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Incidence of Trihalogenmethanes in Drinking Water

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***Abstract*—**Trihalogenmethanes are the most significant by-products of the reaction of disinfection agent with organic precursors naturally present in ground and surface waters.Their incidence negatively affects the quality of drinking water in relation to their nephrotoxic, hepatotoxic and genotoxic effects on human health. Taking into consideration the considerable volatility of monitored contaminants it could be assumed that their incidence in drinking water would depend on the distance of sampling from the area of disinfection. Based on the concentration of trihalogenmethanes determined with the help of gas chromatography with mass detector and the analysis of variance (ANOVA) such dependence has been proved as statistically significant. The acquired outcomes will be used for assessing the non-carcinogenic and genotoxic risks to consumers.

***Keywords*—**disinfection byproducts, drinking water, trihalogenmethanes

I. Introduction

WATER goes through series of treatments before it becomes drinking water. The treatments are aimed at achieving proper physical-chemical characteristics and health non-harmfulness. In the course of disinfection, the aim of which is to achieve microbiological non-harmfulness of drinking water, many disinfection by-products (DBPs) are produced and quite a few of them have significant toxic effects [12]-[2].

The DBPs are produced by the interaction of an oxidizing agent with organic substances commonly present both in ground and surface waters [18]. The DBPs occurring in the highest concentrations and which may have a serious impact on consumers´ health include chloroform, ($CHCl_3$), bromdichlormethane($CHBrCl_2$),dibromchlormethane ($CHBr_2Cl$), and bromoform ($CHBr_3$).

The above mentioned pollutants belong into the group of organic halogenderivates, commonly indicated as trihalogenmethanes (THMs) [2].

Therefore it is necessary to monitor continuously the THMs concentrations in drinking water and implement adequate countermeasures in case the increased concentrations are detected.

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II. The Analysis of Current State

The requirements for non-harmfulness of drinking water are defined in legislation on both national and supranational levels. The WHO states in its earlier handbook on the quality of drinking water, that international limits for THMs range from 25 to 250 $\mu g.dm^{-3}$ [19]. Limit for the total amount of THMs in drinking water in the Czech Republic is 100 $\mu g.dm^{-3}$and is in compliance with the requirements of the European Union [14]. The U.S. EPA sets the limit for THMs as not harmful to health at 80 $\mu g\ dm^{-3}$ [16].

The WHO does not mention any particular amount, but the sum of weighted averages for the most significant THMs [20]. Besides the total amount of THMs the standards define also the limit concentrations for individual compounds classified into the group of THMs. The acceptable concentration of the sum of THMs is higher in the Czech Republic than in the U.S. EPA. However, the limits for chloroform are lower than those set by the U.S. EPA and WHO.

Mainly chlorination and ozonisation, or their combination, are used for water disinfection not only in the Czech Republic, but in most countries around the world [2]. Recently the application of UV radiation and ozone is on the increase, mainly due to the high efficiency of ozone against resistant pathogens such as *Cryptosporidium*oocysts and a lower potential for the production of DBPs. However, all disinfection agents are oxidants producing DBPs [10].

The types and amounts of chlorination intermediates depend on the ways of disinfection and water properties. The research conducted by Chinese scientists has shown that the total amount of THMs increases at certain pH values.Temperature is another factor influencing the amount of DBPs. When exceeding the so called key temperature the quantity of produced DBPs decreases. The amount of produced DBPs is also the function of some ions being present in treated water. It has been proved that the cations Mo^{2+}, Na^{+} and K^{+} increase the total production of THMs, while the occurrence of the cations Fe^{2+}, Mn^{2+} and Ca^{2+} has the opposite effect [5]. The speed of reaction and the range of produced DBPs depend on the type and dose of disinfection agent being used, concentration and chemical composition of organic precursors present in water or the distribution network, water delay during disinfection, etc. [19], [17]. The THMs are present in the interval from 37 to 58% [11] depending on the conditions of disinfection. Other authors state that the occurrence of THMs may be up to 90% with chloroform being the dominant product [3]. The THMs are not the only group of DBPs, halogen acetic acids, cyanogen chloride, halogenacetonitriles, chloral hydrate (2,2,2-trichloro-1,1-ethandiol), chlorophenols, bromates, etc., have also been identified [13], [1].

The THMs are absorbed through inhalation, ingestion and dermal contact, and have neurotoxic, immunotoxic, cytotoxic, hepatotoxic and nephrotoxic effects [9],[15]. Carcinogenic, mutagenic, teratogenic and embryotoxic effects are not excluded, either [15].

The studies are carried out all over the world with the aim to discover particular effects of THMs on human organism. There are suspicions that bromdichlormethane in higher concentration causes spontaneous abortions, reduces the natal weight of children and increases the risk of development defects, although this information has not been sufficiently proved yet [3], [10].

Chloroform and bromdichlormethane are classified into the 2B group as probably carcinogenic to humans according to the International Agency for Research of Cancer. On the contrary, bromoform and dibromchlormethane are classified in the group 3 as substances or mixtures not carcinogenic to humans [6], [7]. It has to be emphasized though, that risk resulting from insufficient inactivation of pathogens in drinking water is of higher order priority in comparison with the health risk resulting from the presence of DBPs [19].

With regard to the fact that THMs are volatile or semivolatile mixtures it may be assumed that their content in drinking water depends on the distance from the area of disinfection. This fact is tried to be verified in this paper with the aim to provide subsequently more reliable health risk assessment.

III. Problem Solution

A. Applied Methods and Devices

The samples of drinking water have been taken and analyzed according to the relevant SOP [19]. The concentration of THMs in the samples of drinking water has been determined by the liquid-gas extraction technology with the help of the TriPlus static head space dosing device and the Trace GC Ultra gas chromatograph with the Trace DSQ mass detector, produced by Thermoelectron Corporation. The limit of determination for individual THMs was 0.1 or 0.5 μg dm-3.

The analysis of variance (ANOVA) has been used for assessing the mutual relation between the content of THMs in a sample and the distance from the site of chlorination. The assumption has been that the data are collected from the normal distribution with constant variance. The method enables us to assess the proportion of intergroup and intragroup variability to the total variability and the significance of impact of explanatory variable on the one being explained. [8].

The intergroup variability $S_V(y)$, given by relation (1), represents the sum of variabilities inside all *k* groups and is caused by a number of effects unexplored for the analysis.

$$S_V(y) = \sum_{k=1}^{m} S_k(y) \quad (1)$$

Where *y* in the equation (1) is random quantity, in this case the concentration of THMs, and *m* is the number of groups, with $k, m \in N \wedge y \in \mathrm{Re}^{+}_{(0)}$, where *N* is the symbol for the set of all natural numbers and $\mathrm{Re}^{+}_{(0)}$ is the symbol for the set of all real positive numbers including zero. At the same time it holds true that the intergroup variability $S_k(y)$ can be expressed by equation (2):

$$S_k(y) = n_k \times s_k^2(y) \quad (2)$$

Where n_k and $s_k^2(y)$ is a number of elements and conditional variance respectively of *k*-group of random variable *y* and at the same time $n_k \in N$. The intergroup variability expresses variability among selected groups, and thus covers the examined dependence of the explanatory variable on the one being explained. The intergroup variability $S_M(y)$ is calculated according to the formula (3):

$$S_M(y) = n \times s^2(\overline{y}) \quad (3)$$

where $n = \sum_{k=1}^{m} n_k$ is the total number of elements and $s^2(\overline{y})$ is the variance of conditional averages of all *m* assessed groups.

The total variability $S_C(y)$ is the sum of intragroup and intergroup variabilities according to the relation (4):

$$S_C(y) = S_V(y) + S_M(y) \quad (4)$$

The value of $B(y)$ of intragroup variability and total variability

$$B(y) = S_M(y) \times [S_C(y)]^{-1} \quad (5)$$

expresses to which extent the intragroup variability has its share in total variability. If the share of intragroup variability in the total variability is $B_y < 0{,}5$, it is possible to hypothe size that the values of measuring *Y* are significantly influenced by explanatory variable *X*.

The above mentioned hypothesis *Hp is* tested with the use of Fisher-Snedecor *F* (p, q) test with *p* and *q* degrees of freedom. The hypothesis is defined in the following way: $H_p: \mu_1 = \mu_2 = \cdots = \mu_k$ and support the statement that explanatory variable has an impact on the one being explained. The *A* alternative is determinedas: $A: \mu_i \neq \mu_j$ and it is enough for it to be accepted when there is a difference between two various means of μ.

The test criterion *F* is in our case in compliance with equation (6):

$$F = \frac{S_M(y)}{k-1} \times \left[\frac{S_V(y)}{n-k}\right]^{-1} \quad (6)$$

The hypothesis *Hp* is rejected on the significance level α, if $F \geq F_{1-\alpha}(k-1,\ n-k)$.

B. Outcomes and Discussion

Sampling has been carried out in the region of Brno town, near the water treatment plant, where the disinfection with gaseous chlorine takes place. The sampling sites have been divided into three groups based on their distance from the site of chlorination. The site 3 has been the closest to the area of chlorination, while the site 1 has been the furthest one. The samples have been taken in various seasons.

TABLE I
CONCENTRATION OF THMS ON INDIVIDUAL SITES AND IN VARIOUS SEASONS

Site	CHCl3 [μg dm-3]	CHCl2Br [μg dm-3]	CHClBr2 [μg dm-3]	CHBr3 [μg dm-3]	Σ THMs [μg dm-3]	n_k
1	<0,1	<0,1	<0,1	<0,1	0,4	4
	0,2	0,1	<0,1	Not detected	0,4	
	0,3	0,2	<0,1	Not detected	0,6	
	<0,5	<0,5*	<0,5*	<0,5*	2	
2	<0,1	<0,1	<0,1	<0,1	0,4	4
	0,5	0,2	<0,1	Not detected	0,8	
	0,7	0,4	0,1	Not detected	1,2	
	<0,5*	<0,5*	<0,5*	<0,5*	2	
3	3,1	2,2	1,9	0,4	7,6	5
	1,8	2,3	2,2	0,6	6,9	
	1,4	2,3	2,9	0,7	7,3	
	1,1	1,6	1,9	0,3	4,9	
	1,2*	1,2*	1,3*	<1*	4,7	

*Analysis with various limit of determinability

TABLE II
INTERGROUP, INTRAGROUP AND TOTAL VARIABILITIES, TOGETHER WITH THE SHARE OF INTRAGROUP VARIABILITY IN THE TOTAL VARIABILITYY

Site	n_k	$s_k^2(y)$	$n_k \times s_k^2(y)$	$S_V(y)$	$\overline{y_k}$	$s^2(\overline{y})$	$S_M(y)$	$S_C(y)$	$B(y)$
1	4	0,448	1,790		0,850				
2	4	0,350	1,400	10,758	1,100	6,264	81,438	92,195	0,883
3	5	1,514	7,568		6,280				

TABLE III
TESTING OUTCOMES

F	$F \geq F_{1-\alpha}(k-1, n-k)$	$F \geq F_{1-0,95}(2, 10)$
37,850	4,103	37,850≥4.103

The Table I shows the concentrations of THMs in individual sites. For the needs of statistical calculations and in compliance with the principle of preliminary precaution the concentrations of THMs being under the limit of determination have been taken on their upper levels, i.e. as the concentrations representing the limit of determinability

The Table II presents the data necessary for the calculation of intergroup variability$S_V(y)$, intragroup variability $S_M(y)$ and total variability $S_C(y)$together with their values. At the same time the portion of intragroup variability $B(y)$from total variability is included. It is obvious from the calculated values, that the discussed portion of $B(y)$is 88,3 %, which means the variability is higher among the groups than inside the groups.

The Table III includes the outcomes of *F*-test in relation to the hypothesis that the THMs concentration is the function of the distance of sampling from the area of chlorination. As the inequation$F \geq F_{1-\alpha}(k-1,\ n-k)$is valid, the *Hp hypothesis* could be rejected and the *A* alternative accepted. It results from the above mentioned that there is a 95% certainty the THMs concentration in drinking water depends on the distance of sampling from the area of chlorination.

IV. Conclusion

Drinking water pollutants occurrence analysis is an important basis for assessing the health risks to the consumers of drinking water. The outcomes acquired from the analysis of variance prove that the concentration of THMs decreases with the increasing distance of water sampling from the area of chlorination. It would be necessary to acquire more data through a more detailed monitoring of THMs concentration in drinking water as a function of distance from the area of chlorination.

The acquired outcomes are relevant in relation to further population health risk assessment. Attention will have to be paid mainly to the areas near the process of disinfection.

With regard to a relatively high variance of measured values it will also be useful to calculate rather the higher limits of reliability interval following the principle of preliminary precaution in risk assessment.

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