3}. Observations of changes in disinfectant concentrations were carried out for 12 hours. The results are shown in Tables 36 and 37.

Table 36

Kinetics of chlorine decay when use was made of post-disinfection of the water samples collected at various distance from WTP Mokry Dwór on 22 April 2009

Time h	Distance from Water Treatment Plant Mokry Dwór, km											
	2.80			7.98			16.54			19.49		
	Initial chlorine dose, mg·dm^{-3}											
	0.3	0.6	0.9	0.3	0.6	0.9	0.3	0.6	0.9	0.3	0.6	0.9
0.1	0.31	0.65	0.89	0.26	0.55	0.82	0.27	0.55	0.80	0.23	0.56	0.85
0.3	0.33	0.60	0.90	0.21	0.50	0.77	0.22	0.52	0.77	0.20	0.51	0.78
0.5	0.29	0.58	0.86	0.19	0.47	0.74	0.20	0.48	0.77	0.12	0.48	0.79
1	0.28	0.57	0.84	0.19	0.43	0.71	0.17	0.43	0.73	0.15	0.44	0.72
2	0.23	0.54	0.80	0.13	0.38	0.68	0.14	0.39	0.67	0.12	0.38	0.66
3	0.22	0.50	0.75	0.12	0.36	0.65	0.12	0.36	0.63	0.09	0.34	0.61
4	0.19	0.48	0.71	0.09	0.34	0.62	0.10	0.34	0.60	0.08	0.32	0.58
5	0.18	0.45	0.67	0.08	0.32	0.60	0.10	0.32	0.58	0.07	0.31	0.56
6	0.16	0.43	0.66	0.08	0.29	0.59	0.08	0.31	0.58	0.07	0.28	0.51
7	0.16	0.42	0.64	0.09	0.28	0.57	0.08	0.30	0.55	0.07	0.26	0.49
8	0.14	0.40	0.61	0.07	0.27	0.54	0.08	0.28	0.53	0.06	0.25	0.48
9	0.13	0.39	0.59	0.06	0.24	0.52	0.06	0.26	0.52	0.07	0.23	0.46
10	0.14	0.37	0.56	0.07	0.25	0.52	0.06	0.26	0.50	0.07	0.23	0.46
11	0.13	0.35	0.54	0.07	0.24	0.50	0.07	0.24	0.50	0.09	0.23	0.44
12	0.12	0.35	0.52	0.08	0.23	0.48	0.08	0.23	0.50	0.08	0.21	0.41

Table 37

Kinetics of chlorine dioxide decay when use was made of post-disinfection of the water samples collected at various distance from WTP Mokry Dwór on 22 April 2009

Time h	Distance from Water Treatment Plant Mokry Dwór, km											
	2.80			7.98			16.54			19.49		
	Initial chlorine dioxide dose, mg·dm^{-3}											
	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
0.1	0.32	0.44	0.69	0.32	0.67	0.46	0.39	0.52	0.72	0.29	0.53	0.65
0.3	0.28	0.50	0.74	0.32	0.74	0.50	0.32	0.47	0.67	0.29	0.47	0.63
0.5	–	0.47	0.65	0.32	0.66	0.45	0.30	0.46	0.66	0.29	0.47	0.60
1	0.27	0.44	0.61	0.29	0.62	0.42	0.26	0.42	0.62	0.27	0.45	–
2	0.23	0.40	0.56	0.25	0.56	0.37	0.25	0.41	0.58	0.24	0.40	0.56
3	0.22	0.39	0.52	0.24	0.53	0.35	0.25	0.40	0.56	0.22	0.40	0.56
4	0.20	0.35	0.47	0.22	0.50	0.32	0.17	0.39	0.55	0.22	0.39	0.54
5	0.19	0.34	0.41	0.21	0.45	0.30	0.23	0.36	0.53	0.22	0.34	0.51
6	0.17	0.30	0.41	0.20	0.44	0.28	0.22	0.34	0.51	0.21	0.35	0.49
7	0.16	0.29	0.37	0.19	0.41	0.25	0.20	0.34	0.49	0.19	0.33	0.47
8	0.14	0.27	0.35	0.17	0.37	0.24	0.20	0.33	0.49	0.17	0.32	0.46
9	0.17	0.25	0.35	0.19	0.37	0.22	0.20	0.34	0.47	0.17	0.31	0.44
10	0.12	0.24	0.32	0.17	0.34	0.22	0.19	0.32	0.47	0.17	0.30	0.44
11	0.12	0.24	0.30	0.17	0.33	0.22	0.19	0.31	0.46	0.17	0.29	0.43
12	0.13	0.21	0.29	0.17	0.32	0.22	0.19	0.30	0.44	0.18	0.29	0.45

Figures 37 and 38 relate the determined values of the coefficients of chlorine decay (k_Cl$_2$) and chlorine dioxide decay (k_ClO$_2$) to initial disinfectant dose and distance of the sampling point fromWTP Mokry Dwór.

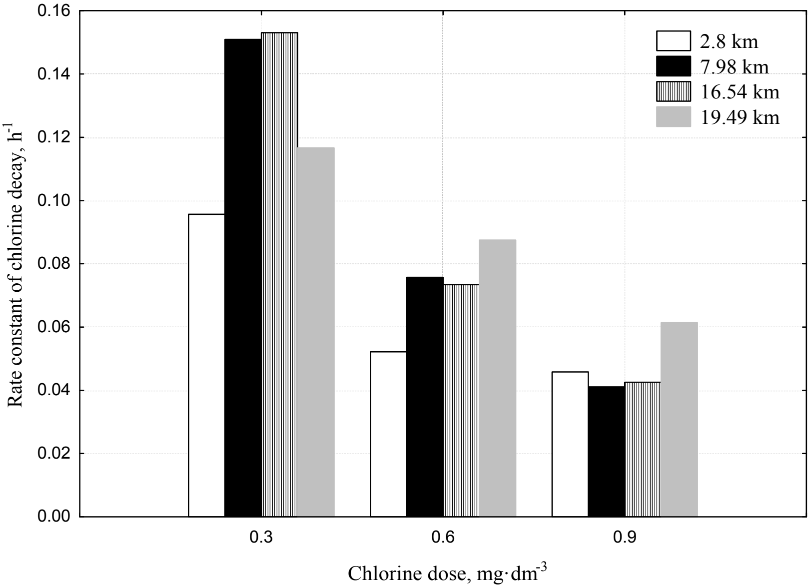

Fig. 37. Effect of disinfectant dose and location of the sampling point along the WTP Mokry Dwór–Oława main conduit on the rate constants of chlorine decay (k_Cl$_2$)

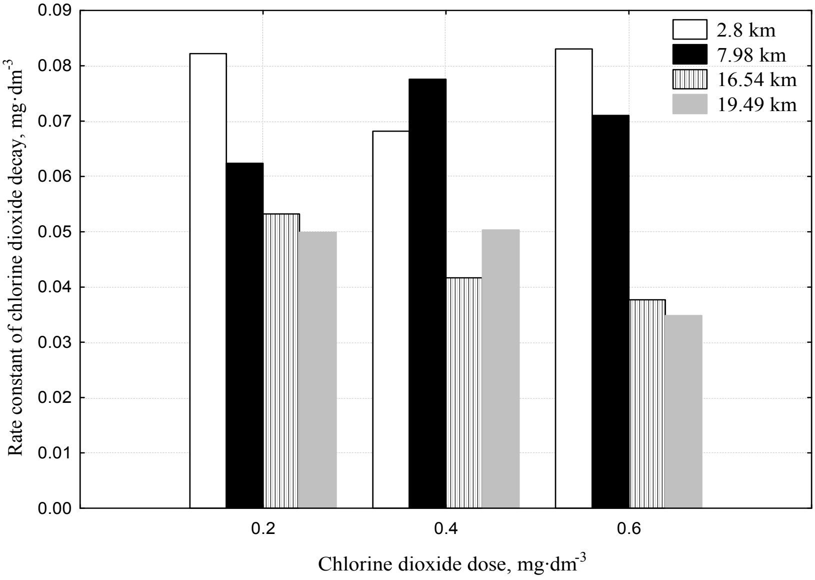

Fig. 38. Effect of disinfectant dose and location of the sampling point along the WTP Mokry Dwór–Oława main conduit on the rate constants of chlorine dioxide decay (k_ClO$_2$)

The initial concentration of the disinfectant exerts a noticeable influence on the rate constant of its decay: as the initial disinfection dose increases, the rate constant of its decay decreases. This holds true for both chlorine and chlorine dioxide. The investigations have revealed that with increasing distance from the water treatment plant the rate constants of chlorine decay increased whereas those of chlorine dioxide decay decreased. The results obtained imply that the assumption of constant values for the rate constants of disinfectant decay when modelling their changes in the water distribution system is misleading.

The results, furthermore, substantiate the need of investigating the rate of decay separately for each disinfectant being used, in order to reliably predict their concentrations in the water distribution system. Technological investigations are indispensable when a disinfectant is to be replaced, or when post-disinfection points are to be established in large water supply systems.

4.5. Effect of water-pipe deposits on the rate of chlorine (chlorine dioxide) decay

It has frequently been observed that upon damage repair in the water distribution system, or after long-lasting stoppage in water supply, turbidity tends to increase and flocs of pipe deposits are present in the water. As yet, no efforts have been reported in the literature to determine the effect of water-pipe deposits on the rate of chlorine or chlorine dioxide decay in tap water. To acquire more detailed knowledge of this phenomenon, an experiment was carried out with samples of deposits which had accumulated on the internal walls of the pipes in the WTP Mokry Dwór–Oława main conduit, and had been collected during repair work. Then a suspension was prepared by making up 10 ml portions of the deposit with distilled water to 1 dm^3. The characteristics of the suspension (suspended solids) is shown in Table 38.

Table 38

Characteristics of the diluted suspension (suspended solids) added to the tap water sample

Turbidity	Total iron	Fe^{2+}	Fe^{3+}	Manganese	pH	Conductivity
NTU	$mg \cdot dm^{-3}$				–	$\mu S \cdot cm^{-1}$
30	3.4	0.9	2.5	0.65	5.9	102.5

Two experimental series were carried out. In the first series, one litre of tap water was treated with 5 and 10 ml of the suspension; in the second series, the volume of the suspension was increased to 20, 30 and 50 ml. The one-litre tap water samples prepared in this way and treated with appropriate portions of the suspension were further treated with 0.65 $mgCl_2 \cdot dm^{-3}$ or 0.4 mg $ClO_2 \cdot dm^{-3}$. Simultaneous experiments were conducted using tap water samples with no suspension. After a defined period, chlorine or chlorine dioxide concentrations were determined. The results are presented in Figures 39 to 42.

Surprisingly, in the tap water samples where suspended solids were present chlorine decay proceeded at a slower rate than in those with no suspended solids (Figs. 39 and 41). The rate of chlorine decay increased with the amount of suspended solids in the sample, but this increase followed a noticeably irregular pattern. The suspension used in the experiments was found to inhibit chlorine decay. The cause behind this inhibition is in the poor ability of chlorine to penetrate the suspension when the organic substances present in the water simultaneously adsorb on the surface. The presence of suspended solids in tap water did not affect the rate of chlorine dioxide decay (Figs. 40 and 42), so the degradation of this disinfectant proceeded at the same rate as in tap water.

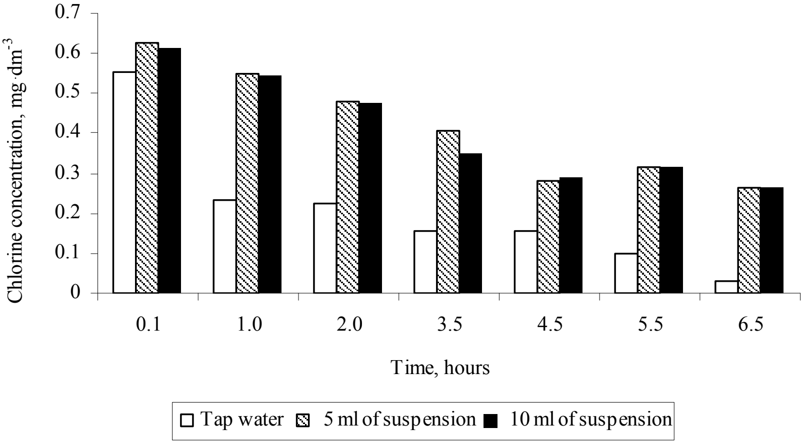

Fig. 39. Change in chlorine concentration with time, at suspension doses of 5 and 10 ml·dm^{-3}

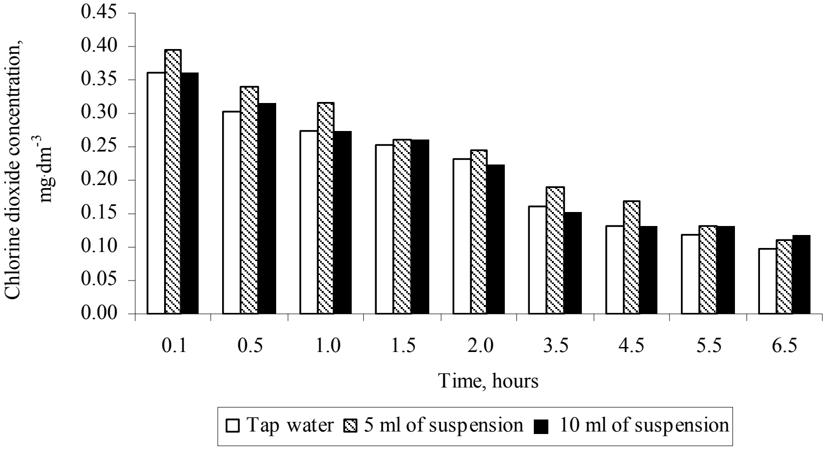

Fig. 40. Change in chlorine dioxide concentration with time, at suspension doses of 5 and 10 ml·dm^{-3}

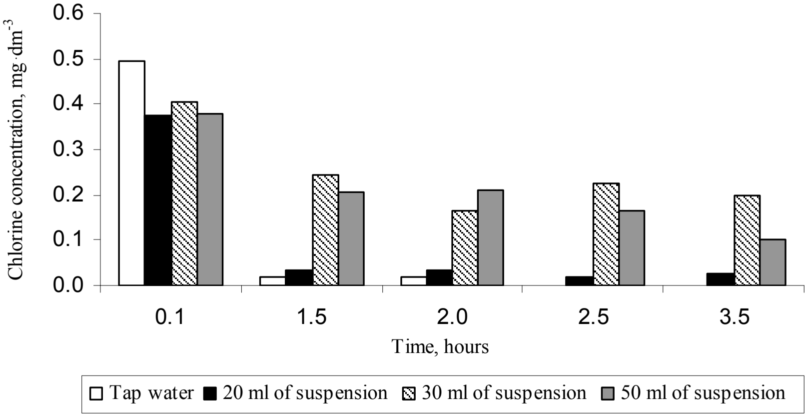

Fig. 41. Change in chlorine concentration with time, at suspension doses of 20, 30 and 50 ml·dm-3

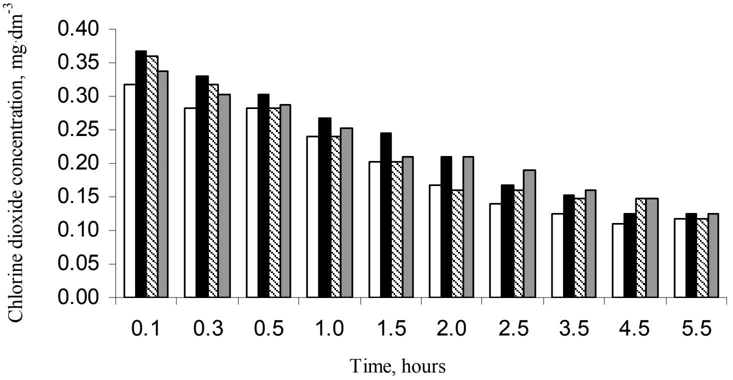

Fig. 42. Change in chlorine dioxide concentration with time, at suspension doses of 20, 30 and 50 ml·dm-3

The results of these experiments clearly show that the deposits washed away from the pipe surface following temporal stoppage of water supply do not increase the chlorine demand of tap water.

5. CONCLUSIONS

- Water composition is a contributing factor in the rates of chlorine and chlorine dioxide decay. Theoretical studies, laboratory tests and full-scale investigations involving real objects have disclosed that the presence of organic compounds, iron(II), manganese(II), ammonia and chlorides, as well as the pH of the water, affect the rate of chlorine decay. The original achievement in this work here consists in demonstrating that chlorine (chlorine dioxide) decay is influenced by the concentration of chlorides in the water being disinfected.
- Differences were found in the kinetics of decay between chlorine and chlorine dioxide during flow in the drinking water distribution system. This is a clear indication that the rates of decay for the two disinfectants should be examined separately in order to reliably predict their concentrations in the water transported to the customers. Technological investigations are indispensable, specifically when the disinfectant is to be replaced with another one, or when post-disinfection points are to be established in large water distribution systems.
- Experiments with treated tap water samples have revealed that changes in chlorine dioxide concentrations occurring in water distribution systems can be quickly predicted in terms of five-minute chlorine demand (PZD_Cl_2). Based on the determined value of (PZD_Cl_2), it is possible to assess the rate constants of chlorine dioxide decay in tap water.
- Research has confirmed that the rate constants of chlorine (chlorine dioxide) decay in tap water are influenced by the disinfectant dose applied.
- Suspended solids entering the water during failure events in the water-pipe network have no significant effect on the kinetics of change in the concentration of chlorine dioxide. As for chlorine, the presence of suspended solids washed away from the pipes reduces the rate of its decay in water.
- When modelling changes in chlorine concentration during flow in main conduits, chlorine decay can be described in terms of the modified equation proposed by Warton et al. [2006]:

$$C(L) = a + b\exp(-d^{*}L)$$

where $d^{*} = \frac{d}{v_{avg}}$ is average velocity of water flow, km·h^{-1};

the constants a, b and d are determined *via* nonlinear estimation based on experimental results, and L stands for the distance from the water treatment plant (km).

- When the mole ratio of hydrochloric acid to sodium chlorite takes values lower than 1, this is concomitant with a significant increase in the concentration of the sum of chlorites and chlorates in tap water disinfected with chlorine dioxide. This finding clearly indicates that the concentrations of the two reagents used for chlorine dioxide generation, as well as the mole ratio between them, require continuous control. Continuous control is also an essential requisite for the chlorine dioxide dose, which cannot exceed the admissible value. If these requirements are fulfilled, the need to control chlorite and chlorate concentrations in drinking water by means of the costly ion chromatography method will be reduced noticeably.

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KINETICS OF CHANGE IN THE CONCENTRATIONS OF CHLORINE AND CHLORINE DIOXIDE IN WATER DISTRIBUTION SYSTEMS

Summary

It is difficult for a distribution system to provide full protection of the water against the loss of biological stability during flow from the waterworks to the consumer. The presence of a disinfectant reduces the risk of microbial growth in the distribution system or recontamination of tap water but the disinfectant dose is crucial. Even though disinfectant residual reduces the number of bacteria, it may provide favourable conditions for the occurrence of compounds with toxic properties. Therefore, the modelling of the disinfection process requires good knowledge and understanding of disinfectant decay. While the kinetics of chlorine decay is well described in the literature, the kinetics of chlorine dioxide decay is still insufficiently understood. This monograph describes chlorine and chlorine dioxide decay in tap water, as well as the influence of the disinfection and treatment processes used on the quality of water transported in the distribution system. The results were obtained from studies performed in 40 different water treatment plants located mainly in Lower Silesia, Poland. The primary objective of these studies was to define the effect of organic substance concentrations on the rate constants of chlorine dioxide decay in tap water. Another major objective was to ascertain if the rate constants of chlorine dioxide decay depend on the rate constants of free chlorine decay and on the five-minute chlorine demand of the water defined as the difference between chlorine dose and chlorine concentration after five-minute contact of water with chlorine. It seemed, furthermore, advisable to examine whether the quantity of chlorites and chlorates that form in the water being disinfected with chlorine dioxide depends on the mode of chlorine dioxide production in generators.

Theoretical studies, laboratory tests and full-scale investigations conducted within the scope of the studies have disclosed that water composition is a major contributing factor in the rates of chlorine and chlorine dioxide decay. The presence of organic compounds, iron(II), manganese(II), ammonia and chlorides, as well as the pH of the water, affect the rate of chlorine decay. The novelty of the work consists in demonstrating that chlorine (chlorine dioxide) decay also depends on the concentration of chlorides in the water being disinfected.

An original achievement in this work is the finding that there are essential differences in the kinetics of decay between chlorine and chlorine dioxide in water distribution systems. This indicates that the decay rates of the two disinfectants should be examined separately to reliably predict their concentrations in the water transported to the customers. Technological investigations are indispensable, when the disinfectant is to be replaced with another one, or when post-disinfection points are to be established in large water distribution systems.

Another achievement was an experiment with treated tap water samples, which has revealed that changes in chlorine dioxide concentrations occurring in water distribution systems can be quickly predicted in terms of five-minute chlorine demand. Based on the determined value of five-minute chlorine demand, it is possible to assess the rate constants of chlorine dioxide decay in tap water. Since there is a risk that chlorine dioxide by-products may form, the concentrations of sodium chlorite and hypochloric acid used for chlorine dioxide generation, as well as the mole ratio between them, require continuous control. Such control is also an essential requisite for the chlorine dioxide dose, which cannot exceed the admissible value. If these requirements are fulfilled, the need to control chlorite and chlorate concentrations in drinking water by means of the costly ion chromatography method will be reduced noticeably.

Key words: tap water, disinfection, chlorine, chlorine dioxide, rate constant, disinfectant decay

KINETYKA ZMIAN STĘŻENIA CHLORU I DWUTLENKU CHLORU W WODACH WODOCIĄGOWYCH

Streszczenie

Utrzymanie stabilności biologicznej wody wodociągowej od stacji uzdatniania wody do odbiorcy stwarza wiele problemów technologicznych. Obecność dezynfekanta ogranicza rozwój mikroorganizmów w systemie dystrybucji i zapobiega ich wtórnemu rozwojowi, lecz dawka dezynfekanta jest bardzo istotna. Chociaż obecność dezynfekanta pozostałego zmniejsza liczbę bakterii w systemie dystrybucji, to stwarza ryzyko wystąpienia związków o właściwościach toksycznych. Dlatego modelowanie zmian stężenia dezynfekanta w wodzie wodociągowej wymaga dobrej wiedzy i zrozumienia tego procesu. Kinetyka szybkości zaniku chloru została dobrze opisana w literaturze, podczas gdy kinetyka szybkości zaniku dwutlenku chloru nie została jeszcze wystarczająco rozpoznana. Monografia opisuje kinetykę zaniku chloru i dwutlenku chloru w wodach wodociągowych, jak również wpływu dezynfekcji i dystrybucji wody na jej jakość. Przedstawione wyniki uzyskano na podstawie badań przeprowadzonych w 40 różnych stacjach uzdatniania wody zlokalizowanych głównie na terenie Dolnego Śląska. Nadrzędnym celem badań było określenie wpływu stężenia substancji organicznych na stałe szybkości zaniku dwutlenku chloru w wodzie. Kolejnym celem było sprawdzenie, czy stałe szybkości zaniku dwutlenku chloru zależą od stałych szybkości zaniku chloru i od pięciominutowego zapotrzebowania na chlor, określonego jako różnica między dawką dezynfekanta a stężeniem chloru po pięciu minutach kontaktu z wodą. Ponadto wykonano badania w celu sprawdzenia, czy ilość powstających chlorynów i chloranów w wodzie poddawanej dezynfekcji dwutlenkiem chloru zależy od sposobu wytworzenia dwutlenku chloru w urządzeniach technicznych.

Badania teoretyczne, laboratoryjne i w skali technicznej wykazały, że skład wody wpływa na szybkość zaniku chloru i dwutlenku chloru. Obecność związków organicznych, żelaza(II), manganu(II), amoniaku oraz chlorków, a także odczyn wody wpływają na szybkość zaniku chloru w wodach. Oryginalnym osiągnięciem jest wykazanie, że na zanik chloru (dwutlenku chloru) ma wpływ stężenie chlorków w wodzie.

Ważnym osiągnięciem pracy jest stwierdzenie, że istnieją różnice w kinetyce zaniku chloru i dwutlenku chloru. Uzyskane wyniki wskazują na potrzebę prowadzenia indywidualnych badań nad szybkością zaniku dezynfekantów w celu prognozowania ich stężeń w wodzie transportowanej systemem wodociągowym. Przeprowadzenie badań technologicznych jest niezbędne zwłaszcza w przypadku zmiany dezynfekanta, a także przy ustalaniu punktów post-chlorowania wody, głównie w rozległych systemach wodociągowych.

Przeprowadzone badania na uzdatnionych wodach wodociągowych wykazały, że istnieje możliwość szybkiej predykcji zmian stężenia dwutlenku chloru w systemie wodociągowym na podstawie pięciominutowego zapotrzebowania na chlor. Według oznaczonej wartości pięciominutowego zapotrzebowania na chlor można oszacować stałe szybkości zaniku dwutlenku chloru w wodzie wodociągowej. Wykazano również potrzebę ciągłej kontroli stężenia reagentów chemicznych używanych do wytwarzania dwutlenku chloru, stopnia ich zmieszania oraz wprowadzenia dopuszczalnej dawki dwutlenku chloru. Ograniczy to potrzebę częstego kontrolowania stężeń chloranów i chlorynów w wodzie wodociągowej przy użyciu drogich metod chromatografii jonowej.

Słowa kluczowe: woda wodociągowa, dezynfekcja, chlor, dwutlenek chloru, stała szybkości, zanik dezynfekanta