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THM FORMATION IN WATER SUPPLY IN SOUTH BOHEMIA, CZECH REPUBLIC

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Abstract—In recent years attention has been drawn to various aspects related to the influence of disinfection by-products in distribution systems. The formation of trihalomethanes (THMs) and its species which form from the reaction of chlorine with humic substances have caused much alarm because of their carcinogenic and dangerous health effects. This article studies the factors affecting THM formation in pipelines transporting drinking water in the south of Bohemia in the Czech Republic. The residual chlorine in water entering these pipelines is in average 0.75 mg l^{-1} and decreases with distance until it reaches zero. The low velocity and the large volume of reservoirs increase the residence time and correspondingly provide conditions for more chlorine decay and accordingly an increase in THM formation. The effect of temperature and organic matters on THM formation was also studied in this article. The residence time and decay of chlorine were used as good predictors for the formation of THM and chloroform in this study. There was a linear correlation between the cumulative chlorine decay and the cumulative THMs formed in the pipelines with $R^2 = 0.913$. Meanwhile, the correlation between THM formation and residence time was exponential with $R^2 = 0.91$. © 2000 Elsevier Science Ltd. All rights reserved

Key words—drinking water, chlorination, chlorine decay, disinfection-by-products, trihalomethane, chloroform

INTRODUCTION

Two of the main reasons for the disinfection of drinking water is to protect the drinking water from the pollution in the distribution systems and to prevent, or at least control, the regrowth of microorganisms in the distribution systems until the water safely reaches the consumers. Chlorination which is the most widely used technique for the disinfection of drinking water, was reported to form trihalomethanes (THMs) as a result of chlorination of natural water (Rook, 1974). The formation of THMs in drinking water results from the reaction of chlorine with naturally occurring organic matters, principally humic and fulvic acids. The presence of THMs and their species—mainly chloroform ($CHCl_3$)—in the nation's drinking water is of concern from a health-related aspect, since these compounds have been linked to the occurrence of human cancer in many instances (Morrow and Minear, 1987). THMs, which represent between 5 and 20% of the chlorinated products formed during the chlorination process (Fayad, 1993), have carcinogenic properties and could affect public health (Jimenez *et al.*, 1993). Consequently, they have raised much concern both at national and international levels (El-Dib and Ali, 1995).

Graun *et al.* (1994) studied the benefits and potential risks in balancing chemical and microbial risks of drinking water disinfection. They found that the risk of infectious waterborne diseases is substantial with health, social and financial implications in all parts of the world, and because of this the potential health risks associated with disinfection by-products (DBPs) pale in comparison with microbial risks, especially in areas with inadequate water supplies, poor sanitation and low socio-economic conditions. They also suggested that additional research was required on DBPs' occurrence and health risks before costly changes were made in water treatment practices to reduce these by-products, and improved methods for quantifying and comparing chemical and microbial risks were needed to provide communities with strategies for reducing these disparate risks to acceptable levels.

Clark *et al.* (1994) described a model which simu-

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lated the propagation of total trihalomethanes (TTHM) and chlorine residuals in a distribution system which was used to evaluate strategies for minimizing TTHM formation while maintaining adequate chlorine residuals in the system. They observed that ultra-violet (UV) absorbance in the 250-nm range and TTHMs were closely related and had a linear correlation with $r = 0.9875$. The formation of chloroform ($CHCl_3$) was also correlated with a decrease in UV absorbance at 272 nm, but the correlation was strongly dependent on the pH value (Korshin *et al.*, 1997). The increase in the pH value and temperature were seen to increase the level of chloroform up to a given temperature (17.3°C), after which a sharp decrease in the chloroform content occurred (Garcia-Villanova *et al.*, 1997).

EXPERIMENTAL WORKS

The pipelines under study are mainly supplied with drinking water from the Plav water treatment plant (WTP) in the city of České Budějovice (Č.Boděj), South Bohemia in the Czech Republic (Fig. 1). The Plav WTP takes its raw water from the Řimov surface water reservoir. The treatment processes in this plant are coagulation with ferric sulfate, flocculation, sedimentation, rapid sand filtration, and disinfection. A lime solution is added between sedimentation and filtration to adjust pH value and reduce the corrosivity of the water. The Plav WTP produces about 915 l/s and serves about 450,000 inhabitants in many cities and small towns in the region of south Bohemia.

This study concentrated on pipelines that take their drinking water from the Plav WTP and transport it to the city of Tábor (Fig. 1). The length of these pipelines is about 80 km and they carry drinking water to the city of Tábor and to the cities and the villages which lie enroute during its transport. The material of these pipelines is steel without any type of coating. They carry about 285 l s^{-1} from the treatment plant; while only 120 l s^{-1} reach the city of Tábor and the surrounding regions. Along these pipelines, there are six reservoirs at different distances with a total capacity of about 48,000 m^3. This paper studies the formation of THMs and the decay of chlorine in these pipelines with the relation between them and the other factors affecting the formation of THMs.

Experimental samples

The samples for this study were taken from six locations along the pipelines traveling to the city of Tábor. The first sample location was directly after the treatment plant, the second location was from the effluent of the Hosin reservoir, the third and fourth locations were from the influent and effluent of the Chotýčany reservoir, respectively, and the fifth and sixth locations were from the effluent of the Šachta Veseli and Svata Anna reservoirs (Fig. 1).

These samples were analyzed for many parameters that could have an effect on the water quality in these pipelines. These analyses included temperature, pH value, chemical oxygen demand (COD), dissolved organic carbon (DOC), chlorine, $CHCl_3$, and THM. Other measured parameters were also included; such as turbidity, dissolved minerals (Ca, Fe, Mn, Mg, etc.), nitrogen compounds (ammonium, nitrites, and nitrates), and others, but their results are not presented here. These analyses were periodically carried out every month during the last 2 years (especially in 1997) and sometimes many times in the same month.

RESULTS AND DISCUSSION

The characteristics of raw water from the Řimov surface water reservoir are presented in Table 1. It can be noted in these characteristics that there was a high concentration of organic matter (represented in COD_{Mn}), while the nitrogenous compounds (NH_4, NO_2 and NO_3) were suitable in comparison to the Czech specifications of the drinking water.

The average results from experiments for some measured parameters are presented in Table 2. This table also represents the range values of these measured parameters and the standard deviations of all measurements taken during 1997.

Chlorine decay

Most water utilities prefer to keep chlorine residual in their distribution system to protect the drinking water and transportation pipelines from micro-organism regrowth and biofilm formation. Some researches (Gatel *et al.*, 1995) stated that a residual free chlorine concentration of 0.2 mg l^{-1} is sufficient to guarantee and control the regrowth of bacteria in a distribution system. Characklis

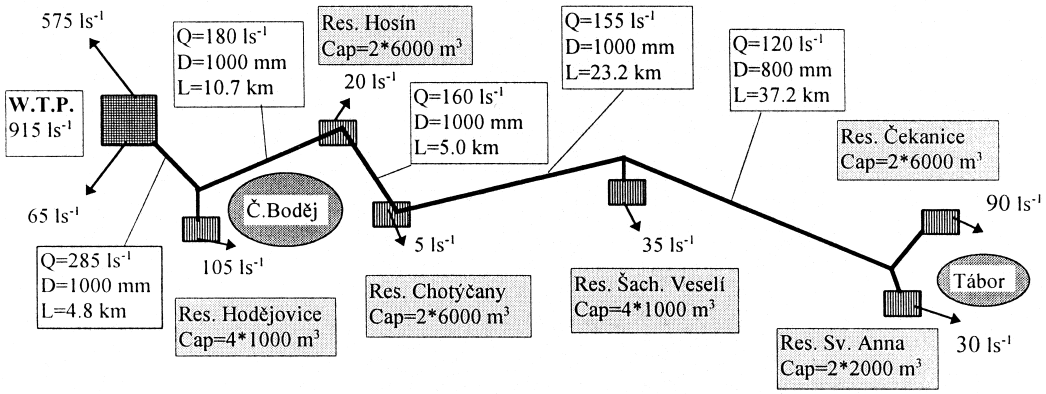

Fig. 1. Water pipleines from the Plav WTP to Tábor.

Table 1. Characteristics of raw water from the Řimov surface water reservoir

pH	COD_{Mn} (mg l^{-1})	Ca^{2+} (mg l^{-1})	$Fe^{2=}/Fe^{3=}$ (mg l^{-1})	Mn^{2+} (mg l^{-1})	NH_4^- (mg l^{-1})	NO_2^- (mg l^{-1})	NO_3^- (mg l^{-1})	Cl^- (mg l^{-1})	SO_4^{2-} (mg l^{-1})	PO_4^{3-} (mg l^{-1})
7.27	5.78	20.73	0.35	0.03	0.19	0.01	12.4	7.77	27.5	0.08

(1981), however, reported that biofilm was formed in distribution systems with a free chlorine residual less than 0.5 mg l^{-1}.

The disinfection of water in the Plav WTP is done by chlorine with a dose of about 1.25 mg l^{-1}. The residual chlorine in water leaving the treatment plant is on average 0.75 mg l^{-1}. This residual decreases with distance until it reaches zero at the end of the pipelines (Fig. 2). It is noted that there was a considerable decrease of the chlorine concentrations inside the reservoirs which is clearly shown in the difference between the chlorine concentrations though the inlet and outlet of the Chotýčany reservoir (see Table 2, and the drop at 20.5 km in Fig. 2)

Chlorine is a relatively unstable chemical and readily reacts with a variety of organic and inorganic compounds (Trussel, 1992), thus causing its gradual dissipation in the distribution system. Four factors that influence chlorine consumption are: (1) reaction with organic and inorganic chemicals in the bulk aqueous phase; (2) reaction with biofilm at the pipe wall; (3) consumption by the corrosion process; and (4) mass transport of chlorine and other reactants between the bulk flow and the pipe wall (Clark, 1998). It should be pointed out that the pipelines under study were undergoing corrosion and had high concentrations of dissolved iron at their ends (Abd El-Shafy *et al*., 1998; Macek *et al*., 1998). It is thought that corrosion, tubercles and biofilm formation on the inside wall consume a great part of the chlorine. Now there are coupons inserted in these pipelines to study the effect of corrosion and biofilm formation on the decay of chlorine and *vice versa*.

The rate of chlorine decrease at the beginning of the pipelines is greater than at the end. In order to predict the decrease of residual chlorine, a first order decay relationship (Clark *et al*., 1994) can be used as follows

$$C_t = C_o \exp(-k_t t)$$

where C_t chlorine concentration in (mg l^{-1}) at any time t (day), C_o = initial chlorine residual (mg l^{-1}), k_t = first order decay coefficient (day^{-1}).

It was evident that the distribution system itself could exhibit a chlorine demand. Vasconcelos (1995) confirmed that chlorine decay in distribution systems could occur both as a result of reactions within the bulk fluid and from reactions with materials associated with the pipe wall.

By using the results of total chlorine concentration through the pipelines, the overall coefficient of chlorine decay k_t was calculated. Its mean value was about 0.30 per day with a range of 0.25–0.34 per day. By using this coefficient, the water quality model in the EPANET program (Rossman, 1994) was calibrated. The overall coefficient of chlorine decay was divided to the water bulk chlorine decay coefficient k_b, and the coefficient of wall chlorine decay k_w by values of 0.10 per day and 0.35 m per day for them, respectively. It has been noted that

Table 2. Average results of analysis parameters in 1997[a]

Places		L (km)	t (day)	T (°C)	pH value	COD_{Mn} (mg l^{-1})	DOC[b] (mg l^{-1})	Chlorine (mg l^{-1})	$CHCl_3$ ($\mu g\ l^{-1}$)[c]	THM ($\mu g\ l^{-1}$)[c]
Plav WTP	Av	0.0	0.0	6.6	7.6	1.8	1.90	0.73	4.61 (3.9)	5.2 (4.25)
	SD			2.2	0.26	0.18	0.07	0.08	4.01 (1.8)	4.45 (2.0)
	R			3.5–11	7.1–8.1	1.4–2.1	1.84–1.94	0.60–0.85	1.0–16.0 (7.1)	1.1–18.0 (7.9)
Hosín Reservoir (outlet)	Av	15.5	1.35	7.8	7.7	1.78	1.94	0.54	5.89 (4.1)	7.1 (5.3)
	SD			2.5	0.17	0.1	0.11	0.13	6.61 (2.0)	7.93 (2.1)
	R			4.0–11	7.4–7.9	1.6–1.9	1.82–2.14	0.25–0.75	1.3–25.0 (7.8)	1.5–30.0 (8.9)
Chotýčany Reservoir (inlet)	Av	20.5	2.28	7.1	7.7	1.82	1.79	0.48	5.91 (4.4)	7.3 (5.7)
	SD			2.4	0.14	0.17	0.08	0.15	6.26 (1.9)	8.20 (2.0)
	R			3.5–11	7.5–8.0	1.6–2.2	1.68–1.98	0.15–0.60	1.4–24.0 (8.1)	1.5–31.0 (9.7)
Chotýčgany Reservoir (outlet)	Av	20.5	2.61	6.9	8.2	1.74	1.82	0.40	7.01 (4.8)	8.6 (6.1)
	SD			2.2	0.21	0.16	0.09	0.19	8.91 (2.3)	11.2 (2.5)
	R			3.5–10	7.9–8.6	1.4–1.9	1.73–1.96	0.10–0.60	1.4–33.0 (10.5)	1.6–41.0 (12.0)
Šach. Veselí Reservoir	Av	43.7	4.45	7.5	8.3	1.86	1.89	0.26	8.15 (6.1)	9.4 (6.5)
	SD			2.5	0.14	0.23	0.11	0.11	8.43 (2.1)	10.6 (2.3)
	R			4.0–10	8.1–8.6	1.5–2.3	1.74–1.99	0.05–0.45	1.6–31.0 (11.0)	1.7–39.0 (12.0)
Sv. Anna Reservoir	Av	80.9	6.83	8.1	8.2	1.82	1.92	0	8.50 (6.0)	10.3 (7.1)
	SD			2.9	0.12	0.24	0.14	0	9.23 (2.4)	11.7 (2.7)
	R			4.0–11	8.0–8.4	1.5–2.4	1.78–2.06	0	2.5–35.0 (13.1)	3.0–44.0 (14.9)

[a]WTP, water treatment plant; L, distance; t, residence time; T, temperature; DOC, dissolved organic carbon; COD, chemical oxygen demand; Av, Average of results; SD, Standard deviation; R, Range of all results during 1997.
[b]Number of measurements were only four. Figure in brackets denotes correct number after excluding the abnormal measurements.

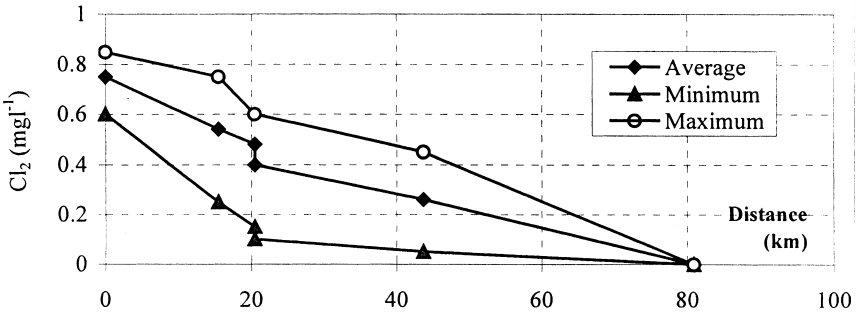

Fig. 2. Decay of chlorine residual with increase of distance.

the average of the measured values of total chlorine concentration and those estimated by the EPANET water quality model have a very strong correlation ($r = 0.994$).

Residence time. The residence time of water in these pipelines is calculated by assuming the plug flow in the pipelines and complete mixing in the reservoirs. Water velocity in the pipelines is determined according to the classic hydraulic survey. By these methods, the residence time and velocity are calculated in the pipelines and reservoirs under study. The velocity in the pipelines ranged from 0.3 to 0.14 m s^{-1} with an average of 0.19 m s^{-1} in 1996 which increased to 0.32 m s^{-1} in 1997 (ranging from 0.2 to 0.45 m s^{-1}). The low velocity was due to the decrease of water consumption during recent years when it reached 190 l per capita per day in 1996, while it was about 290 l per capita per day in 1988. This low consumption might be because of the increase in the price of drinking water for consumption during recent years.

This very low velocity and the large volume of reservoirs increased the residence time (more than 10 days with very slow velocity) and correspondingly increased the decay of residual chlorine. The residence time of water in any distribution system changes the quality of the water according to the long or short of the residence time. That is because many parameters undergo decay or growth as a result of chemical and biological actions according to the environment in the distribution system (Reddy *et al.*, 1995).

THM formation

It is known that the chlorination of drinking water results in the formation of THMs in treatment plants and distribution systems. As stated above, the formation of THMs and its species were observed to cause many health problems.

In the pipelines under study, there is no problem with the concentration of THMs where the maximum concentration of it at any place is less than the indicative limit in the Czech specifications (0.1 mg l^{-1}). This may be because of the relatively low content of THM precursors. In addition, the presence of ammonia in the raw water (Table 1) and in the treated water (data not shown) might be another reason for the relative low concentration of THMs as stated elsewhere (Muttamara *et al.*, 1995; Myers, 1990). It has been noted that the formation of THMs increased with an increase in distance from the Plav WTP (Fig. 5). The formation of THMs in the treatment plant only represented about 45% of the THMs found at the end of the pipelines, while the rest was formed in the pipelines. The percentage of the THMs formed in the WTP was formed after a contact time of about 7 h between the adding of the chlorine dose and the first sampling locations in the effluent of the WTP.

The main species of THM formation is chloroform ($CHCl_3$), which represents about 82% of the THMs formed. It is noted that the standard deviation (SD) was very high for both THMs (4–11 μg l^{-1}) and $CHCl_3$ (4–9 μg l^{-1}). This is because there

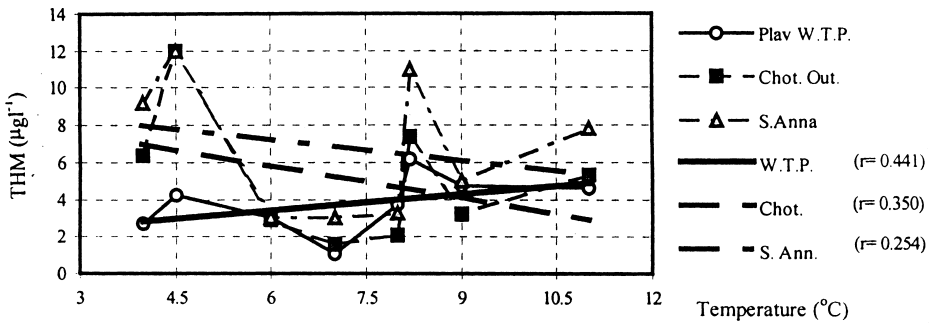

Fig. 3. Formation of THM in different temperature.

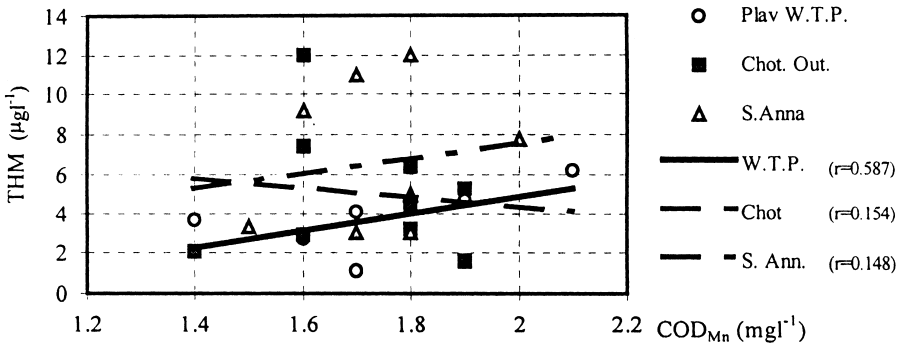

Fig. 4. Relation between THM formation and COD_{Mn}.

was one sampling day with very high and abnormal results for both THMs and $CHCl_3$. If we exclude these abnormal results, SD will be in the normal range as shown in parentheses in Table 2. These abnormally high results of THMs and $CHCl_3$ in one day might have been due to an abnormal increase of THM precursors or inaccuracy in the measuring apparatus. Therefore these abnormal results were not taken into consideration in discussion and in the figures.

Effect of COD, temperature and residence time. It is known that many factors can affect THM formation, such as organic matter, pH value, temperature, etc. (El-Dib and Ali, 1995). In this study pH values were relatively constant at every sampling location (Table 2). In the Chotýčany reservoir, however, there was an increase in pH value from 7.7 at the inlet to 8.3 at the outlet due to the addition of a lime solution for corrosion control. This increase in pH value was accompanied with an increase of THMs in this reservoir, and it might also have been due to the residence time and chlorine consumption. There was also an increase in THM formation due to the increase of temperature and chemical oxygen demand determined by a manganese solution (COD_{Mn}) at the WTP, as stated in other researches (El-Dib and Ali 1995; Garcia-Villanova *et al.* 1997), but the correlation between them was not clear (for COD_{Mn} $r = 0.587$ and for temperature $r = 0.441$; Figs 3 and 4). But as shown in these Figures, this correlation was not found in other sampling locations.

A very good correlation was found between the residence time and THM and $CHCl_3$ formation (Fig. 5). The increase of THM and $CHCl_3$ concentrations can be formulated as exponential functions of the residence time t (or first order increase) as the following:

$$THM_t = THM_o \exp(kt)$$

$$CHCl_{3t} = CHCl_{3o} \exp(kt)$$

where k is the coefficient of first order increase, THM_t and $CHCl_{3t}$ are the concentrations of trihalomethane and chloroform (respectively) at any time, and THM_o and $CHCl_{3o}$ refer to the concentrations of them at the initial time. These formulae can be used to predict the concentration of THM and $CHCl_3$ in the transporting pipelines after the determination of the coefficient k.

It has also been noted that there is a very good linear correlation between the cumulative THM formed at the beginning of the pipelines and the

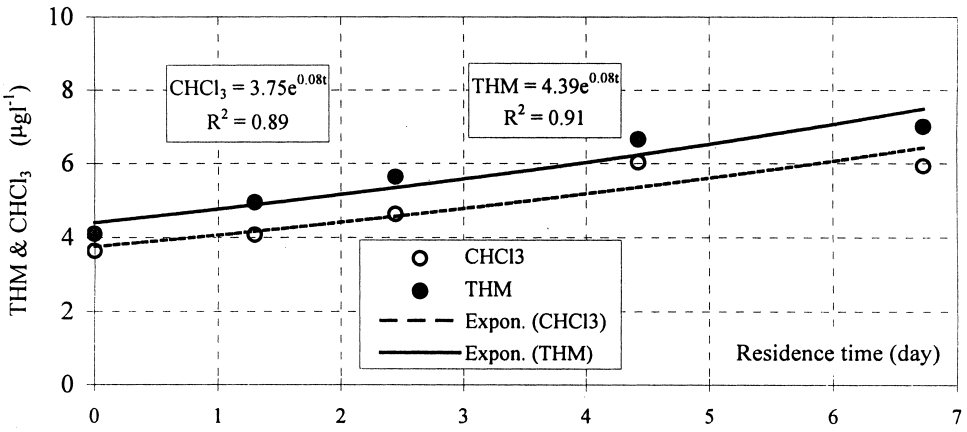

Fig. 5. THM and $CHCl_3$ concentration at different residence times.

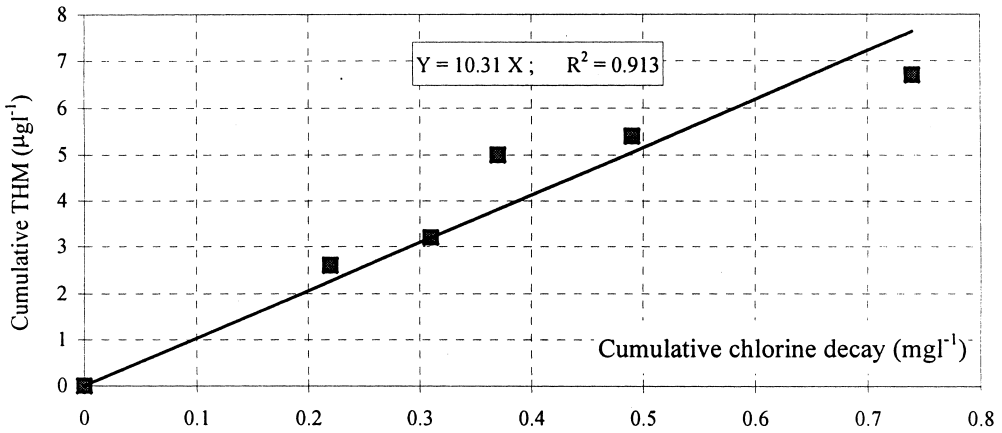

Fig. 6. Relation between the cumulation of chlorine decay and THM formation.

cumulative decrease of chlorine residual through them (Fig. 6).

This relationship can be described as the following:

$$THM = A + B^{*}\Sigma DCl$$

where THM is the trihalomethane concentration at any place in pipelines [$\mu g\ l^{-1}$] and ΣDCl is the cumulative decay of chlorine residual from the beginning of the pipeline to this place [mg l^{-1}], A and B are constant coefficients to be calibrated according to THMs formed in the WTP and other water characteristics. An application of this formula in our case resulted in constants of 4.25 $\mu g\ l^{-1}$ and 10.31 μg per mg for the coefficients A and B, respectively. The coefficient of correlation in this application was very high ($R^2 = 0.913$). This linear relationship can also be used to predict THM formation from the decay of chlorine through drinking water pipelines after its calibration in each case.

CONCLUSION

The formation of THMs in pipelines transporting drinking water is one reason for the depletion of the chlorine residual. The THMs formed inside the pipelines in our case was more than 120% of that formed in the treatment plant. This may be because of the low velocity in the pipelines and the correspondingly high residence time inside them. The limit of residual chlorine at the end of the pipelines is thought to be the reason for no formation of more THMs.

In this study the effect of temperature and organic matter on the THM formation was not clear because of the small change of these parameters during the study. However there was a general trend in increasing THM formation with an increase of these parameters at the effluent of the treatment plant. A very good correlation was found between the formation of THMs and the cumulative chlorine decay and residence time in the pipelines. There was a linear correlation between the cumulative chlorine decay and the cumulative THMs formed in the pipelines with $R^2 = 0.913$. Meanwhile, the correlation between THM formation and residence time was exponential with $R^2 = 0.91$.

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