

Formation of Haloforms during Chlorination of Natural Waters

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Recent drinking water regulations have lowered the standards for disinfection by-products and have added new disinfection by-products for regulation. Natural organic matter (NOM), mainly humic compounds, plays a major role in the formation of undesirable organic by-products following disinfection of drinking water. Many disinfection by-products have adverse carcinogenic or mutagenic effects on human health. This paper deals with the formation potential of disinfection by-products in water samples taken from different places in the Flaje catchment.

Keywords: water, chlorination, disinfection by-product formation potential.

1 Introduction

Disinfection by-products (DBPs) comprise of several organic and inorganic compounds that are formed by reactions between chlorine, naturally occurring organic matter (NOM) and bromide in drinking water [1]. The major halogenated DBPs that are commonly identified from chlorine treatment are trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitrile (HANs), cyanogen halides, and halopicrins. Some of the major species of these DBPs are listed in Tab. 1 [2].

Tab. 1: Chlorinated DBPs

Chemical class	Chemical compound
Trihalomethanes (THM)	Chloroform
	Bromodichloromethane
	Dibromochloromethane
	Bromoform
Haloacetic acids (HAAs)	Monochloroacetic acid (MCAA)
	Dichloroacetic acid (DCAA)
	Trichloroacetic acid (TCAA)
	Monobromoacetic acid (MBAA)
	Dibromoacetic acid (DBAA)
	Tribromoacetic acid (TBAA)
	Bromochloroacetic acid (BCAA)
	Bromodichloroacetic acid (BDCAA)
Haloacetonitrile (HANs)	Chlorodibromoacetic acid (CDBAA)
	Dichloroacetonitrile
	Trichloroacetonitrile
	Dibromoacetonitrile
Cyanogen halides	Bromochloroacetonitrile
	Cyanogen chloride

Trihalomethanes (THMs) and haloacetic acids (HAAs) are the two major classes of DBPs commonly found in waters disinfected with chlorine. Early studies have mainly focused on the formation of THMs and HAAs. The levels of these compounds formed after chlorination of natural waters depend on several operational conditions, such as chlorine dosage and free chlorine contact time, as well as water quality conditions such as natural organic matter content (NOM), bromide concentration, temperature and pH.

The US Environmental Protection Agency (USEPA) has set a maximum contaminant level (MCL) of $100 \mu\text{g}\cdot\text{l}^{-1}$ for total THMs and has set a new MCL of $80 \mu\text{g}\cdot\text{l}^{-1}$ in stage 1 of the disinfection (disinfection by-product rule (USEPA 1998)). In addition to these standards, an MCL for HAAs of $60 \mu\text{g}\cdot\text{l}^{-1}$ was proposed in the stage 1 rule. Stage 2 of the D/DBP Rule may lower the MCLs for THMs and HAAs to $40 \mu\text{g}\cdot\text{l}^{-1}$ and $30 \mu\text{g}\cdot\text{l}^{-1}$, respectively. Hence, techniques to rapidly determine the problematic organic fractions most responsible for DBP formation within NOM are important for the minimization of DBP formation in water treatment systems.

The aggregate concentration of all halogenated DBPs is sometimes characterised as the total organic halide concentration (TOX).

To date, most DBP research has focused on THMs and HAAs [3]. NOM is considered to be the primary organic precursor to DBP formation and it is present in nearly all-natural waters.

Previous studies have shown the importance of many parameters for the formation of THMs and HAAs, such as dose of chlorine, concentration of bromide and ammonia, pH, temperature, content and type of natural organic matter (NOM) [4].

The NOM of most source waters comprises humic substances (humic and fulvic acids), hydrophilic acids, carboxylic acids, aminoacids, carbohydrates and hydrocarbons in the approximate proportions of 50, 30, 6, 3, 10 and 1 %, respectively [5]. However, in highly colour waters, the humic substance content may be as high as 50 to 90 %. The portion of NOM that can be biodegraded is sometimes defined as biodegradable dissolved organic carbon (BDOC) or assimilable organic carbon (AOC), which are measured by two distinct techniques [6].

Extensive research has been conducted to understand NOM composition. Much of this research has relied on the

fractionation of natural waters into operationally defined discrete fractions based on adsorption chromatography employing synthetic resins. However, questions have been raised about such isolation and fractionation techniques because NOM is cycled through large changes in pH (2 to 10), which may chemically alter its structure. NOM can be characterised by non-specific parameters; important examples include organic carbon content (i.e. dissolved organic carbon DOC) and UV-absorbance in the range of 254 to 280 nm ($UV_{254-280}$). Among all the different parameters for characterizing NOM of given water, UV_{254} and specific ultraviolet absorbance ($SUVA_{\lambda} = UV_{\lambda}/DOC$) at a particular wavelength (λ) has often correlated well with DBP formation [7].

A number of studies have used linear regression techniques to correlate THMs formation potential (THMFP) with TOC and UV_{254} [8, 9].

THMFP is the difference between the final THM concentration and the initial THM concentration in a sample at standard reaction conditions. Standard reaction conditions are as follows: free chlorine residual at least $3 \text{ mg} \cdot \text{l}^{-1}$ and not more than $5 \text{ mg} \cdot \text{l}^{-1}$ at the end of a 7-d reaction (incubation) period, with sample incubation temperature of $25 \text{ }^{\circ}\text{C}$ and pH controlled at $7,0 \pm 0,2$ with a phosphate buffer [10].

This paper discusses DBP formation potential in surface waters of the Flaje catchments and its relationship to the properties of the humic substances in these waters. The focus of this discussion is on reactions with chlorine and on the formation of halogenated DBPs – THMs and HAAs.

2 Samples

Five sampling points in the Flaje catchment were chosen: Rašeliník stream (No. 1), Flaje water reservoir (No. 2), Radní stream (No. 3), Flájský stream (No. 4) and Mackovský stream (No. 5). The locations of the sampling points are given in Fig. 1.

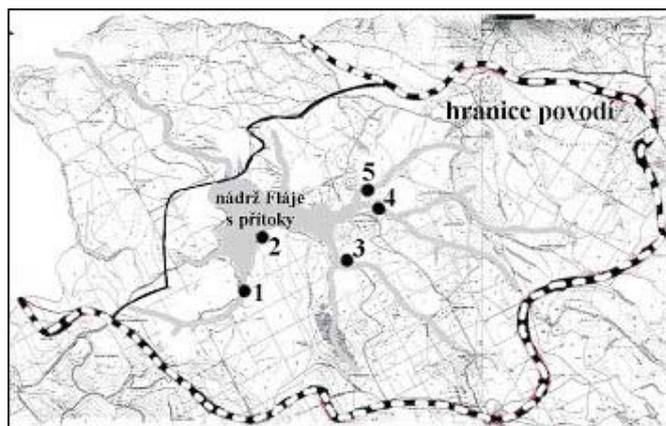


Fig. 1: Flaje catchments and the locations of sampling points

3 Materials and methods

THM and HAA formation potential (THMFP and HAAFP) tests were conducted in accordance with Czech method TNV 757549 [10], which corresponds with method 5710, given in the Standard Methods for the Examination of Water and Wastewater [11].

THMs were determined by head-space solid phase micro-extraction, using a Carboxen coated fiber (Supelco). HAAs were analysed by liquid – liquid extraction from an acidified sample into methyl t-butylether (MTBE) after esterification by boron trifluoride. Gas chromatography – mass spectrometry (GC 8000/MD 800 Fisons) was used as a final analytical technique. Other parameters such as TOC, A_{254} , were tested in all samples.

The results for THMFP and HAAFP measured in given samples are summarized in Tab. 2.

Tab. 2: Results of THMFP and HAAFP tests – Flaje catchment. Sampling period September – December 2001

Sampling place	1	2	3	4	5
THMFP ($\text{mg} \cdot \text{mg}^{-1} \text{DOC}$)	0,061	0,107	0,024	0,120	0,107
	0,139	0,159	0,070	0,146	0,055
	0,104	0,106	0,069	0,044	0,106
	0,258	0,164	0,191	0,170	0,109
HAAFP ($\text{mg} \cdot \text{mg}^{-1} \text{DOC}$)	0,009	0,030	0,024	0,017	0,009
	0,211	0,099	0,105	0,208	0,201
	0,108	0,114	0,147	0,076	0,128
	0,134	0,113	0,057	0,103	0,112

Tab. 3: Evaluation of THMFP and HAAFP tests in surface water from the Flaje catchment

No	Sampling place	THMFP ($\text{mg} \cdot \text{mg}^{-1} \text{DOC}$)			HAAFP ($\text{mg} \cdot \text{mg}^{-1} \text{DOC}$)		
		Min.	Max.	\emptyset	Min.	Max.	\emptyset
1	Rašeliník	0.061	0.258	0.140	0.009	0.211	0.033
2	Reservoir surface	0.106	0.164	0.134	0.030	0.114	0.089
3	Radní stream	0.024	0.191	0.088	0.024	0.147	0.083
4	Flájský stream	0.044	0.170	0.120	0.017	0.208	0.101

Table 3 shows the average, minimum and maximum values of measured parameters.

The results are compared in Fig. 2 and Fig. 3.

The values of other measured parameters are given in Tab. 4.

As can be seen from Fig. 2, the maximum potential of THM formation presented was in the Rašeliník stream ($\emptyset 0.140 \text{ mg} \cdot \text{mg}^{-1} \text{DOC}$), while the minimum was in the water from Radní stream ($\emptyset 0.088 \text{ mg} \cdot \text{mg}^{-1} \text{DOC}$). The maximum formation potential of HAA was in water from Flájský stream ($\emptyset 0.101 \text{ mg} \cdot \text{mg}^{-1} \text{DOC}$), whereas the minimum was in water from Radní stream ($\emptyset 0.083 \text{ mg} \cdot \text{mg}^{-1} \text{DOC}$). The seasonal evolution of THMFP in the water under study was also observed. The results of tests measured in December were the highest, and the overall trend advanced from

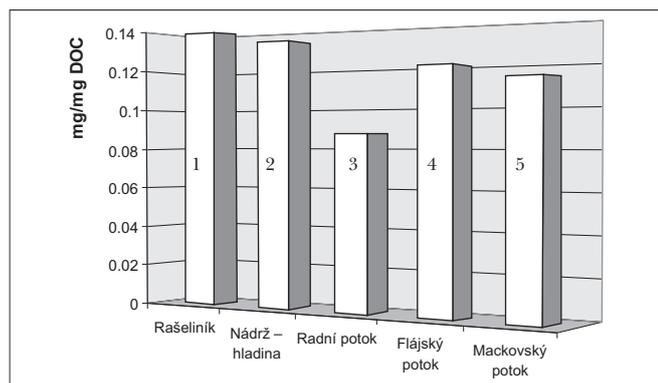


Fig. 2: Average values of THMFP in water under study

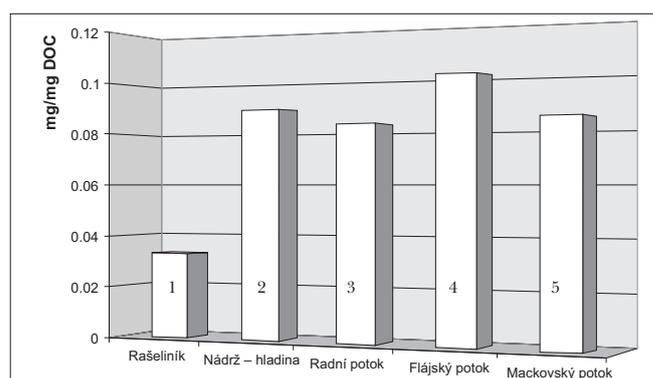


Fig. 3: Average values of HAAFP in water under study

Tab. 4: Content of organic compounds in water samples from the Flaje catchment

Sample No.	Sampling place	1	2	3	4	5
1	DOC ($\text{mg}\cdot\text{l}^{-1}$)	15.9	6.55	8.15	9.33	9.53
	COD _{Mn} ($\text{mg}\cdot\text{l}^{-1}$)	22.7	8.00	10.70	11.00	10.7
	A ₂₅₄ (cm^{-1})	0.685	0.25	0.327	0.385	0.376
2	DOC ($\text{mg}\cdot\text{l}^{-1}$)	6.55	3.51	6.00	7.20	10.91
	COD _{Mn} ($\text{mg}\cdot\text{l}^{-1}$)	14.40	8.00	4.60	9.30	7.00
	A ₂₅₄ (cm^{-1})	0.483	0.278	0.131	0.327	0.245
3	DOC ($\text{mg}\cdot\text{l}^{-1}$)	10.69	6.29	10.23	16.55	5.73
	COD _{Mn} ($\text{mg}\cdot\text{l}^{-1}$)	14.00	10.00	15.50	22.00	8.90
	A ₂₅₄ (cm^{-1})	0.445	0.263	0.446	0.748	0.231
4	DOC ($\text{mg}\cdot\text{l}^{-1}$)	4.62	6.79	2.07	3.92	4.55
	COD _{Mn} ($\text{mg}\cdot\text{l}^{-1}$)	5.60	8.60	1.90	4.20	4.70
	A ₂₅₄ (cm^{-1})	0.185	0.269	0.061	0.140	0.146

September to December 2001. This was not the case for HAAFP. It should be noted that these conclusions need to be verified by analysing further samples. It should be noted, that the average values of THMFP in the given waters were higher than those in the data presented for surface water by Fox et al [7].

4 Summary and conclusions

This paper discusses the use of THMFP and HAAFP as a predictive tool for disinfection by-product formation due to the presence of natural organic matter (NOM), mainly of humic and fulvic acids in water. The limited number of samples used means that the conclusions and the use of THMFP and HAAFP as an interest parameter should be regarded with caution.

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