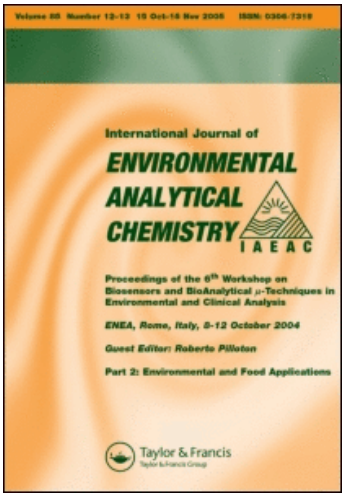

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Differences in Chloroform Levels from Drinking Water Samples Analysed Using Various Sampling and Analytical Techniques

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DIFFERENCES IN CHLOROFORM LEVELS FROM DRINKING WATER SAMPLES ANALYSED USING VARIOUS SAMPLING AND ANALYTICAL TECHNIQUES

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During an investigation of disinfection by-products in drinking water from Canadian treatment facilities, chloroform was determined using either Purge & Trap or liquid-liquid extraction techniques on water samples treated with different dechlorinating preservatives and/or pH adjustment. The addition of dechlorinating preservatives to the sampled water altered the sample pH which had a significant effect on the chloroform levels. Initial results indicated lower chloroform levels for water samples where the pH was decreased by the addition of acid or preservative. The effect due to pH adjustment was usually greatest for samples taken at the treatment plant and diminished with distance (time) in the distribution system. The magnitude of the differences appeared to be also dependent on other variables such as water source quality and water treatment processes. To obtain an accurate estimation of human exposure to chloroform from drinking water, samples should be collected at the consumer tap and not at the treatment plant.

KEY WORDS: Chloroform, drinking water, disinfection by-products, purge & trap, liquid-liquid extraction.

INTRODUCTION

Chloroform, a major disinfection by-product (DBP) found in chlorinated drinking water, has been determined by a number of different analytical techniques including Purge and Trap (P&T)[1,2], liquid-liquid extraction (LLE)[2,3] and direct aqueous injection[4]. Some of the techniques are known to give different values; for example, chloroform levels in water analysed by direct aqueous injection technique are usually higher than levels determined by the P&T technique. The variation is attributed to the formation of chloroform from the breakdown of chlorinated DBP precursors in the gas chromatograph hot injection port used for the direct aqueous injection technique. Trichloroacetic acid, a known DBP, has been shown to degrade to chloroform at elevated temperature[5]; the formation of chloroform during water chlorination is also enhanced at higher pH[6].

During a national survey [1993] of DBPs in drinking water from Canadian treatment facilities, replicate samples were collected for analyses using purge and trap/gas chromatography/mass spectrometry (P&T/GC-MS) {sample pH not adjusted and $Na_2S_2O_3$ preservative added} and using liquid-liquid extraction/gas chromatography/electron capture detection (LLE/GC-ECD) {sample pH adjusted to 4.5–5.0 and NH_4Cl preservative added}. The results obtained using the two analytical procedures differed significantly and the magnitude of the differences varied with the

location of the sample in the distribution system. The differences were not primarily due to the different analytical techniques but appeared, however, to be associated with the pH of the sample or the dechlorinating preservative used. A more detailed investigation of the impact of pH adjustment, dechlorinating preservative and sampling location was, therefore, carried out using replicate samples collected from the distribution systems of plants using different drinking water treatment processes.

EXPERIMENTAL

Sampling and extraction

For the Purge & Trap analyses, precleaned 40 ml VOC vials were used and either (i) 0.2 ml of $Na_2S_2O_3$ solution (61.3 mg ml^{-1}), (ii) ascorbic acid (20 mg per vial) or (iii) ammonium chloride (44 mg per vial) were added as dechlorinating preservative. For the liquid-liquid extraction technique, 62 ml amber bottles were used and either (i) 0.3 ml sodium thiosulfate solution (61.3 mg ml^{-1}), (ii) ascorbic acid (30 mg per bottle) or (iii) ammonium chloride (62 mg per bottle) were added as dechlorinating preservative.

During the period January to March, 1994, replicate samples of raw and treated water were collected from well flushed taps at three water treatment plants and at various points in the distribution systems. The treatment processes at each plant were: Plant #1 – prechlorination, flocculation, sedimentation, multimedia filtration, pH correction (lime), chloramination; Plant #2 – mechanical screening, flocculation, chlorination, sand filtration, post chlorination; Plant #3 – mechanical screening, flocculation, chlorination (summer months), sand filtration, ozonation and post chlorination. Plants #1 and #2 draw their raw water from the same river, Plant #3 draws its water from a second river. For sampling and storage consistency the pH of the water samples was adjusted, when needed, at the time of collection. For pH adjustment of samples, the volume of acid (0.1N HCl) required to adjust the sample to pH 4.5 (or other pH) was determined using an equivalent volume of a replicate sample. For those water samples requiring pH adjustment, the required amount of acid was added to the sample container and, using a very gentle stream of water, the vials or bottles were filled just to overflow to prevent any headspace and/or dilution of the added preservatives. The vials and bottles were capped with teflon-lined seals to eliminate any head space, returned to the laboratory in a cooler and stored in a cold room until analysed (usually 1–4 days).

For P&T/GC-MS analyses, the water samples were analysed directly from the sample vial, no other sample preparation was required. For the LLE/GC-ECD analyses, a 12 ml aliquot was withdrawn, 16 g NaCl was added to the remaining 50 ml sample, and the solution was extracted for 3 min with 3 ml of methyl t-butyl ether (MTBE) containing dibromomethane and 1,2-dibromopropane (50 and 250 pg μl^{-1} respectively) as internal standards (IS). After transfer to a precalibrated (3.0 ml) vial, the MTBE solution was fortified with a quantification standard (15 µl 1,3-dibromopropane, 50 ng μl^{-1} in MTBE) and analysed by GC-ECD.

Identification and quantification

The P&T analyses were conducted using a Tekmar LSC 2000 system interfaced to a Varian Saturn II GC-MS (ITD) system equipped with a J&W DB-624 75 m × 0.53 mm (3 µm film) column. The P&T was also interfaced to a Tekmar AQUATeq 50

autosampler (sample chamber maintained at 8°C using a cooling bath) set for automatic addition of internal standards solution. The quantification was done automatically using the Saturn II autoquan software and was based on response factors established by multilevel calibration runs with fortified samples operated under identical conditions.

The GC-ECD analysis were conducted using a Varian Vista 6000 GC equipped with an on-column injector and a J&W DB-5 30 m × 0.32 mm id (1 μm film) column. Response factors, developed from the analyses of multi-level fortified water samples, were used to calculate the amounts in the water samples.

Quality control

All solvents used were analysed to verify the absence of interferences. The samples were collected in duplicate or triplicate and blank water samples were included for each field sampling excursion. The analytical methods incorporated the use of surrogate internal standards and the quantification was based on response factors established by multi-level calibration runs with fortified samples analyzed under identical conditions. Therefore, the results are automatically corrected for recovery rates. Additional fortified samples were also analyzed at scheduled intervals. Any sample with a concentration value outside the determined experimental linear range [0.2–50 μg l^{-1} for LLE/GC-ECD and 0.5–125 μg l^{-1} for P&T/GC-ITD] was reanalysed using one of the replicate samples. The confirmation of data was further established by use of appropriate analytical techniques, i.e, mass spectrometry detection or reanalysis of selected samples on a secondary (DB-17 liquid phase) GC column. The results presented in the Table 1 and figures 2(a), 2(b) and 2(c) represent the mean or duplicate or triplicate water samples analysis.

RESULTS AND DISCUSSION

There is no single sampling and/or analytical procedure which is suitable for all of the disinfection by-products which have been reported in chlorinated drinking water. Haloacetonitriles, chloroacetones, chloral hydrate, chloropicrin and cyanogen chloride require the correct choice of preservative and pH adjustment to maintain sample integrity[7–9]. Little comment has been made, however, on the effect of these various preservatives and sampling procedures on the level of chloroform, which is the major disinfection by-product. Initial results from a national survey [1993] of disinfection by-products in drinking water, using two different sampling and analysis procedures indicated lower chloroform levels for those water samples which were adjusted to pH 4.5 at the time of collection (LLE/GC-ECD analysis) compared to pH unadjusted samples (pH 7 to 9; P&T/GC-MS analysis). For samples taken at the treatment plant, the chloroform levels for pH adjusted (pH 4.5) samples were, on average, 39% lower in winter and 25% lower in summer compared to pH unadjusted samples. For samples collected a few kilometers along the distribution system the chloroform levels for pH adjusted (pH 4.5) samples were, on average, 32% lower in winter and 16% lower in summer compared to pH unadjusted samples. Although it is known that some compounds will degrade to chloroform when analysed using the P&T technique, this could not explain the large differences seen between the two analytical procedures, When water samples, fortified with either chloral hydrate, trichloroacetonitrile, chloropicrin and 1,1,1,-trichloro-2-propanone (DBPs with CCl_3 moiety), were analysed only 1,1,1-trichloro-2-propanone was found to convert efficiently to chloroform (ca. 60%

conversion) under our P&T operating conditions. In fact, when the same sample (or replicate) was analysed using the P&T/GC-MS and the LLE/GC-ECD techniques, the chloroform results obtained were generally in good agreement (< 10% difference).

The differences in chloroform levels were clearly associated with the sample pH and/or dechlorinating preservative used. In order to evaluate these factors treated water from two water treatment facilities (plants #1 and #2), taken at the treatment plant and at the end of the distribution system were sampled using a combination of pH adjustment and dechlorinating preservatives. It was found that the addition of ascorbic acid to water samples from both plants decreased the pH to pH 3.8 (Table 1). The pH decrease from the use of ascorbic acid is dependent on the raw water quality; a similar amount of ascorbic acid added to a "hard" groundwater sample reduced the pH from pH 8.5 to pH 4.8. The addition of sodium thiosulfate to water samples from both plants resulted in a slight increase in sample pH while the addition of ammonium chloride caused a slight decrease in sample pH. The pH of additional water samples, treated with sodium thiosulfate or ammonium chloride preservative, was adjusted to give intermediate pH values (Table 1) by addition of acid. Most samples were then analysed by both LLE/GC-ECD and P&T/GC-MS; the analytical data for chloroform and 1,1,1-trichloro-2-propanone are presented in Table 1.

The results clearly indicate that for samples with similar pH and the same preservative, the P&T/GC-MS and LLE/GC-ECD techniques gave comparable chloroform levels. The slightly higher chloroform levels obtained using the P&T/GC-MS

Table 1 Chloroform and 1,1,1-trichloro-2-propanone (μg l^{-1}) in drinking water.

Preservative	*pH*	*Adjust*		*Treated (plant)*			*Distribution systems (end)*		
				LLE		*P&T*	*LLE*		*P&T*
				$CHCl_3$	*TCP**	*$CHCL_3$*	*$CHCl_3$*	*TCP**	*$CHCl_3$*
WATER TREATMENT PLANT #1 [CHLOR (AM) INATION]; water pH 8.9									
Sodium Thiosulfate	NO		9.2**	13.7	0.3	14.4	14.6	0.3	14.8
Sodium Thiosulfate	YES	Field	5.0	10.3	1.2	11.3	14.1	0.7	14.3
Sodium Thiosulfate	YES	24 hr	5.1	13.8	0.3	13.7	13.7	0.3	14.1
Ammonium Chloride	NO		7.6	11.5	1.2	12.6	14.7	0.7	14.2
Ammonium Chloride	YES	Field	7.1	10.8	1.3	11.7			
Ammonium Chloride	YES	Field	6.3	10.5	1.2	11.5			
Ammonium Chloride	YES	Field	4.6	10.5	1.2	11.2	13.1	0.8	14.1
Ammonium Chloride	YES	24 hr	4.5	11.5	1.3	11.6	13.5	0.7	14.7
Ascorbic Acid	NO		3.8	10.6	1.2	10.9	13.8	0.7	14.3
WATER TREATMENT PLANT #2 [CHLORINATION]; water pH 8.0									
Sodium Thiosulfate	NO		8.2	21.7	1.3	21.2	31.4	1.4	33.8
Sodium Thiosulfate	YES	Field	4.9	11.7	1.6	13.4	29.7	1.5	30.1
Sodium Thiosulfate	YES	24 hr	4.8	20.7	1.4	18.7	29.5	1.4	31.2
Ammonium Chloride	NO		7.4	18.1	1.6	18.8	30.5	1.5	31.2
Ammonium Chloride	YES	Field	7.0	14.2	1.6	15.8			
Ammonium Chloride	YES	Field	5.9	12.5	1.6	13.0			
Ammonium Chloride	YES	Field	4.7	12.3	1.6	12.6	27.8	1.6	29.5
Ammonium Chloride	YES	24 hr	4.7	17.0	1.7	16.1	28.6	1.5	30.5
Ascorbic Acid	NO		3.8	12.3	1.6	10.8	29.2	1.6	29.2

* TCP = 1,1,1-trichloro-2-propanone

** measured pH of water sample

technique can be accounted for by the conversion of 1,1,1,-trichloro-2-propanone to chloroform. It can also be seen that at similar sample pH the chloroform levels were essentially the same whichever of the three dechlorinating preservatives was used. Quite obviously it was the pH of the sample that had the major impact on the chloroform levels in the samples. This is clearly illustrated in Figures 1(a) and 1(b) which plot the P&T

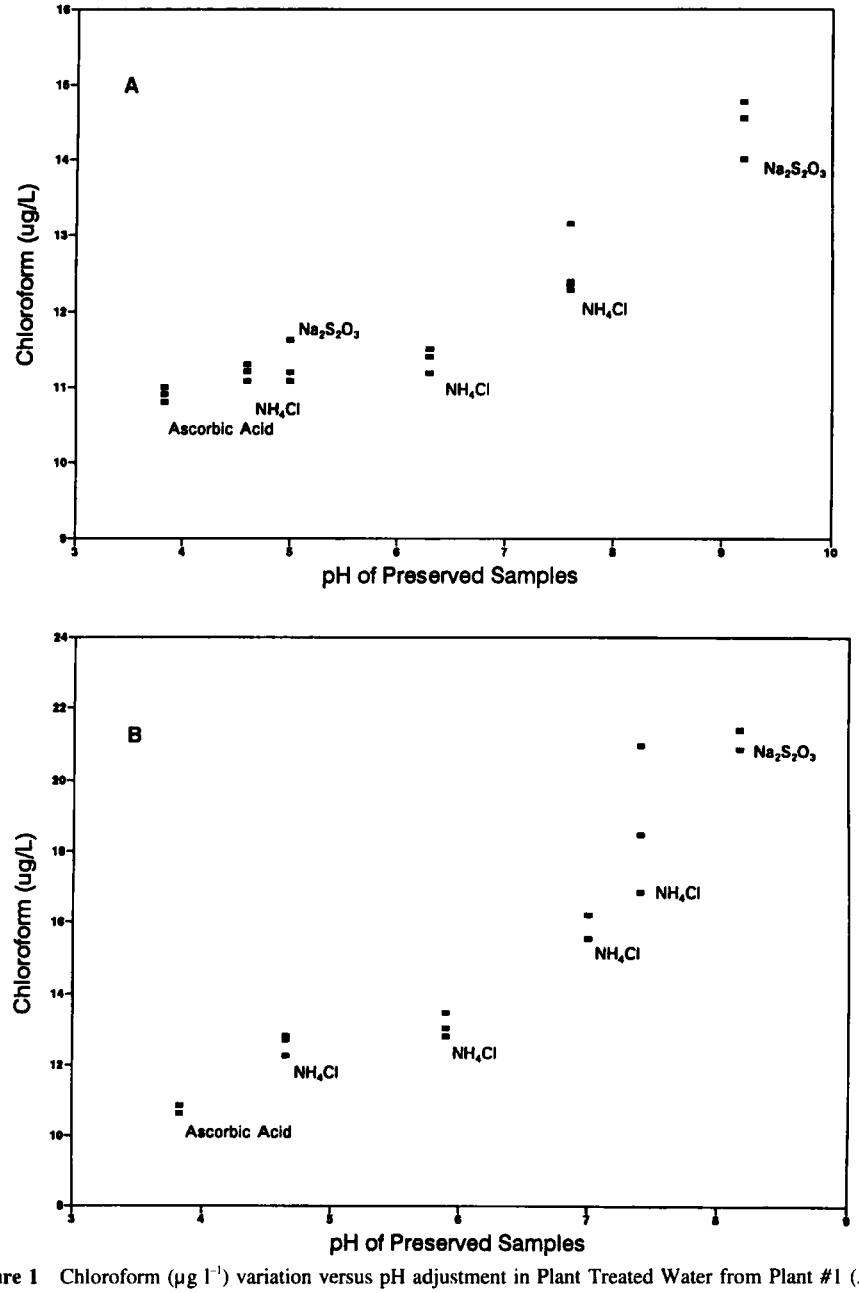


Figure 1 Chloroform ($\mu g\ l^{-1}$) variation versus pH adjustment in Plant Treated Water from Plant #1 (A) and Plant #2 (B).

chloroform levels of the treatment plant water samples versus sample pH. Figures 1(a) and 1(b) also show the precision for the analysis of replicate samples. The dependence on pH can be explained by postulating that the samples contain chlorinated intermediates which are stable at low pH but, at higher pH, break down to chloroform over time. This is supported by the data for the samples collected at the end of the distribution system for Plant #2. The chlorination reactions have essentially gone to completion during the residence time in the system, chloroform levels are much higher and the pH effect is far less. A similar, though smaller, increase in chloroform levels is seen in samples that are stored for 24 hours before analysis with or without pH adjustment (Table 1).

Since the magnitude of the differences appeared to be site and water type dependent, a series of samples were collected at three water treatment plants using different treatment processes; (i) chloramination (Plant #1), (ii) chlorination (Plant #2) and (iii) ozonation/chlorination (Plant #3). At several points along the distribution lines served by the three treatment plants, samples were collected using different preservatives (ascorbic acid, NH_4Cl and $Na_2S_2O_3$) and pH adjustment. The samples were then analysed using both the P&T/GC-MS and the LLE/GC-ECD analytical techniques.

The analytical data are illustrated in Figures 2(a), 2(b) and 2(c) and indicate that the pattern of chloroform variation was different for the three water treatment systems. However, in all three cases, the variation was always greatest from water taken at the plant and minimal from water taken at the end of the distribution system (Figures 2(a), 2(b) and 2(c)).

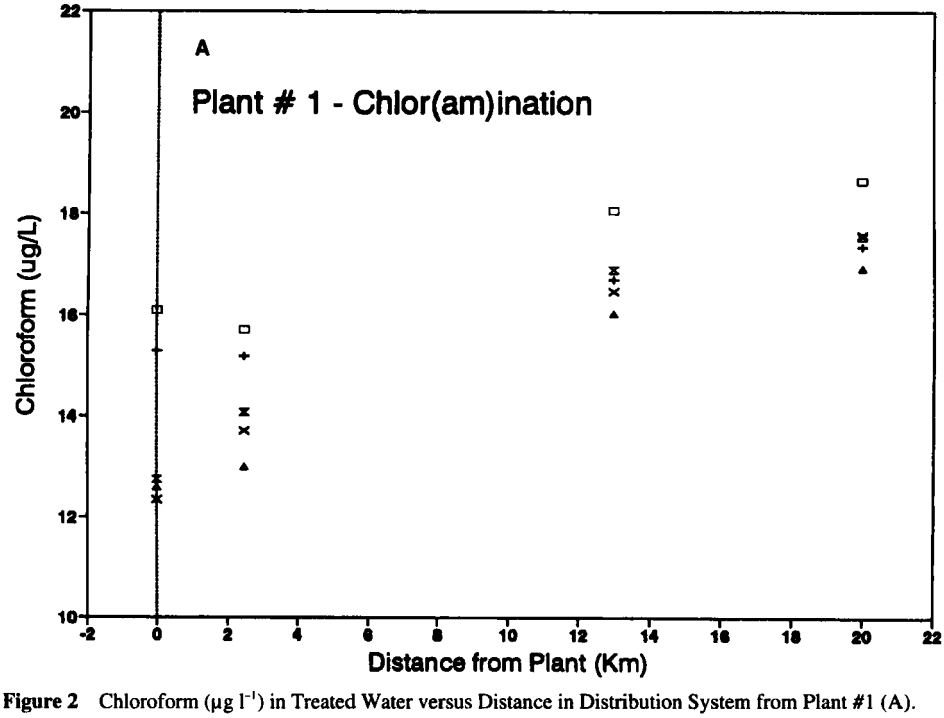
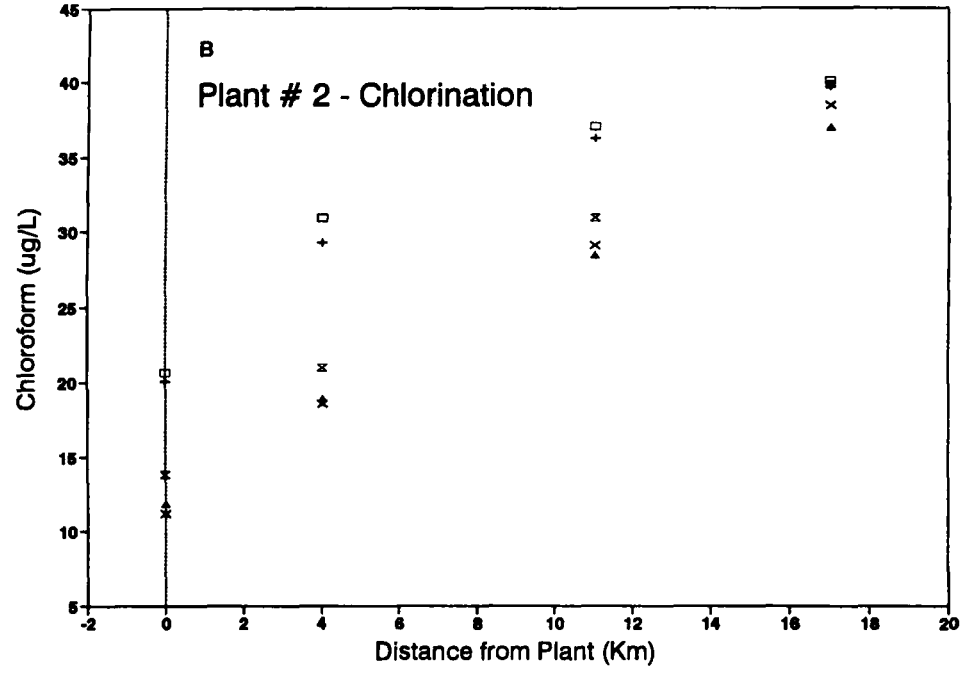


Figure 2 Chloroform ($\mu g\ l^{-1}$) in Treated Water versus Distance in Distribution System from Plant #1 (A).



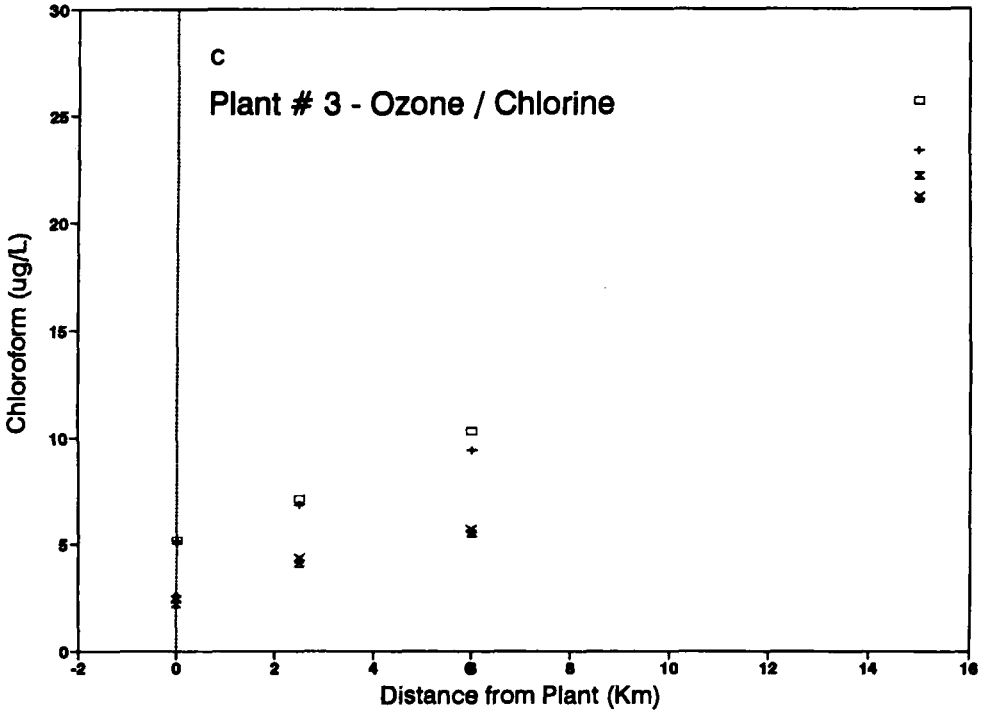


Figure 2 *(cont.)* Plant #2 (B) and Plant #3 (C). The legends are: □ (P&T; no pH adjust); + (LLE, no pH adjust); ⧖ (P&T, pH adjust); △ (LLE, pH adjust) and x (ascorbic acid). The initial pH of the treated water were: Plant #1–8.3; Plant #2–7.7; Plant #3–7.3.

CONCLUSIONS

Both the P&T/GC-ITD and LLE/GC-ECD techniques can be used for the determination of chloroform in drinking water samples. The P&T technique gives slightly higher values due to breakdown of some chlorinated intermediates. If the pH of the sample is controlled, either sodium thiosulfate, ammonium chloride or ascorbic acid can be used as a dechlorinating preservative. The best choice of preservative will depend on which other disinfection by-products are also being analysed. It is essential to adjust the water sample to pH 4.5 or below to prevent further production of chloroform during sample storage; the effect due to pH diminished with time (distance) in the distribution system. However, the magnitude of the effect may also be dependent on other variables such as water source quality and treatment processes. To obtain an accurate estimation of human exposure to chloroform from drinking water, samples should be collected at the consumer tap and not at the treatment plant.

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