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Relationships Between Raw Water Quality, Treatment, and Occurrence of Organics in Canadian Potable Water

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The occurrence of organic contaminants in potable water is of concern since ingestion of such compounds may pose a hazard to human health. To aid in health hazard assessment, Canadian potable water supplies have been surveyed for the occurrence of organic compounds, such as, the trihalomethanes (WILLIAMS et al. 1980) and nitrilotriacetic acid (MALAIYANDI et al. 1979). A wide range of organics have been reported to occur in potable water (GARRISON et al. 1978) and sources of such contaminants have been discussed (e.g., DEINZER et al. 1978, WAGGOTT & WHEATLAND 1978). The relationships between the occurrence of organics, raw water quality, and treatment practices have been investigated (e.g. SYMONS et al. 1975, WILLIAMS et al. 1980, OTSON et al. 1981). However, such studies have been limited, generally, to the occurrence of trihalomethanes (THM).

During a recent survey of water at 30 Canadian potable water treatment facilities, the occurrence of about 40 volatile organics was investigated (OTSON et al. 1982). Subsequently, data obtained from questionnaires completed during the survey were used to explore the relationships between the occurrence of organics, water quality, and treatment practices. Results of these investigations are now reported.

EXPERIMENTAL

Survey scope. Thirty potable water treatment plants, in 29 municipalities were selected across Canada. During August-September, 1979, grab samples of raw and treated water were collected within 1 hr at a particular plant. An additional treated water sample was collected 24 hr later. In November-December, raw and treated water samples were collected on one day only. Information on raw water source, water quality measurements, treatment practices, and chemical dosages and levels was obtained from questionnaires completed at the treatment plants.

Analyses. Grab samples of water were analyzed for total organic carbon (OTSON et al. 1979) and for volatile organics by dynamic head space (OTSON & WILLIAMS 1982), static head space (OTSON et al. 1982), and liquid-liquid extraction (OTSON & WILLIAMS 1981) techniques.

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RESULTS AND DISCUSSION

Analytical techniques and levels and frequency of occurrence for 43 compounds which were investigated are reported and discussed elsewhere (OTSON et al. 1982). The 27 compounds which were detected in water samples and their frequency of occurrence are summarized in TABLE I.

TABLE I. Frequency of Detection for Compounds Found in Water Samples.

Compound	Frequency Raw[a]	Frequency Treated[b]	Compound	Frequency Raw[a]	Frequency Treated[b]
$CHCl_3$	28	87	C_6H_5Cl	3	16
$CHBrCl_2$	4	73	CHClCHCl	2	11
$CHBr_2Cl$	1	22	p-$C_6H_4Cl_2$	5	6
$CHBr_3$	0	8	$CHCl_2CH_3$	2	7
CH_2Cl_2	18	40	CH_3Cl	1	2
CH_2ClCH_2Cl	10	25	$CHClCHCH_2Cl$	1	2
CCl_2CHCl	48	51	CCl_2F_2	1	1
CCl_2CCl_2	24	39	CH_2CHCl	1	1
C_6H_6	32	55	$CHCl_2CH_2Cl$	0	2
$C_6H_5CH_3$	27	46	$CHCl_2CHCl_2$	1	1
$C_6H_5C_2H_5$ & p-$C_6H_4(CH_3)_2$	14	21	m-$C_6H_3Cl_2$	1	1
			CH_2CCl_2	0	1
m-$C_6H_4(CH_3)_2$ & o-$C_6H_4(CH_3)_2$	7	22	$CH_2ClCHClCH_3$	0	1

[a] Frequency in 30 summer plus 30 winter water samples.
[b] Frequency in 60 summer (day 1 & day 2) plus 30 winter water samples.

A mean concentration exceeding 1 ug/L for treated water samples from the 30 treatment plants was only found for CH_2Cl_2, CHClCHCl, CH_2ClCH_2Cl, $CHCl_3$, $C_6H_5CH_3$, C_6H_6, and $CHBrCl_2$. Only for $CHCl_3$ did the mean value exceed 10 ug/L. Mean levels for CH_2Cl_2, $CHCl_3$, CH_2ClCH_2Cl, C_6H_6, and CCl_2CHCl exceeded 1 ug/L in raw water but values were generally lower than for treated water.

As shown in TABLE II, generally the occurrence of the identified organics was more frequent and at a higher total concentration in treated water than in raw water. The difference was not quite as evident for the total identified compounds when THM values were excluded. The formation of THM during chlorination of natural waters has been demonstrated (ROOK 1974) and the appearance of other organics, such as, aromatic hydrocarbons (SMILLIE et al. 1978) and chlorinated hydrocarbons (SYMONS et al. 1975) has been observed. The totals for identified compounds also demonstrate seasonal differences in mean concentration, with the highest concentrations found for the summer months. The observed decrease of trihalomethane levels from summer to winter has been reported in other studies (e.g. OTSON et al. 1981). Mean total organic carbon values, which include many less volatile compounds, did not show much seasonal difference for the same water type. However, a reduction of total organic carbon was evident upon treatment of the raw water.

TABLE II. Mean Concentration ($\bar{c}$) and Frequency (f) of Occurrence[a] of Organics in Water

Sample type	Total Identified Compounds All $\bar{c}$(ug/L)	f	No THM c(ug/L)	f	TOC[b] (mg/L)
Aug.-Sept.					
Day 1-Raw	18	120	13	102	4.10
Day 1-Treated	66	202	25	135	3.36
Day 2-Treated	65	172	26	109	3.48
Nov.-Dec.					
Raw	7	111	5	96	4.41
Treated	32	167	9	107	3.33

[a] Sum of frequencies for all compounds in all samples.
[b] Total Organic Carbon measured by Dohrmann Model DC-54 Instrument.

Water quality and treatment practices. Information on raw water quality and treatment practices was obtained from the completed questionnaires. The raw water source was river water at 17 plants, lake water at 10 plants, and ground water at 3 plants. For water entering the 30 plants, the pH ranged from 5.2 to 8.8 and the pH was 7.0 at 19 of the plants. Hardness ranged from 5 to 300 ppm, turbidity ranged from 0.3 to 230 JTU, and colour ranged from about 1 to 95 Hazen units. The order and type of treatment, i.e. flocculation, sedimentation, filtration, carbon adsorption, aeration, chlorination, ozonation, fluoridation, etc., chemical dosages for chlorine, ozone, fluoride, alum, and lime, and residual chlorine levels were recorded. Eleven facilities used no flocculation, sedimentation, and filtration. The total dosage of chlorine, applied at all 30 plants, ranged from 0.1 to 9.0 mg/L and the dosage of ozone, applied at 3 of the plants, ranged up to 1.7 mg/L.

The mean concentration of organics in raw and treated water are listed according to raw water source in TABLE III. Raw and treated groundwater showed the lowest levels of organics. The highest mean concentrations of trihalomethanes, aromatic hydrocarbons, and other organics were found in raw and treated river water during August-September.

TABLE III. Mean Concentration (ug/L) of Organics by Water Source

Sample type		Source	THM	Aromatic HC	Other	TOC (mg/L)
Aug.-Sept.	Raw	lake	4.0	0.9	1.7	3.5
		river	8.5	4.4	25.0	5.3
		ground	0.2	0.3	2.0	1.7
	Treated	lake	34.3	5.0	22.0	3.6
		river	58.4	10.0	25.2	3.9
		ground	6.6	3.1	11.7	1.9
Nov.-Dec.	Raw	lake	0.5	0.5	3.0	4.6
		river	2.2	1.1	5.0	5.2
		ground	2.2	2.4	1.9	2.0
	Treated	lake	23.2	4.2	17.4	3.8
		river	31.4	0.9	2.1	3.5
		ground	1.3	0.7	1.9	2.0

Generally, levels of total identified organics increased upon treatment of the raw water, but total organic carbon measurements decreased or remained the same. With the exception of untreated ground water, the levels of identified organics were lower in the winter raw and treated water than in corresponding summer raw and treated water. The decrease was most noticeable for river water. Dichloromethane, chloroform, trichloroethylene, tetrachloroethylene, bromodichloromethane, and the aromatic hydrocarbons were frequently detected in both raw and treated water from all three sources. Mean total organic carbon levels in raw water decreased in the order of river to lake to groundwater. TOC levels in treated ground water were about one half the levels in treated river and lake water.

Treated water at 12 plants, including 6 river, 3 lake, and 3 groundwater supplies, showed chloroform levels of <10 ug/L in winter and, usually, also in summer. Two of the plants supplied with groundwater showed chloroform levels ≤1 ug/L in treated water and unusually low TOC levels (<1.4 ug/L). Seven of the 12 plants used no flocculation, sedimentation, and filtration and included 1 river, 3 lake, and the 3 groundwater supplies. Five of these plants, including 2 with lake water and the 3 with groundwater supplies, showed particularly low TOC and chloroform levels as compared to mean values obtained for the 12 plants. Other studies (SYMONS et al. 1975, WILLIAMS et al. 1980) have also shown the occurrence of lower THM levels in treated water when the raw source is groundwater rather than surface water and suggest also that, often, low THM levels are associated with low TOC levels.

A high chlorine dosage usually resulted in high chloroform levels in treated water at the 30 plants. This relationship has been observed previously (SYMONS et al. 1975, WILLIAMS et al. 1980) when attempts have also been made to relate THM formation with other treatment practices. However, in this study no other relationships between water quality, treatment practices, and occurrence of organics were evident upon comparison of the tabulated data by visual inspection.

Correlation coefficients. Since identification of factors influencing the levels of organics in water was difficult by visual comparison of the tabulated data, computer assisted statistical treatment of the data was applied. For many of the variables which had a large number of zero or near zero values, the normality assumption could be violated and the significance levels for correlation coefficients could become meaningless. Therefore, three types of coefficients were used in the determination of significant correlations. First, Kendall's non-parametric correlation coefficients, which make no assumptions about the distribution of values, were calculated and only those pairs of variables with a coefficient significantly different from zero at the $p = 0.05$ level were considered subsequently. Then Pearson's coefficient was calculated for the pairs having both values greater than zero, that is, approximately normally distributed values were considered. For those pairs which were significant at $p = 0.1$, Pearson correlation coefficients using all values were then calculated. Pairs of variables showing a strong relationship were then determined from the three correlation coefficients and scattergram plots of all values of a pair. In the following discussions, only the Pearson coefficient for all values will be reported.

Since some of the compounds were quantitated by more than one analytical technique, it was possible to compare values obtained by the techniques. In general, best correlation was found upon comparison of analytical results for compounds showing a mean concentration, in water, of greater than 1 ug/L at the 30 plants. That is, when a good analytical precision was obtained because many values were above the quantitation limit. Techniques used to measure three such compounds, chloroform, bromodichloromethane, and dichloroethane, showed correlation coefficients which were usually above 0.80. Although relatively poor correlation between techniques was found for some infrequently occurring compounds, all analytical data were considered in the following statistical analyses.

Correlation between levels of different compounds in the same water type were investigated and significant relationships found for summer treated water are shown in TABLE IV. Dichloromethane, dichloroethane, chloroform, bromodichloromethane, benzene and toluene showed only a few strong relationships in both summer and winter raw water samples. However, in treated water, ethylbenzene, the xylene isomers, bromoform, chlorodibromomethane and the aforementioned compounds showed additional and more complex relationships. Notably, the aromatics showed strong correlation with each other in treated water. Dichloromethane and dichloroethane were correlated with each other and with the aromatics in treated water. In summer, in treated water, the brominated trihalomethanes showed some correlation with each other and chlorobenzene, but not with chloroform. The above results suggest that levels of many of these frequently detected compounds in treated water, and in a few instances raw water, are often directly related. However, levels of some compounds, such as tri- and tetra- chloroethylene which also occurred frequently and at levels above 1 ug/L, did not show significant correlations with any compounds.

TABLE IV. Compounds Showing Strong Correlation ($p \leq 0.001$) in August-September Treated Water

	Compound	2	3	4	5	6	8	9	10
1.	CH_2Cl_2	0.93	0.85	0.92	0.85	0.84			
2.	CH_2ClCH_2Cl		0.94	0.94	9.92	0.84			
3.	C_6H_6			0.96	0.92	0.80			
4.	$C_6H_5CH_3$				0.98	0.96			
5.	EtBz & p-Xy					0.97			
6.	m- & o-Xy								
7.	$CHBrCl_2$						0.86	0.71	
8.	$CHBr_2Cl$							0.91	0.76
9.	$CHBr_3$								
10.	C_6H_5Cl								

Significant correlations found for levels of organics in different water types are summarized in TABLE V. For chloroform, bromodichloromethane, and chlorodibromomethane only, there was some correlation between levels in summer and levels in winter treated water. These correlations and evaluation of the scattergrams suggested a consistency in the decrease of trihalomethane levels in treated water from summer to winter. Only dichloromethane, dichloroethane, benzene, and toluene showed some correlation between levels in raw and treated water in the summer. The scattergrams showed that, although there is correlation between occurrence of these compounds, their levels in treated water are almost always greater than in raw water and cannot, therefore, be entirely attributed to their occurrence in the raw water. In addition to the results shown in TABLE VI it was found that total organic carbon levels showed strong correlation ($r \geq 0.70$, $p < 0.001$) for summer raw water with summer treated and winter raw water at the plants and, in fact, levels in all water types were interrrelated. These results, evaluation of the scattergrams, and the observed reduction of mean TOC levels upon water treatment suggest a consistency in raw water TOC levels and removal at the individual treatment plants.

As shown in TABLE VI, some correlations were observed for chlorine dosages and demand with chloroform and bromodichloromethane levels in treated water. Strongest correlations were found for chlorine demand and total dosage with levels of the two trihalomethanes, particularly chloroform. Such results were also found in a 13 month study of water at two of the treatment plants (OTSON et al. 1981) and in a previous survey including 70 Canadian municipalities (WILLIAMS et al. 1980).

TABLE V. Correlation of Compound Levels in Different Sample Types[a]

Compound	Treated water Aug.-Sept./Nov.-Dec	Aug.-Sept. Raw/Treated Water
$CHCl_3$	0.72	
$CHBrCl_2$	0.58	
$CHBr_2Cl$	0.66	
CH_2Cl		0.86
CH_2ClCH_2Cl		0.91
C_6H_6		0.91
$C_6H_5CH_3$		0.56

[a] Pearson coefficient ($p \leq 0.001$) - zero values included.

For raw water, no significant correlations of dosages and water quality measurements with levels of organics were found. However, weak correlations occurred for TOC with colour, hardness, total chlorine dosage, and alum dosage. For summer treated water, weak correlation was found for turbidity with TOC, and for pH with chlorodibromomethane levels.

A disadvantage in this and similar studies (WILLIAMS et al. 1980, SYMONS et al. 1975), wherein a large number of water supplies are surveyed, has been that the frequency of sampling was limited. Also, since the number of variables which can be identified and measured is limited, precise and accurate interpretation of the statistical results is difficult. Usually, only bivariate statistical analyses are done, whereas relationships between some variables may actually be multivariate. However, results of bivariate analyses of data, such as in this study, do provide useful information and indicate the direction of further studies.

TABLE VI. Correlation of Chlorine Values With Trihalomethane Levels in Treated Water[a]

Chlorine	THM	Aug.-Sept.	Nov.-Dec.
predosage	$CHCl_3$	0.45	0.62
	$CHBrCl_2$	0.60	0.74
post dosage	$CHCl_3$	0.58	0.57
total dosage	$CHCl_3$	0.77	0.84
	$CHBrCl_2$	0.65	0.64
demand	$CHCl_3$	0.82	0.87
	$CHBrCl_2$	0.65	0.66

[a] Pearson coefficient - all values; $p \leq 0.01$

CONCLUSIONS

Some interesting results obtained from this survey of water at 30 Canadian potable water treatment plants are summarized. 1. Generally, levels of organics were highest during summer and in raw and treated river water and were lowest in raw and treated groundwater. The levels of total identified organics increased upon water treatment, but TOC levels decreased or remained the same. 2. Strong correlations were found for chloroform and bromodichloromethane levels with chlorine dosages and demand. 3. Several compounds, in particular chloroform, bromodichloromethane, dichloromethane, 1,2-dichloroethane, benzene, and toluene showed complex relationships for their occurrence in raw and/or treated water samples.

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