A National Survey of Chlorinated Disinfection By-Products in Canadian Drinking Water

Environmental Health Directorate
Health Protection Branch

Our mission is to help the people of Canada maintain and improve their health.
Health Canada

Published by authority of the
Minister of National Health and Welfare
1995

Également disponible en français sous le titre
Étude nationale sur les sous-produits de désinfection chlorés dans l'eau potable au Canada

Cat. H46-2/95-197E
ISBN 0-662-24295-5

Copies of this report can be obtained from:
Publications, Health Canada
Communications and Consultation Directorate
Ottawa, Ontario
K1A 0K9

95-EHD-197

Appendices

Appendix 1 – Questionnaire

National Study on Disinfection By-Products in Water

1. Treatment Plant Address: _____
2. Plant Telephone No.: _____
3. Questionnaire completed by: _____
4. Title: _____
5. Telephone No.: _____
6. Population served by Plant: _____ Date completed: _____

7. Water Source Lake _____ River _____ Well _____ Other _____
   Name _____ Name _____ No _____

8. Raw Water Quality pH _____ TOC _____ ppm
   Turbidity _____JTU Colour _____Hazen
   Temperature Range _____^{o}C (winter) _____^{o}C (summer)

9. Type of treatment: listed below are several typical unit operations. Number the operations in the sequence at the plant.

_____	Pre-chlorination	_____	Filtration (Multi Media)
_____	Screening	_____	Filtration (Sand)
_____	Flocculation (Lime)	_____	Aeration
_____	Flocculation (Alum)	_____	Carbon Adsorption
_____	Flocculation (Iron)	_____	Ozone
_____	Flocculation (_____)	_____	Fluoridation
_____	Sedimentation	_____	Chloramine
_____	Post-chlorination	_____	Other

   For example, a plant with pre-chlorination, sedimentation, sand-filtration and post-chlorination would insert 1,2,3,4 beside the above operation in the sequence they are found in the plant.

10.

Chemical Added	Average conc. Added (ppm)	Residual Conc. in treated water
Pre Chlorine (as Cl_2)	_____	_____
Post Chlorine (as Cl_2)	_____	_____
Ozone (as O_3)	_____	_____
Fluoride (as F)	_____	_____
Alum (as ___)	_____	_____
Lime (as CaO)	_____	_____
Iron (as ___)	_____	_____
Other (as ___)	_____	_____
Other (as ___)	_____	_____
Carbon	_____	

11. Explain variation in treatment process, if any, between summer (Aug.-Sep.'93) and winter sampling (Feb.-Mar.'93)

12. Treated water Quality TOC _____ppm pH _____
    Temperature Range _____^{o}C (winter) _____^{o}C (summer)

13. Residence time in system _____

14. Sampling location (required for same location sampling for winter and summer'93)

    Raw water (prior to any treatment) _____
    Treated water (plant effluent) _____
    Distribution water (5-10 km from plant) _____

Please return completed questionnaire with sampling kit or send to:
Monitoring and Criteria Division
Environmental Health Directorate
Health Canada
EHC Room B-19
Tunney's Pasture
OTTAWA, Ont.
K1A 0L2

Appendix 2– Sampling Protocol and Analytical Methodology

Experimental

Reagents. Silica gel (chromatography grade, 100-200 mesh) was washed with diethyl ether (DEE) and dried at 110°C; sodium sulphate was heated at 400°C for 4 hours, washed with DEE and dried at 110°C and glass wool was acidified with sulphuric acid, washed with DEE and oven dried at 110°C. Diazomethane was prepared as required according to the Aldrich Diazald method. Groundwater, free of DBPs, obtained from a local well was used for blanks and the preparation of fortified standards.

Sample Collection and Extraction. During two periods, February-March 1993 and August-September 1993, replicate water samples were collected at fifty-three water treatment plants across Canada. Samples requested were raw water, treatment plant water (after final disinfection but before distribution) and treated water from a well-flushed tap at a point near the middle of the distribution system.

Water samples for the analysis of THMs, HANs, chloropropanones, chloral hydrate and chloropicrin were collected in 62 mL amber bottles containing ammonium chloride (62 mg per bottle). The water sample was adjusted to pH 4.5 at the time of collection; the volume of acid (0.1N HCl) needed to adjust the pH was determined using a 62 mL water sample which was then discarded. The determined amount of acid was added to each sampling bottle and, using a gentle stream of water, the bottles were filled just to overflow to prevent any headspace and dilution of the added preservatives. The bottles were capped with Teflon-lined seals, returned to the laboratory in a cooler and stored in a cold room until analyzed (usually within 1-4 days). For the analyses, a 12 mL aliquot was withdrawn and discarded, 16 g NaCl was added to the remaining sample (ca 50 mL; the accurate volume of the sample bottle was determined later using a volumetric cylinder), and the solution was shaken for 3 minutes with 3 mL of methyl t-butyl ether (MTBE) containing dibromomethane (IS-1) and 1,2-dibromopropane (IS-2) (50 and 250 pg/µL respectively) as internal standards. After transfer to a precalibrated (3.0 mL) vial, any residual water was removed with a pasteur pipet and the volume adjusted to 3 mL. Sodium sulphate was then added to the extract and the MTBE solution fortified with 1,3-dibromopropane (IS-3) (15 µL of 50 ng/µL in MTBE) and analyzed by GC-ECD. Quantification was based on response factors relative to IS-2 (IS-1 was added in case there were interferences with IS-2, however this did not occur). IS-3 was used to determine the percent recovery of IS-2 (95 ± 4%). Data from the first replicate sample was evaluated before analysis of other replicates and if the chloroform concentration in the sample exceeded the ECD linear range (0.2-50 µg/L), only an aliquot of the other replicate samples was used for analysis.

For the HAAs, the sampling vials used for water collection, field blanks and fortified samples were prepared by adding sodium thiosulphate solution (100 µL of 125 µg/µL) to each vial, which was then oven dried at 110°C for 2 hours. The vials were filled just to overflow with samples, sealed with Teflon-lined caps, returned to the laboratory in a cooler and stored in a cold room until analyzed (usually within 1-4 days). For analysis of HAAs the 30 mL water sample was transferred to a 60 mL separatory funnel containing NaCl (8 g) and the recovery standard (5.0 µl of 100 ng/µL 2-bromo-n-butyric acid (MBBA) in acetone) was added. The accurate volume of the sample vial was then determined using a volumetric cylinder. The solution was made basic (pH = 11.5) by adding 1 N sodium hydroxide (100 µL or as determined on representative replicates), shaken and left to stand for 5 minutes. The sample vial was rinsed with 6 mL DEE, the rinsing transferred to the separatory funnel and the sample extracted. After phase separation (ca 5 minutes) the aqueous layer was transferred from the separatory funnel into a 50 mL disposable centrifuge tube. The organic phase was discarded and, after washing the separatory funnel with a small amount of DEE (also discarded), the aqueous phase was returned to the separatory funnel. The solution was acidified to pH 0.5 by adding sulphuric acid (1.2 mL, 1:1) and left to stand for 5 minutes. The 50 mL tube was washed with 6 mL of DEE which was transferred to the separatory funnel and used to extract the aqueous solution. This process was repeated with a second 6 mL of DEE; the separatory funnel was washed with 2 mL DEE after each extraction and the combined DEE extracts were passed through a drying tube containing 2.8 grams of sodium sulphate (washed with 20 mL DEE prior to use). The eluent was collected in disposable centrifuge tubes (15 mL; pre-calibrated at the 2 mL mark) and the volume reduced to 1.8 mL using a nitrogen gas evaporator. The GC/MS quantification standard (5.0 µL of 200 ng/µL*para* bromochlorobenzene in DEE), methanol (10 µL, dried), diazomethane (60 µL) were added and the volume adjusted to 2 mL with DEE. After 30 minutes with minimal exposure to light, silica gel (50 mg) was added and the samples allowed to stand for at least 30 minutes before they were analyzed by GC/MS.

Water samples were collected for the analysis of total organic carbon (300 mL samples collected in prewashed polycarbonate bottles containing 1 mL of 10% H_2SO_4) and total organic halogen (500 mL samples collected in prewashed amber glass bottles containing sodium thiosulfate). Water samples (60 mL in prewashed polypropylene bottles) were collected for the determination of bromide ion.

Gas chromatography. GC/ECD analysis was conducted using a Varian Vista 6000 GC with an on-column injector and a J&W DB-5 30 m × 0.32 mm id (1 µ film) column. The GC was interfaced to a Vista 402 chromatography data system. The operating parameters were: oven temperature program; 50°C (3 min), 1.5°C/min to 65°C (1 min), 5°C/min to 120°C, 20°C/min to 180°C (10 min); on-column injector program: 100°C, 140°C/min to 240°C (15 min); detector 290°C. The helium carrier gas was set at 1 mL/min (ambient) with nitrogen make-up gas set at 25 mL/min.

The confirmation analyses were conducted on a DB-17 column (J&W DB-17 30 m × 0.32 mm id (0.25 µ film). The oven temperature program was: 35°C (3 min), 0.5°C/min to 40°C (1 min), 6°C/min to 100°C (1 min), 15°C/min to 160°C (1 min). All other GC/ECD settings remained unchanged.

Response factors, obtained by analyses of multi-level fortified water samples, were used to calculate DBP concentrations in the samples.

Gas chromatography – mass spectrometry. GC/MS analysis for HAAs was carried out by selected ion monitoring using a Finnigan MAT 90 GC/MS fitted with a DB-1701 30m × 0.32 mmid (0.25 µ film) column by injection of 3 µL aliquots (Varian SPI injector). The GC operating parameters were: injector – 100°C increased to 240°C at 100°/min, hold 24 min; oven – 40°C held for 3 min, increased to 140°C at 3.3°/min, then to 180°C at 23°/min. The ions monitored (mass resolution 1000) for each target HAA were: monochloroacetic acid – 49,77,79; dichloroacetic acid – 83,85; trichloroacetic acid – 117,119,121; monobromoacetic acid – 93,95; dibromoacetic acid – 171,173,175; tribromoacetic acid – 251,253; bromochloroacetic acid – 127,129; bromodichloroacetic acid – 141,161,163; chlorodibromoacetic acid – 207,209. DBP quantification was carried out by using relative response factors derived from the analysis of fortified water samples.

Auxiliary parameters. Auxiliary chemical parameters were determined by NOVAMANN (Ontario) Inc. Bromide ion concentration was determined by chromatography using a DIONEX 2000i ion chromatograph; for the summer samples, the detection limit was improved by a 10:1 preconcentration.

Total organic carbon (TOC) was determined using a SKALAR SK 12 organic carbon analyzer. After sparging with nitrogen to remove inorganic carbon or volatile organics, the organic carbon of the sample was converted to CO_2 by UV/persulfate oxidation followed by catalytic conversion (H_2; Ni/400°C) to methane. The methane was then detected by flame ionization detector (FID) and quantified by reference to a standards calibration curve.

The total organic halogen (TOX) was determined using a Mitsubishi TOX-10 analyzer using coulometric/activated charcoal techniques. The samples were passed through TOX adsorbing activated charcoal (AC) tubes and washed with a nitrate solution to remove any adsorbed inorganic halide ions. The TOX adsorbing AC tube was then transferred to a combustion chamber where the TOX was converted (O_2 / (800-900°C) to halogenated hydrogen. The generated halogenated hydrogen was then titrated automatically with silver ions generated coulometrically.

Quality Control. All samples were collected at least in duplicate and control samples were included for all groups of target analytes (usually one field blank per two sites). All DBP analytical methods incorporated surrogate internal standards and quantification was based on response factors established by multi-level calibration with fortified samples analyzed under identical conditions.

For the THMs, HANs, chloropropanones, chloral hydrate and chloropicrin analyses, the response factors were initially set by triplicate analyses of DBP-free groundwater fortified at 0, 0.2, 1, 2, 5 and 10 µg/L [chloroform = 5×]. Additional fortified samples were also analyzed at scheduled intervals. A total of 12 replicates (four sets of triplicate samples spiked at each fortification levels) were analyzed during each season. The response factors were not changed if variation was less than 10%. In addition, several raw water samples (unused raw replicates from all regions) from different water sources (matrix spikes; n=14) were analyzed at a fortification level of 5 µg/L (chloroform = 25 µg/L). The overall percent recovery was 99.4% (range 87.4 – 107.2) with standard deviation of 3.5. The results are shown in Table 7.

The accuracies of the analytical methods were estimated (TTHMs ± 5%, HAAs ± 20%) from the periodic analysis, throughout the study, of water samples fortified with known levels of target analytes. The mean recovery of HAAs was typically 96% as estimated from the recovery of the added MBBA internal standard.

Samples with a chloroform concentration exceeding the ECD linear range (0.2-50 µg/L) were reanalyzed using an aliquot from a replicate sample. DBPs identified by GC-ECD were confirmed by GC-MS or by GC-ECD analysis on a second GC column (DB-17). Each week during the analytical period, duplicate 30 mL groundwater samples were spiked with a HAA standard mixture of known concentration (6 µL of 80 ng/µL), stored in a refrigerator until the following week and analyzed as described above.

Table 7
Recoveries (%) from fortified raw water (n=14)

Compounds	Spking Level (µg/L)	RT	RF	Mean % Recovery	SD
Chloroform	25	5.80	0.73	98.4	3.1
Bromodichloromethane	5	8.97	4.82	99.9	1.8
Chlorodibromomethane	5	14.20	4.16	100.1	1.8
Bromoform	5	19.77	1.53	92.3	2.3
Trichloroacetonitrile	5	7.71	8.63	104.7	3.1
Dichloroacetonitrile	5	9.13	4.74	96.5	1.9
Bromochloroacetonitrile	5	15.05	3.88	102.7	1.7
Dibromoacetonitrile	5	20.83	3.10	107.0	2.3
1,1-dichloro-2-propanone	5	10.24	2.78	92.3	1.9
1,1,1-trichloro-2-propanone	5	17.27	4.09	107.2	1.9
Chloral Hydrate	5	9.30	4.88	104.5	4.1
Chloropicrin	5	13.20	9.20	87.4	16.4

RT – retention time in minutes
RF – response factor based on IS-2
SD – standard deviation

Appendix 4 – Drinking Water Guidelines

Excerpted from "*Guidelines for Canadian Drinking Water Quality*"

Total Trihalomethanes (TTHM)

The new lower guideline for TTHM was approved in 1993 by the Federal-Provincial Subcommittee on Drinking Water, and its parent Committee on Environmental and Occupational Health. Specific wording was approved for the new guideline which is reproduced below.

"*The interim maximum acceptable concentration (IMAC) for total trihalomethanes (THMs) in drinking water is 0.1 mg/L (100 µg/L) expressed as a running annual average of quarterly samples. This IMAC is based on the risk associated with chloroform, the THM most often present and generally found in the greatest concentration in drinking water. The guideline is designated as interim until such time as the risks from other disinfection by-products are ascertained. It is not expected that all water systems will be able to meet the revised THMs guideline immediately. When water systems are expanded or upgraded, every effort should be made, not only to meet the revised guideline, but to reduce concentrations of THMs to as low a level as possible. The preferred method of controlling disinfection by-products is precursor removal, however, any method of control employed* ***must not*** *compromise the effectiveness of water disinfection.*

Since the measurements made in our survey were only conducted in summer and winter, they cannot be used to calculate directly a "running annual average of quarterly samples" as described in the guideline. Nevertheless, if the TTHM value is in excess of the 0.1 mg/L (100 µg/L) guideline, you may wish to determine the annual average by taking quarterly samples. The risk associated with TTHM is due to some of them being classified as probable human carcinogens based on positive animal studies, and some positive, but weak, epidemiological data in humans. The risk of cancer at or close to the guideline value is very low with the estimated risk from lifetime exposure (70 years) being close to one in a million.

Excerpted from *Guidelines for Drinking-Water Quality 2nd Edition Volume 1 Recommendations, World Health Organization, Geneva 1993*.

Dichloroacetic Acid (DCAA)

DCAA produced neuropathy and liver toxicity in laboratory animals. The available evidence of liver tumour formation in mice was considered insufficient to classify DCAA as a carcinogen, and the WHO drinking water guideline was based on a no-observed-adverse-effect-level (NOAEL) for liver toxicity in mice. A provisional guideline was set at 50 µg/L.

Trichloroacetic Acid (TCAA)

TCAA has been shown to produce toxic effects in the liver of laboratory animals. It also induced tumours in the liver of mice and was reported to produce chromosomal aberrations, but was negative in *in vitro* mutagenicity assays. Due to the evidence of carcinogenicity being limited to one species, the WHO drinking water guideline was based on a lowest-observed-adverse-effect-level (LOAEL) for liver toxicity in mice. A provisional guideline was set at 100 µg/L.

Chloral Hydrate (CH)

CH has been used as a sedative or hypnotic drug in humans at doses up to 14 mg/kg body weight. No long-term study in animals was identified by the WHO and the guideline was based on a 90-day study in mice where liver toxicity was observed. The lowest-observed-adverse-effect-level (LOAEL) in the mouse study was used as the basis for setting a WHO drinking water guideline at 10 µg/L. The guideline value is designated as provisional because of the limitations of the available database.

Dichloroacetonitrile (DCAN)

DCAN has been shown to be teratogenic and to have body weight effects in rats. The no-observed-adverse-effect-level (NOAEL) in the rat study was used as the basis for setting a WHO drinking water guideline at 90 µg/L. The guideline value is designated as provisional because of the limitations of the available database.

Dibromoacetonitrile (DBAN)

DBAN has been shown to produce effects on body weight in a 90-day study in rats. The no-observed-adverse-effect-level (NOAEL) in the rat study was used as the basis for setting a WHO drinking water guideline at 100 µg/L. The guideline value is designated as provisional because of the limitations of the available database.

Trichloroacetonitrile (TCAN)

TCAN has been shown to be teratogenic and to have body weight effects in rats. The no-observed-adverse-effect-level (NOAEL) in the rat study was used as the basis for setting a WHO drinking water guideline at 1 µg/L. The guideline value is designated as provisional because of the limitations of the available database.