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The optimization of chlorine dose in water treatment process in order to reduce the formation of disinfection by-products

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ABSTRACT

The main threat to human health is associated with organic compounds, which are found in the natural water ecosystem. The law relating to drinking water quality protects consumers' health. Thus, the need to remove disinfection by-products (DBP) precursors requires the application of high-efficient water treatment processes. Usually, chlorine is used to disinfection, and then, haloforms are generated. Well-calibrated model, estimating the concentration of DBP in treated water, can be a useful tool for predicting the quantity of trihalomethanes in water in the distribution network. Such a model makes it also possible to identify the critical control points in the monitoring process. This paper presents the statistical analysis of chloroform formation in treated water, based on laboratory tests. The chloroform concentration is expressed as a function of factors, which determine kinetics of the chemical reaction of organic compounds with chlorine. Two new variables—the ratio of total organic carbon and chloroform and the ratio of chlorine consumption and chlorine dose, both obtained after 1 h of the reaction—were taken into account. From the function predicting the chloroform concentration, one can determine the optimal dose of chlorine in the disinfection of water in dynamic operational conditions.

Keywords: Chloroform; Trihalometanes; Water treatment; Multiple regression

1. Introduction

Surface and underground water are reservoirs exposed to various contaminants of natural origin and anthropogenic. Natural organic compounds in water occur due to processes in the catchment. Mentioned above natural organic matter includes humic substances, peptides, amino acids, tannins, chlorophyll *a*, and various metabolites of aquatic organisms. The main threat to human health (resulting from the consumption of water) is associated with organic compounds of anthropogenic origin, which are found in a natural aquatic system. Approximately, one-third of organic compounds produced in the national economy goes into the environment, including water.

Development of analytical methods, especially gas chromatography, a particle capture detector, and mass

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spectrometry, enabled researchers to identify the substances found in micrograms per liter of water. Laboratory tests are also focused on disinfection by-products (DBP). All data obtained from the analytical study of water and growing toxicology are permanently used to verify current legal regulations related to the quality of water intended for human consumption. The legislation [1] protects the consumers' health because of numerous scientific confirmations of carcinogenic or mutagenic effects of DBP, including chloroform. In 1996, the World Health Organization at the request of the International Agency for Research on Cancer placed the chloroform to the group 2B.

The discovery in 1974 of the presence of DBP in chlorinated water made it necessary to look at the issue of water treatment due to the fact that coagulation and filtration processes do not guarantee the efficient removal of DBP precursors, which makes the increment of risk of formation of trihalometanes (THM) in chlorinated water. The need for removal of precursors of THM makes the processes of sorption on an activated carbon be preceded by coagulation, filtration as well as the initial and secondary ozonation, which constitute an important part of modern water treatment plants (WTP). Chlorine is still an indispensable disinfection agent because of the assurance of a high microbiological stability of water in the distribution subsystem as well as of economic calculation of waterworks operation.

Most threats concerning the operation of water supply systems (WSSs) come from the fact that the THM formation in drinking water occurs not only in the place of treatment but also in the water transported by wide pipe networks. Harmful effects of THM on human health and also the inability to eliminate THM formation during the transport of chlorinated water make it necessary to develop the methodology for determining the THM concentration in the water supplied to the consumer. Such a model might be an important tool in the decision-making in order to determine the technological parameters of water treatment processes. So, well-calibrated model can also be helpful to monitor the process—apart from the complex laboratory analyzes, which require time and money.

There have been a few attempts made in order to define a mathematical model, which describes changes of THM concentration generated in chlorinated water. The scientific background of construction of these models is derived from the application of the methods of mathematical statistics. In 1987, the first important result, in which the prediction of THM concentration was based on quality parameters of water and reaction conditions, was published [2]. The authors predicted the concentrations of trihalometanes formation potential $PTHM$ [mol/l] as a function of a content of organic compounds—TOC [mgC/l], UV-254 nm, chlorine dose D_{Cl_2} [mgCl$_2$/l], contact time of water and chlorine t [h], the temperature T [°C], and pH as well as the concentration of bromide Br [mgBr/l] in water. The model estimates it by the following formula:

$$PTHM = 0.00309\,(UV \cdot \mathrm{TOC})^{0.440} \cdot (D_{\mathrm{Cl}_2})^{0.409} \cdot (t)^{0.205} \cdot (T)^{1.06} \cdot (\mathrm{pH} - 2.6)^{0.715} \cdot (\mathrm{Br} + 1)^{0.0356} \tag{1}$$

Above model was obtained in laboratory studies and was based on standard solutions that contained humic maters. Most of the models described in the literary sources are based on laboratory tests in fixed conditions [2–4]. This is the reason why these models cannot be directly applied to a real exploitation WSS; every time, they need verifying. However, one can find examples of the research on the actual concentration of THM in real distribution networks [5–8]. The comparison of published models indicates that parameters in the prediction formula are always related to individual internal and external conditions of the study.

From the point of view of operation of WSSs, it is important to recognize the process of formation of THMs in close relation to the working conditions of the distribution network.

2. Materials and methods

This paper presents the scientific research results from analysis of a large WSS of Wroclaw city in the southern-west of Poland. The WSS operates on the basis of surface water from the Olawa River, with a high concentration of organic substances that are DBP precursors. It is the reason for high costs of monitoring the water quality both in water intake, in a technological system as well as in a large distribution network. Thus, a developed mathematical model of DBP formation is a useful tool in management of such WSS. The mathematical model allows to decrease significantly the cost of water production and all costs related to water quality monitoring.

Wroclaw with about 680 thousands inhabitants is one the biggest and most important industry, cultural and scientific centers of Poland. Such a highly developed city requires a large amount of water to meet needs of its inhabitants and industry. The intensive development of the Wroclaw WSS is connected with building the water treatment plant Na Grobli in 1871. At the beginning, Na Grobli plant supplied water to the city from the Odra River. Water was pumped through sand filters, and after treatment, it was directed to the water tower at the height of 38 m and then gravitationally by a pipe of diameter 762 mm to the municipal WSS. At that time, the daily production was about 11,000 m^3.

At present, Wroclaw's WSS consists of two subsystems: the water production subsystem and the water distribution subsystem (WDS). The distribution subsystem is connected with two big WTP: Na Grobli and Mokry Dwór, and one small Lesnica, which operate basing on independent high-effective technological lines. The primary assignment realized by WTP is to maintain the continuity and reliability of supplied water characterized by standardized quality and required pressure. Plants continuously supply water to meet city demand. WTP have total production capacity at the level of 219,000 m^3/d, which is a double value of water consumption (Table 1).

The WSS in Wroclaw takes water from the Olawa River, which is supplied by switching the water system from the Nysa Klodzka River. Enriched Olawa's River water resources are taken in Czechnica and then that water is over pumped to water-bearing areas of Wroclaw's WSS, which are located in southeastern outskirts of city along the left bank of the Odra River. The water intake system includes irrigation ditches and canals with a total length of 21 km, by which water is supplied to 63 infiltration ponds (total area of approximately 60 ha). That water is a source of raw water for the WTP Na Grobli. Moreover, the Czechnica pumping station is the first-degree pumping system providing raw water by two pipes with diameter 1200 mm to water treatment plant Mokry Dwor. In addition, the water intake system based on the water taken from Olawa River has an independent water source for WTP Lesnica (groundwater resources) in the north west of city, which are nearly 1% of the total current water production of Wroclaw WSS.

Table 1
Water production of WTP of Wroclaw city

Water treatment plant	Average production [m^3/d]	Percent fraction [%]	Maximal water production [m^3/d]
WTP Mokry Dwor	58,000	48	98,000
WTP Na Grobli	61,000	51	120,000
WTP Lesnica	1,000	1	1,100
WSS	120,000	100	219,000

Total length of Wroclaw water-pipe network is 1,800 km. The WDS consists of about 200 km of main network, 1,200 km of distribution network, and about 30 thousands of terminals of length 390 km. It is a ring system. Owing to this, there exists the possibility of delivering water to specified places from other directions of supply in case some parts of the network are cut off due to some failure or modernization. The location and the working conditions of WPD and WDS as well as the characteristics of the terrain in Wroclaw are the reasons for separating four water supply zones in the city.

The reason for selecting Mokry Dwor WTP as an object of research presented in this paper is that the plant intakes surface water from the Olawa River. The water in the Olawa River has both solids (turbidity, suspended matter), chemical (compounds of iron, manganese, ammonia) and organic compounds (bacteria, diatoms, green algae, plankton) with a high level of THM precursors. These waters are characterized by high levels of volatility of pollutants concentration during the year. To be treated in accordance with the global and Polish standards relating drinking water, it is treated on the technological processes, such as classic coagulation using aluminum compounds (PAC-10WA), sedimentation, rapid filtration on sand bed, intermediate ozonization, sorption on activated carbon, and disinfection using chlorine and chlorine dioxide. The treatment technology applied in Mokry Dwor WTP guarantees the high quality of drinking water in accordance with the standard. However, the usage of chlorine as a disinfectant increases the risk of THM formation during a long transport to consumers. Indeed, constant laboratory water analyses confirm irregular occurrence of THM in the WDS.

The exploitation practice of the WSS shows that insignificant amounts of organic matter remain in treated water (they do not exceed the level required by law), but the consequence of this may be a significant content of THM in the water delivered to customers. Taking that into consideration, some laboratory research has been undertaken. It was focused on looking for the parameter of water quality that could be the best factor of predicting THM concentration in water-pipe network. This parameter would allow the operator of WTP to determine the range of water quality change in the WSS in the function of THM formation as a side effect of water chlorination. For this purpose, a series of laboratory tests have been done in order to define the parameters determining the reaction of the chloroform formation.

The results of these tests were subjected to statistical analysis. Different sets of variables and their transformations were studied using statistical methods. A good model, which would explain the relationships between studied variables, was searched using multiple regression.

3. Experimental procedure

The water samples for tests were taken from a technological line of Wroclaw WTP before the disinfection process. The concentration of the water sample was 50 times smaller in a flow system with membrane (membrane model: TW 30-2012-75 GDP, series nr JD 0701210 with pump Booster Pump PJ-V 6005), to extract the water of total organic carbon concentration equal to 20 mg C/l. The final water samples of different concentrations of total organic carbon (1.02, 2.11, 3.04, 4.0, and 8.17 mg C/l) obtained by the dilution methods. These water samples were subjected to the disinfection process, in which the dose of chlorine was respectively 2.0, 6.0, 4.0, and 8.0 mg Cl_2/l. In those samples, the concentrations of residual chlorine and the amount of chloroform were determined appropriately after 1, 2, 8, 24, 48, and 72 h of reaction.

The following variables were considered (in parentheses, the procedures according to which water samples' quality was specified are given):

- pH [dimensionless] (PN-90/C-04540.01, multifunction apparatus inoLab MultiLevel1),
- T [°C]—temperature (PN-77/C-04584, mercury thermometer),
- D_{Cl_2} [mgCl_2/l]—the total chlorine dose (PN-ISO 7393–2:1997, photometer PC Compact Chlor),
- R_{Cl_2} [mgCl_2/l]—residual chlorine (PN-ISO 7393–2:1997, photometer PC Compact Chlor),
- TOC [mgC/l]—total organic carbon (PN-EN-1484–1999, analyzer TOC 5050 Shimadzu), and
- $CHCl_3$ [μg/l]—the concentration of chloroform (75-PB-NJL-W-06, gas chromatograph HP-5890GC/5970MSD).

4. Results and discussion

The basic descriptive statistics (i.e. mean, median, minimum and maximum values, and standard deviation) of studied variables are collected in Table 2.

Table 3 shows correlation coefficients between considered variables. Statistically significant coefficients (with) are indicated by bold font. These results confirm the following known facts:

- the longer reaction time, the greater the concentration of chloroform (high correlation),
- the greater chlorine dose, the greater the concentration of chloroform (average correlation),
- the higher temperature, the greater the concentration of chloroform (weak correlation), and
- the lower concentration of residual chlorine (i.e. the greater chlorine consumption), the greater the concentration of chloroform (average correlation).

It follows also from Table 3 that there is a very weak (or not at all) linear association between total organic carbon and chlorine dose, reaction time, pH, and temperature. It was to be expected since we had only the content of total organic carbon at the beginning (so there is no correlation with reaction time), whereas other correlation coefficients are irrelevant because the values of chlorine dose, pH, and temperature were forced (also at the beginning of the experiment). On the other hand, the statistically significant correlation between total organic carbon and residual chlorine is noticed, and it follows from the fact that the greater content of organic compounds causes the greater chlorine consumption and thus there is less residual chlorine.

The main aim of presented research was to obtain a formula, which approximates the value of chloroform concentration based on input parameters. One of the possible and frequently employed methods is the multiple regression based on the least square method [4]. It was noticed that a dependent variable $CHCl_3$ was not normally distributed—at the significance level, the Kolmogorov–Smirnov and χ^2 tests [9] indicated that the null hypothesis about normal distribution had to be rejected. However, the transformed variable is normally distributed, so this variable was considered in further research.

The first hour is the most important in trihalomethanes formation, so the two new variables were considered: the ratio of total organic carbon and chloroform and the ratio of chlorine consumption and chlorine dose, both obtained after one hour of the reaction. These variables have statistically significant sample correction coefficients with variable (i.e. –0.32 and 0.44, respectively).

The analysis of results of standard multiple regression, backward elimination as well as forward selection, calculated for various combinations of considered explanatory variables results in the following model:

Table 2
Basic descriptive statistics of considered variables

	Mean	Median	Minimum	Maximum	Standard deviation
TOC (total organic carbon)	3.80	4.00	1.02	8.17	1.90
D_{Cl_2} (chlorine dose)	4.82	6.00	2.00	8.00	1.96
R_{Cl_2} (residual chlorine)	1.85	1.66	0.03	5.36	1.54
t (time of reaction)	25.83	16.00	1.00	72.00	26.36
pH	7.28	7.30	6.50	8.00	0.27
T (temperature)	19.41	20.00	5.00	25.00	3.81
$CHCl_3$ (chloroform)	41.74	29.55	7.60	134.00	30.60

Table 3
Sample correlation coefficients between considered variables

	TOC	D_{Cl_2}	R_{Cl_2}	t	pH	T	$CHCl_3$
TOC	1.00	0.04	**–0.29**	0	–0.01	–0.02	0.19
D_{Cl_2}	0.04	1.00	**0.67**	0	–0.05	–0.09	**0.31**
R_{Cl_2}	**–0.29**	**0.67**	1.00	**–0.45**	–0.07	**–0.23**	**–0.44**
t	0	0	**–0.45**	1.00	0	0	**0.67**
pH	–0.01	–0.05	–0.07	0	1.00	0	0.06
T	–0.02	–0.09	**–0.23**	0	0	1.00	**0.24**
$CHCl_3$	0.19	**0.31**	**–0.44**	**0.67**	0.06	**0.24**	1.00

$$\ln CHCl_3 = 0.63001 + 0.85787 \ln TOC + 0.32713 \ln t + 0.67185 \ln T + -2.30347 \left(\frac{TOC}{CHCl_3}\right)_{after\,1h} - 0.80701 \left(\frac{D_{Cl_2} - R_{Cl_2}}{D_{Cl_2}}\right)_{after\,1h} \pm 0.333 \qquad (2)$$

Only the free term is not statistically significant at the significance level $\alpha = 0.05$. The model was obtained by excluding the cases, for which $t = 1$. Eq. (2) has the value of F-test equal to 49.68 (which corresponds to p-value less than 10^{-5}). Thus, the test confirms that there is a significant relationship among independent variables and variable $\ln CHCl_3$. The differences between observed and predicted values of $\ln CHCl_3$ are small, and they are contained in interval $\langle -0.7978, 0.7305\rangle$. They are approximately normally distributed (Fig. 1). The analysis of residuals ($R = 0.870$, $R_a^2 = 0.743$) leads to the conclusion that 74% of the variability in $\ln CHCl_3$ is explained by relationship (2).

Directly from (2), we have

$$CHCl_3 = 1.87763 \cdot (TOC)^{0.85787} \cdot t^{0.32713} \cdot T^{0.67185} \cdot \exp\left(-2.3034 \left(\frac{TOC}{CHCl_3}\right)_{after\,1h} - 0.80701 \left(\frac{R_{Cl_2} - D_{Cl_2}}{D_{Cl_2}}\right)_{after\,1h} \right) \qquad (3)$$

For the last model, applied to complete data, errors are greater which is related to the properties of logarithmic function. The residuals, shown in Fig. 2, are contained in interval $\langle -33.53, 19.80\rangle$, but as many as 70% of the observations lie in the range from –10 to 10. This is quite a good result if we take into account a big range of variation of input variables.

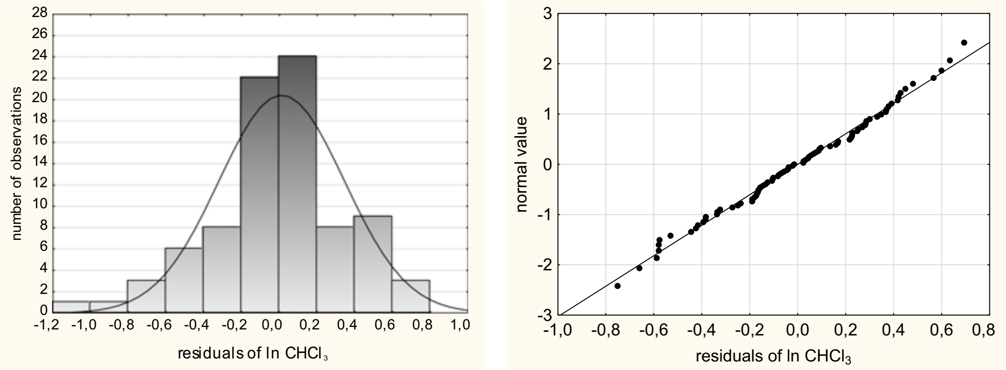

Fig. 1. Residuals for model (2).

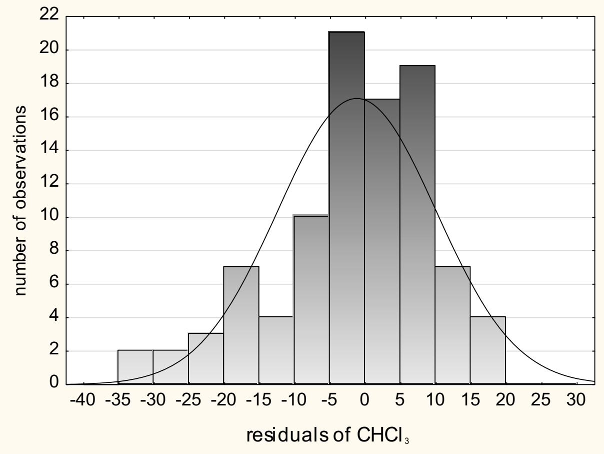

Fig. 2. Residuals for model (3).

5. Conclusion

Optimizing the dose of chlorine in order to reduce the formation of chloroform is significant in economy, technology, and health areas. Statistical analysis is a useful tool for predicting DBP concentration in treated water. The method does not involve large costs and may be applied in order to improve management and decision processes. The research should be focused more on the concentration of chloroform rather than on the sum of THMs because there are more restrictive norms for chloroform. Simultaneously, the chloroform is a significant fraction of the sum of THMs.

The new parameters considered in the paper allow obtaining a very good equation used for predicting the chloroform concentration. The model obtained by multiple regression applied to data from laboratory tests provides a better adjusted coefficient of determination R_a^2 in comparison with the ones obtained from data collected during the exploitation—in the latter cases, values of R_a^2 were about 0.3–0.55, which means that only up to about 50% of variability of dependent variables may be explained by those statistical models [4,8]. It is possible that the application of a described method (using defined new parameters) in real WSSs will provide more precise estimations, however; it still requires some further research.

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