Trihalomethane formation during water disinfection in four water supplies in the Somes river basin in Romania

Dumitru Ristoiu · Urs von Gunten · Aurel Mocan ·
Romeo Chira · Barbara Siegfried ·
Melinda Haydee Kovacs · Sidonia Vancea

Received: 25 April 2008 / Accepted: 5 December 2008 / Published online: 14 February 2009
© Springer-Verlag 2009

Abstract

Background, aim and scope After the discovery of chloroform in drinking water, an extensive amount of work has been dedicated to the factors influencing the formation of halogenated disinfections by-products (DBPs). The disinfection practice can vary significantly from one country to another. Whereas no disinfectant is added to many water supplies in Switzerland or no disinfectant residual is maintained in the distribution system, high disinfectant doses are applied together with high residual concentrations

in the distribution system in other countries such as the USA or some southern European countries and Romania. In the present study, several treatment plants in the Somes river basin in Romania were investigated with regard to chlorine practice and DBP formation (trihalomethanes (THMs)). Laboratory kinetic studies were also performed to investigate whether there is a relationship between raw water dissolved organic matter, residual chlorine, water temperature and THM formation.

Materials and methods Drinking water samples were collected from different sampling points in the water treatment plant (WTP) from Gilau and the corresponding distribution system in Cluj-Napoca and also from Beclean, Dej and Jibou WTPs. The water samples were collected once a month from July 2006 to November 2007 and stored in 40-mL vials closed with Teflon lined screw caps. Water samples were preserved at 4°C until analysis after sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) had been added to quench residual chlorine. All samples were analysed for THMs using headspace GC-ECD between 1 and 7 days after sampling. The sample (10 mL) was filled into 20-mL headspace vials and closed with a Teflon-lined screw cap. Thereafter, the samples were equilibrated in an oven at 60°C for 45 min. The headspace (1 mL) was then injected into the GC (Cyanopropylphenyl Polysiloxane column, 30 m×53 mm, 3 µm film thickness, Thermo Finnigan, USA). The MDLs for THMs were determined from the standard deviation of eight standards at 1 µg/L. The MDLs for CHCl_3 , CHBrCl_2 , CHBr_2Cl and CHBr_3 were 0.3, 0.2, 0.3 and 0.6 µg/L, respectively. All kinetic laboratory studies were carried out only with water from the WTP Gilau. The experiments were conducted under two conditions: baseline conditions (pH7, 21°C, 2.5 mg/L Cl_2) to gain information about the change of the organic matter in the raw water and seasonally variable conditions

Responsible editor: Walter Giger

ESPR Special Issue - ESTROM

D. Ristoiu (✉) · B. Siegfried · M. Haydee Kovacs
Faculty of Environmental Science,
University Babes-Bolyai Cluj-Napoca,
P-ta Ștefan cel Mare 4,
400084 Cluj-Napoca, Romania
e-mail: dristoiu@enviro.ubbcluj.ro

U. von Gunten · B. Siegfried
Eawag, Swiss Federal Institute of Aquatic Science
and Technology,
8600 Dübendorf, Switzerland

A. Mocan
Institute of Public Health Cluj-Napoca,
400349 Cluj-Napoca, Romania

R. Chira
Water and Sewerage Company Cluj,
Bulevardul 21 Decembrie 1989 nr.79,
400604 Cluj-Napoca, Romania

S. Vancea
Garda de mediu, Comisariatul Județean Cluj,
str.G-ral T. Mosoiu nr.49,
400609 Cluj-Napoca, Romania

to simulate the actual process at the treatment plant and the distribution system.

Results and discussion This study shows that the current chlorination practice in the investigated plants complies with the THM drinking water standards of the EU. The THM concentrations in all samples taken in the four treatment plants and distributions systems were below the EU drinking water standard for TTHMs of 100 µg/L. Due to the low bromide levels in the raw waters, the main THM formed in the investigated plants is chloroform. It could also be seen that the THM levels were typically lower in water supplies with groundwater as their water resource. In one plant (Dej) with a pre-ozonation step, a significantly lower (50%) THM formation during post-chlorination was observed. Laboratory chlorination experiments revealed a good correlation between chloroform formation and the consumed chlorine dose. Also, these experiments allowed a semi-quantative prediction of the chloroform formation in the distribution system of Cluj-Napoca.

Conclusions CHCl_3 was the most important trihalomethane species observed after the chlorination of water in all of the sampled months. However, TTHM concentrations did not exceed the maximum permissible value of 100 µg/L (EU). The THM formation rates in the distribution system of Cluj-Napoca have a high seasonal variability. Kinetic laboratory experiments could be used to predict chloroform formation in the Cluj-Napoca distribution system. Furthermore, an empirical model allowed an estimation of the chloroform formation in the Gilau water treatment plant.

Keywords Chlorination · Disinfection by-products · Electron Capture Detector · Gas chromatography · Headspace sampling · Trihalomethanes

1 Background, aim and scope

Water disinfection with chlorine to improve the hygienic quality of water by eliminating waterborne bacterial pathogens such as dysentery and diarrhoeal diseases, cholera, typhoid fever, hepatitis A, etc. has been the major disinfection process for municipal drinking water since the early twentieth century. However, in 1976, it was discovered that disinfections by-products (DBPs) were produced during the disinfection process (Marhaba and Washington 1998). Chlorine, which exists as hypochlorous acid and hypochlorite in water reacts with natural organic compounds—such as humic and fulvic acids—to form a wide range of undesired halogenated organic compounds, including trihalomethanes (THMs), haloacetic acids, chlorophenols, chloral hydrate and haloacetonitriles (Gallard and von Gunten 2002). THMs have been found to be the most prevalent organic contaminants in drinking water and

typically occur at higher concentrations than other disinfection by-products. The four THMs (chloroform, dichlorobromomethane, dibromochloromethane and bromoform) are formed when chlorine-based disinfectants are added to source waters. Previous investigations have shown that the major variables that affect THM formation are chlorine dose and residual, concentration and type of NOM, contact time, pH, temperature of water, and the presence of inorganic compounds such as bromide and ammonia (Najm et al. 1994). In general, higher THM concentrations are expected if the parameters above are higher (except ammonia; Nikolaou and Lekkas 2001; Nikolaou et al. 2004a, b; USEPA 1999b). Chloroform is usually the most widespread by-product formed in drinking water after chlorination processes, although brominated THMs can occur at higher concentrations when waters with high bromide concentrations are chlorinated (Najm et al. 1994). The concern of DBPs formed during disinfection processes is based on the evidence that they have some adverse health effects, in particular cancer and reproductive disorders (Arora et al. 1997; Woo et al. 2002). Research on health effects showed a relationship between THMs exposure and bladder cancer. Recently, THMs were suspected to cause not only cancer but also liver and kidney damage, retarded foetus growth, birth defects and possibly miscarriage (Wright et al. 2004). The US Department of Health and Human Services has determined that chloroform (CHCl_3) may be anticipated to be a carcinogen (USEPA 2001a). Also, it has been shown that dibromochloromethane (CHClBr_2) and bromoform (CHBr_3) could damage the nervous system. Disinfected drinking water from surface waters generally contains higher concentrations of DBPs than groundwater due to the higher concentration of natural organic material (NOM).

The objective of this study is an overview concerning chlorination and THM formation in four water treatment plants in Transylvania (Romania). It is the first study of this kind for Romania and it is connected to the request to comply with EU drinking water regulations. Furthermore, the formation of THMs was assessed in laboratory experiments, in which chlorination experiments were performed under seasonally varying conditions.

THM legislation in Romania and other countries The first legislation (interim total THMs standard) to limit the concentration of total THMs (TTHMs) in drinking water was promulgated on November 29, 1979 by the USEPA (2001a, b). Not only the USEPA, but also the other governmental agencies of various countries—such as the World Health Organization (WHO; 1993), Health Canada (2001), UK Health Agency (2000), Aus-NZ Health Agency (2000)—have focussed on THMs and promulgated regulations. Currently, the MCL is set at 80 µg/L by the USEPA and 100 µg/L by the EU. In Romania, the regulation and

monitoring of THMs has become a current issue in connection with Romania's entry to the EU and the fulfilment of the required drinking water standards. In order to minimise cancer risk, Romania has adopted the maximal permissible value (100 µg/L) fixed in the EU drinking water directive in 2002, granting the water companies a transition time of 10 years to meet the requested standards and accepting a TTHM value of 150 µg/L in the first 5 years. In terms of monitoring, the Romanian water law stipulates a minimal number of samples per year depending on the magnitude of the treatment plant. The local health authorities carry out the monitoring (Government of Romania 2005; Guvernul Romaniei 2004; Parlamentul Romaniei 2002).

2 Materials and methods

2.1 Water supplies

In this study, four water treatment plants from four cities situated in the Somes river basin were investigated: Cluj-Napoca, Dej, Jibou and Beclean. The largest WTP is located in Gilau at about 18 km to the west of Cluj-Napoca and provides drinking water for approximately 600,000 people. Its principal water sources are the storage lakes Gilau and Somesul Cald River. The chlorine dose is regulated manually to achieve a free chlorine residual at the exit of the reservoir (where the water arrives approximately 12 min after chlorination) of 0.5–0.7 mg/L in the winter season and 0.7–0.9 mg/L in the summer season. Dej city is located about 60 km to the north of Cluj-Napoca. In this WTP, pre-ozonation and post-chlorination are used. In Dej, the target chlorine concentration at the exit of the reservoirs is between 0.3–0.6 mg/L. In the WTP Beclean, gaseous chlorine is used with a target chlorine concentration at the exit of reservoir in the range between 0.6 and 1.0 mg/L. In Jibou, the water source is groundwater from a depth of 8–12 m. Chlorine gas is applied with a target chlorine concentration at the exit of the reservoir in the range of 0.5–0.8 mg/L.

2.2 Sampling

Samples were collected monthly from different sampling points at the WTPs Gilau and the distribution system in Cluj-Napoca, Beclean, Dej and Jibou. Samples were taken in raw water, sand-filtrated water, chlorinated water and chlorinated water after ozonation (Dej). The water samples were collected once a month from July 2006 to November 2007, quenched with sodium thiosulfate (Na₂S₂O₃) and stored in 40-mL vials closed with Teflon-lined screw caps

at 4°C until the analysis. All samples were measured between 1 and 7 days after sampling. For kinetics experiments, filtered water was taken monthly from the WTP Gilau. The sand-filtrated water was stored in 5-L plastic containers at 4°C without adding any preservatives until the chlorination experiments were performed.

2.3 Reagents

A standard stock solution containing 2,000 µg/mL of each trihalomethane was obtained from Restek (Bellefont, U.S.). THM working standard solutions (100 mg/L, 4 mg/L) were prepared through dilution of the stock solution in 10 mL methanol. Methanol, NaNO₂, NaB₇O₅ and Na₂S₂O₃ were obtained from Reactivul Bucuresti (Bucuresti, Romania). KI and a DPD solution (*N,N*-diethyl-1,4-phenyldiammoniumsulfat) were purchased from Merck (Darmstadt, Germany). NaH₂PO₄ and EDTA were obtained from DBH Chemicals (Poole, England). ABTS (2,2-azino-bis(3-ethylbenzo-thiazoline)-6-sulfonic acid diamonium salt) was purchased from Fluka (Buchs, Switzerland). Aqueous chlorine solutions were prepared from a chlorine solution for cleaning purposes (95% purity of Cl₂, Sun Industries, Ilfov, Romania).

2.4 THM analysis

THMs were measured by a Thermo Finningan U.S. Trace GC Ultra gas chromatography system with an electron capture detector (GC-ECD) is equipped with a TriPlus HS auto sampler. The analyses were made using the headspace technique. The sample (10 mL) was filled into 20-mL headspace vials and closed with Teflon-lined screw caps. After that, the samples were equilibrated in an oven at 60°C for 45 min. The headspace (1 mL) was then injected into the GC (Cyanopropylphenyl Polysiloxane column, 30 m × 53 mm, 3 µm film thickness, Thermo Finnigan, USA). The column programme was 35°C (hold time 3 min), 15°C/min to 200°C (hold time 3 min). The inlet was set at 200°C. The calibration standards were prepared using the THM test mixture produced by Restek. The calibration standards were prepared for the range 0–100 µg/L in the mineral water Izvorul alb. Samples of 1 mL volume of headspace were injected into the GC column with TriPlus HS auto sampler, and four peaks were detected belonging to the four THM compounds. Calibration curves were obtained by plotting the areas under the peaks of each standard THM solution versus their concentration as shown in Fig. 1. The THM concentrations of the samples were determined using these calibration curves. The specifications of the TriPlus HS auto sampler were as follows: agitator temperature 60°C, incubation time 45 min, syringe temperature 80°C.

The relative standard deviations of 20 and 80 µg/L spiked samples were between 1.25% and 3.01% (*n*=10).

Fig. 1 Calibration curves for the four trihalomethane compounds

Recovery of 1, 20 and 80 µg/L spiked samples was between 93% and 120% ($n=10$). The MDLs were determined from the standard deviation of eight standards at 1 µg/L. The MDLs for CHCl_3 , CHBrCl_2 , CHBr_2Cl and CHBr_3 were 0.3, 0.2, 0.3 and 0.6 µg/L, respectively.

2.5 Chlorine analysis

For the kinetic studies, chlorine was measured colourimetrically according to the standard 8021 DPD method (powder pillow) for free chlorine and the standard 8167 DPD method (powder pillows) for total chlorine using a Hach Dr 2800 analyser. A 25-mL cell was filled with samples, and the DPD free chlorine reagent was added (powder pillow). After mixing, chlorine was determined at a wavelength of 530 nm. The chlorine concentration was also determined by the ABTS method at a wavelength of 405 nm with a molar absorption coefficient ϵ of 28,500 $\text{M}^{-1} \text{cm}^{-1}$ monochloramine; total and free chlorine are measured with the ABTS method. Monochloramine and HOCl react with ABTS to a green-coloured product, which can be measured at a wavelength of 405 nm. Both HOCl and NH_2Cl react rapidly with ABTS and are impossible to be distinguished (Pinkernell et al. 2000):

To determine NH_2Cl , HOCl is destroyed by the addition of nitrite prior to ABTS addition. Nitrite rapidly reacts with HOCl , but only slowly with NH_2Cl . Nitrite does not react with ABTS and does not interfere in the determination of NH_2Cl . Four minutes are sufficient for completing the destruction of HOCl by nitrite (Pinkernell et al. 2000).

The concentration of free chlorine is calculated by subtracting monochloramine from the total chlorine concentration. In Table 1, the concentrations (milligrams per litre) obtained for total chlorine, free chlorine and NH_2Cl in laboratory kinetic experiments are shown for the DPD and the ABTS methods. The agreement between the two methods is quite good. In general, the values differ by <10%.

2.6 Chlorination experiments

2.6.1 Experimental conditions

Kinetic laboratory chlorination experiments were carried out monthly with sand-filtrated water collected at the Gilau treatment plant. The experiments were conducted under two conditions: *baseline conditions* (pH 7; 21°C and 2.5 mg/L Cl_2) to gain information about the influence of change in the organic matter and *seasonally variable conditions* to simulate the actual process at the treatment plant for a given time point. Experiments under seasonally variable conditions were carried out at the same pH, temperature and chlorine dose as in the pretreated water on the sampling day.

2.6.2 Sample preparation

Sand-filtrated water (500 mL) collected after one of the sand filters from the WTP Gilau was filled into a Schott bottle, and the pH was adjusted to the desired value by addition of NaOH or H_2SO_4 (0.5 M and 0.1 M, respectively). For experiments under baseline conditions, the water was buffered with 12.5 mL of a $\text{Na}_2\text{B}_4\text{O}_7$ solution (0.5 M) to pH 7. A diluted chlorine solution was prepared, and its concentration was determined by the ABTS method (Pinkernell et al. 2000) and checked also with the DPD

Table 1 Comparison of results from total chlorine, free chlorine and NH_2Cl determination by the ABTS and DPD method

Time (min)	ABTS method			DPD method		
	Total chlorine (mg/L)	Free chlorine mg/L)	NH_2Cl (mg/L)	Total chlorine (mg/L)	Free chlorine (mg/L)	NH_2Cl (mg/L)
0.333	1.62	1.584	0.036	1.661	1.619	0.042
0.666	1.32	1.258	0.062	1.339	1.268	0.071
1	1.26	1.192	0.068	1.287	1.212	0.075
3	1.1	1.034	0.066	1.14	1.067	0.073
6	0.92	0.845	0.075	0.985	0.903	0.082
15	0.81	0.733	0.077	0.857	0.769	0.088
40	0.7	0.621	0.079	0.792	0.7	0.092
60	0.62	0.566	0.054	0.659	0.596	0.063
90	0.56	0.532	0.028	0.624	0.59	0.034
120	0.52	0.499	0.021	0.547	0.517	0.03
240	0.46	0.444	0.016	0.482	0.461	0.021
600	0.26	0.251	0.009	0.291	0.281	0.01
690	0.19	0.185	0.005	0.208	0.2	0.008
780	0.12	0.119	0.001	0.154	0.151	0.003

method. The respective chlorine dose was added to the sand-filtrated water and stirred for 40 s. For each desired reaction time, two 8 mL samples were taken with a dispenser, and total chlorine, free chlorine and monochloramine concentrations were determined. After chlorine addition, the headspace vials were filled with 10 mL of the chlorinated water, closed immediately with Teflon-lined screw caps and put into the water bath. At each desired reaction time, one vial was removed, and a thiosulfate solution was injected through the septum to quench chlorine and stop THM formation. The vials were then stored at 4°C and analysed. In order to determine seasonal variations, experiments were conducted with sand-filtrated water from March 2006 to November 2007. To determine the effect of chlorine dose on THM formation, two different initial chlorine doses were applied to each water sample. At the end of each of the predetermined time intervals, THM, total chlorine, free chlorine and monochloramine concentrations were measured.

3 Results and discussion

3.1 Factors affecting THM formation in full-scale plants

Figure 2 shows the evolution of CHCl_3 in (a) WTP Gilau and (b) WTP Jibou. It can be seen that there is a distinct trend over the year. When the temperature increases in the warmer summer months, reactions are faster and a higher chlorine dose is required for disinfection, leading to a higher formation of THMs. Subsequently, THM concentrations are expected to be higher in summer than in winter

(Fayad 1993). The observations in both plants confirm this assumption. Furthermore, it can be seen that the absolute values for THM formation are much smaller in the WTP Jibou than in Gilau. This can be explained by the different water resources used for the two WTPs. Whereas the WTP Gilau uses surface water, the WTP Jibou uses groundwater. The maximum level of chloroform in the WTP Jibou does not exceed 10 µg/L for the whole duration of the study, whereas it can get up to 80 µg/L for the WTP Gilau.

Also in Dej, with an ozonation step in the treatment scheme prior to chlorination, trihalomethane formation was lower by almost 50% as compared to Gilau (Cluj). In Cluj, the chloroform varies between 60 and 80 µg/L in the distribution system, whereas it was only about 40 µg/L in the Dej distribution system. This is a clear indication that ozonation is a successful measure to remove the THM precursors partially. Recent studies have examined the relationship between bromide concentration in a drinking water supply and disinfection by-products formation (von Gunten and Hoigné 1992, 1996). When bromide is present, chlorine as hypochlorous acid (HOCl) oxidises bromide to hypobromous acid (HOBr). A mixture of HOCl and HOBr can lead to the formation of both chlorinated and brominated by-products (Gallard and von Gunten 2002). Based on the difference in bromide concentrations, substantial variations in THM formation (and THM species) can be expected. Studies have shown that as the concentration of bromide increases, the concentration of TTHMs increases and more brominated THMs are formed. In the four WTPs from the Somes river basin, the concentrations of brominated and mixed chloro-bromo trihalomethanes were typically very low, which can be explained with a low

Fig. 2 Chloroform concentration (micrograms per litre) measured in water samples from **a** the Cluj-Napoca distribution system in 2006–2007 and **b** a sampling point in the Jibou distribution system. *Numbers* represent the location of the sampling: 1 Chemistry Faculty, 2 Institute of Public Health, 3 Environmental Faculty (for details see Fig. 5)

bromide concentration of 5–7 µg/L in the investigated waters. In Gilau and Cluj-Napoca, dichlorobromomethane never exceeded 20 µg/L. In Jibou, all four THMs were detected but the TTHM concentration never exceeded 10 µg/L.

3.2 Kinetics of chlorine consumption and THM formation

Figure 3 shows results from kinetic laboratory experiments for the consumption of chlorine for variable seasonal conditions for water from the WTP Gilau (experimental details are given in the captions of Fig. 3). A characteristic

fast decrease followed by a slower chlorine consumption can be observed. This is possibly due to reactions with ammonia and NOM, respectively. There is no clear trend in the data; however, after a contact time of 10 min, the initially large differences in chlorine residual level out to 0.2–0.5 mg/L. In Fig. 4, the corresponding formation of THMs is shown with a very similar pattern. However, in this case, the differences are much larger and span over almost a factor of 4.

Based on the data shown in Figs. 3 and 4, the concentration of chloroform obtained in chlorination experiments under seasonally variable conditions were

Fig. 3 Laboratory experiments for chlorine stability in sand-filtered water from the Gilau plant under seasonally variable conditions in 2006 (pH, temperature and chlorine doses were the same as in the plant at the sampling day) *March* pH7, 4°C, 1.2 mg L⁻¹; *April* pH7.2, 4°C, 0.9 mg L⁻¹; *May* pH7.3, 8°C, 1.2 mg L⁻¹; *June* pH7.1, 8°C,

1.2 mg L⁻¹; *July* pH7, 12°C, 1.4 mg L⁻¹; *August* pH7.2, 14°C, 1.6 mg L⁻¹; *September* pH7.2, 13.5°C, 1.6 mg L⁻¹; *October* pH7, 14°C, 1.4 mg L⁻¹; *November* pH7, 9°C, 1.3 mg L⁻¹; *December* pH7, 7°C, 1.1 mg L⁻¹

linked to the chlorine consumed. The resulting linear correlation had an $R^2=0.8742$ (data not shown). This could be explained by the changing composition of the organic matter and the varying ammonium concentration in the raw water: Ammonia reacts rapidly with free chlorine to

chloramine, which shows much lower reactivity with organic substances. For the same chlorine consumption, a higher ammonium concentration therefore leads to lower THM yields. A slightly better correlation could be obtained by taking into account only the free chlorine concentration.

Fig. 4 Laboratory experiments for chloroform formation in sand-filtered water from the Gilau plant under seasonally variable conditions in 2006 (pH, temperature and chlorine doses were the same as in the plant at the sampling day) *March*: pH 7, 4°C, 1.2 mg L⁻¹; *April*: pH 7.2, 4°C, 0.9 mg L⁻¹; *May*: pH 7.3, 8°C, 1.2 mg L⁻¹; *June*:

pH 7.1, 8°C, 1.2 mg L⁻¹; *July*: pH 7, 12°C, 1.4 mg L⁻¹; *August*: pH 7.2, 14°C, 1.6 mg L⁻¹; *September*: pH 7.2, 13.5°C, 1.6 mg L⁻¹; *October*: pH 7, 14°C, 1.4 mg L⁻¹; *November*: pH 7, 9°C, 1.3 mg L⁻¹; *December*: pH 7, 7°C, 1.1 mg L⁻¹

Fig. 5 Relationship between chlorine consumption and chloroform formation in sand-filtered water from the Gilau plant under seasonally variable conditions (13°C , $1.6 \text{ mg L}^{-1} \text{ Cl}_2$ and $\text{pH} 7.2$) and base line

condition (21°C , $2.5 \text{ mg L}^{-1} \text{ Cl}_2$ and $\text{pH} 7$) in September 2007. NH_2Cl concentration was subtracted from the total chlorine concentration

This was done by correcting for the monochloramine concentration. The corresponding results are shown in Fig. 5 for the kinetic experiments from September 2007 for seasonally variable conditions and the baseline conditions. For both conditions, a reasonable linear correlation between the chloroform formation and the chlorine consumed could be obtained (see Fig. 5).

3.3 THM formation: comparison of laboratory experiments with a full-scale system

Figure 4 shows clearly that THMs increase gradually as a function of time as long as there is a chlorine residual concentration. Therefore, the influence of reaction time on trihalomethane formation was investigated in the Gilau WTP and distribution system (Fig. 6). Samples were taken at various sampling points as described in the legend of Fig. 6. Both the pattern (initially faster increase) and the absolute concentrations are very similar to the laboratory experiments. For the sampling campaign in July 2006 (see Fig. 6), the CHCl_3 concentration after post-chlorination is about $10 \mu\text{g/L}$, which is reached after a few minutes in the laboratory experiments (see Fig. 4). Then, it increases to around $40 \mu\text{g/L}$ after a distance in the distribution system of about 19 km. This is roughly the same end concentration as is observed in the laboratory experiments for that particular date. For the last sampling point, a decrease in CHCl_3 was measured. The nature of this observation is unclear.

Results from laboratory experiments were compared to full-scale results, for all the data obtained in the sampling campaigns. Figure 7 shows a plot of simulated CHCl_3 concentrations (laboratory experiments) versus measured

CHCl_3 concentrations in the distribution system of Cluj-Napoca. For comparison, CHCl_3 concentrations at calculated approximate residence times in the full-scale system were plotted against the corresponding CHCl_3 values for the same reaction time in the laboratory experiments. A relatively good linear correlation ($R^2=0.9161$) could be obtained.

Fig. 6 Chloroform concentration in the WTP Gilau and distribution system as a function of distance (1 raw water, 2 sand-filtrated water (15 m), 3 chlorinated water (60 m), 4 Sapca Verde (12 km), 5 beer factory (16 km), 6 Chemistry faculty (18 km), 7 Institute of Public Health (19 km) and 8 Environmental Faculty (20 km))

Fig. 7 Comparison of chloroform formation in seasonally variable laboratory experiments with sand-filtrated water from the Gilau plant (simulated CHCl_3 formation) with data from the treatment plant Gilau and the distribution system (measured CHCl_3) during the experimental

study in 2006 and 2007. The chloroform data are compared based on reaction times in the laboratory study and estimated residence times in the Gilau plant and the distribution system

3.4 Empirical modelling of THM formation

Chlorine decrease in the bulk phase is characterised by a first-order kinetic model as follows:

$$dC/dt = -kt \quad (1)$$

Where C is the chlorine concentration (milligrams per litre), k is the first-order decay constant (per minute) and t is the time (minutes; Amy et al. 1987; Duong et al. 2003; Rathbun 1996). A plot of the integrated form of Eq. 1 results in a straight line with the slope representing the first-order decay constant. The chlorine decrease follows almost first order. The results obtained with Gilau WTP waters

showed that the first-order decay provides a good correlation ($r^2=0.9788$) with a k value of 0.0015 min^{-1} . However, looking more carefully at the data, it could probably be better described by a two-phase behaviour (see discussion above). It is also observed that the rate of reaction depends on the concentration of chlorine (milligrams per litre). Chlorine consumption was very rapid during the initial phase with higher resulting decay rate constants in the range of $0.067\text{--}0.17 \text{ min}^{-1}$. In addition to the chlorine stability, THM formation depends on temperature, nature and concentration of organic matter, pH, reaction time and inorganic species like bromide and ammonia (Golfonopoulos and Arhonditsis 2002; Nikolaou et al. 2004a; Singer 1999).

Fig. 8 Comparison between observed and predicted chloroform concentration in water from the Gilau treatment plant for data from August to December 2006. The predictions are based on an empirical model described in the text

By including these factors, the USEPA developed an empirical simulation model for predicting the THM formation (Adin et al. 1991). The form of a multiple power function was taken for the sand-filtrated water in this study:

$$\text{THMs} = k(\text{temp})^a (\text{Cl}_2)^b (\text{pH})^c (\text{time})^d \quad (2)$$

Where the independent parameters are as follows: temp is the water temperature, Cl_2 is the chlorine dose, pH is the chlorination pH, and time is the reaction time; k is the pseudo-first-order rate constant for the chlorine decrease; a , b , c and d are the empirical constants. This equation was used to predict the formation of THMs for the laboratory experiments of this study. It can help to see if there is a risk for high THMs in a water treatment plant after a certain chlorine dose was applied for the disinfection of water. As shown in Fig. 8, the model and the actual data correlate quite well with quite high R^2 values of 0.85 for the following parameters: $k=0.00441$, $a=3.172$, $b=0.538$, $c=0.722$ and $d=0.309$. That parameters were determined using a Levenberg–Marquardt statistical method. The linear relationship between the predicted and measured chloroform concentration shows a reasonable correlation with some significant deviations for certain sampling events.

4 Conclusions

For the investigated water utilities Gilau, Beclean, Dej and Jibou in Romania, CHCl_3 was the most important THM species observed after the chlorination of reservoir water in all of the sampled months. In all of the sampling points, CHCl_3 and TTHM concentrations did not exceed the maximum permissible value of $100\mu\text{g/L}$ of the European Union. The THM formation rates in the distribution system of Cluj-Napoca have a high seasonal variability. THM concentrations depended on the applied initial chlorine dose. Although both low and high chlorine doses are higher than the chlorine demand of the water samples, higher chloroform concentrations were found for increasing chlorine doses. For THM formation, the overall yield (TTHM/total Cl_2 consumed during the entire reaction period) as well as the average yield (micrograms TTHM formed per milligram Cl_2 consumed between two reaction times) differed through sampled months. This may be attributed to the variations in the nature of organic matter. In all the months, the formation yields were highest during the first hours of reaction time, showing a rapid THM formation and chlorine decay. Kinetic laboratory experiments could be used to predict chloroform formation in the Cluj distribution system. Furthermore, an empirical model allowed an estimation of the chloroform formation in the Gilau water treatment plant.

Acknowledgements This work was financed by the Swiss National Science Foundation, the Swiss Agency for Development and Cooperation and the Romanian Ministry for Education and Research within the framework of the Swiss–Romanian cooperation programme on ‘Environmental Science and Technology in Romania—ESTROM’. The reported study was performed in the project WAQUA focussing on the formation of trihalomethanes and bromate during disinfection of drinking water in water treatment plants and distribution systems in Cluj, Romania.

References

- Adin A, Katzhendler J, Alkaslassy D, Rav-Acha C (1991) Trihalomethane formation in chlorinated drinking water. A kinetic model. *Water Res* 25:797–805
- Amy GL, Chadik PA, Chowdhury ZK (1987) Developing models for predicting trihalomethane formation potential kinetics. *J Am Water Works Ass* 79:89–96
- Arora H, LeChevallier MW, Dixon KL (1997) DBP occurrence survey. *J Am Water Works Ass* 89:60–68
- Aus-NZ Health Agency (2000) Australian Drinking Water Guidelines. Australian National Health and Medical Research Council, Australia
- Duong HA, Berg M, Hoang MH, Pham HV, Gallard H, Giger W, von Gunten U (2003) Trihalomethane formation by chlorination of ammonium- and bromide-containing groundwater in water supplies of Hanoi, Vietnam. *Water Res* 37:3242–3252
- Fayad NM (1993) Seasonal variations of THMs in Saudi Arabian drinking water. *J Am Water Works Ass* 85:46–50
- Gallard H, von Gunten U (2002) Chlorination of natural organic matter: kinetics of chlorination and of THM formation. *Water Res* 36:65–74
- Golfopoulos SK, Arhonditsis GB (2002) Multiple regression models: a methodology for evaluating trihalomethane concentrations in drinking water from raw water characteristics. *Chemosphere* 47:1007–1018
- Government of Romania (2005) Annex 8.6 to the implementation plan of Directive 76/464/EEC and ‘daughter directives’ on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Accession Treaty Romania-European Union, 25 April
- Guvernul Romaniei (2004) Hotarare pentru aprobarea Normelor de supraveghere, inspectie sanitara si monitorizarea a calitatii apei potabile. 669/26.VII.2004. Annex 1, Table 1–2
- Health Canada (2001) Summary of Guidelines for Drinking Water Quality. Federal-Provincial Subcommittee
- Marhaba TF, Washington MB (1998) Drinking water protection and byproducts: history and current practice. *Adv Environ Res* 2:103–115
- Najm I, Patania NL, Jacangelo JG, Krasner SW (1994) Evaluating surrogates for disinfection by-products. *J Am Water Works Ass* 86:98–106
- Nikolaou AD, Golfopoulos SK, Lekkas TD, Kostopoulou MN (2004a) DBP levels in chlorinated drinking water: effect of humic substances. *Environ Monit Assess* 93:301–319
- Nikolaou AD, Lekkas TD (2001) The role of natural organic matter during formation of chlorination by-products: a review. *Acta Hydrochim Hydrobiol* 29:63–77
- Nikolaou AD, Lekkas TD, Golfopoulos SK (2004b) Kinetics of the formation and decomposition of chlorination by-products in surface waters. *Chem Eng J* 100:139–148
- Parlamentul Romaniei (2002) Lege nr. 458/2002 privind calitatea apei potabile. Annex 1, Table 3

- Pinkernell U, Nowack B, Gallard H, von Gunten U (2000) Photometric determination of reactive bromine and chlorine species with ABTS. *Water Res* 34:4343–4350
- Rathbun RE (1996) Regression equations for disinfection by-products for the Mississippi, Ohio and Missouri Rivers. *Sci Total Environ* 191:235–244
- Singer PC (1999) Humic substances as precursors for potentially harmful disinfection by-products. *Water Sci Technol* 40:25–30
- UK Health Agency (2000) Water Supply (water quality) Regulations 2000 for England and Wales
- USEPA (1999b) Alternative Disinfectants and Oxidants Guidance Manual, United States Environmental Protection Agency. EPA 815-R-99-014
- USEPA (2001) National Primary Drinking Water Standards. United States Environmental Protection Agency, EPA 816-F-01-007
- USEPA (2001) Controlling Disinfection By-Products and Microbial Contaminants in Drinking Water. United States Environmental Protection Agency, EPA 600-R-01-110
- von Gunten U, Hoigné J (1992) Factors controlling the formation of bromate during ozonation of bromide-containing waters. *Aqua* 41:299–304
- von Gunten U, Hoigné J (1996) Ozonation of bromide-containing waters: bromate formation through ozone and hydroxyl radicals. In: Minear RA, Amy G (eds) *Disinfection By-products in water treatment, The chemistry of their formation and control*. CRC Press, Boca Raton
- WHO (1993) Guidelines for drinking-water quality, 2nd ed, Vol. 1, Recommendations, World Health Organization, Geneva, 1993
- Woo Y-T, Lai D, McLain JL, Manibusan MK, Dellarco V (2002) Use of Mechanism-Based Structure-Activity Relationships Analysis in Carcinogenic Potential Ranking for Drinking Water Disinfection By-Products. *Environmental Health Perspectives*. Supplements Volume 110, No S1, February
- Wright JM, Schwartz J, Dockery DW (2004) The effect of disinfection by-products and mutagenic activity on birth weight and gestational duration. *Environ Health Persp* 112:920–925